(16)

SYNTHESIS AND REACTIVITY OF RHENIUM AND TECHNETIUM POLYARYL COMPLEXES

by

CHRISTOPHER ALAN MORSE

A.B., Chemistry, Dartmouth College (1993)

SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SEPTEMBER 1998

Signature of Author_____
Department of Chemistry
August 5, 1998

Certified by_____
Alan Davison
Thesis Supervisor

Accepted by_____
Dietmar Seyferth, Chairman
Departmental Committee
on Graduate Students

Science

This doctoral thesis has been examined by a committee of the Department of Chemistry as follows:

Professor Daniel G. Nocera — Chairman

Professor Alan Davison — Thesis Supervisor

Professor Stephen J. Lippard — Department Chairman

To my family for their unwavering support
and love over the years

Harry Chapin's "Flowers are Red"

The little boy went first day of school; he got some crayons, and he started to draw.
He put colors all over the paper for colors was what he saw.

And the teacher said "What you doin', young man?"
"I'm paintin' flowers," he said.
She said "It's not the time for art young man, and anyway flowers are green and red.
There's a time for everything young man, a way it should be done.
You've got to show concern for everyone else for you're not the only one."

And she said "Flowers are red, young man, green leaves are green.
There's no need to see flowers any other way
Than they way they always have been seen."

But the little boy said "There are so many colors in the rainbow,
So many colors in the morning sun,
So many colors in the flower, and I see every one."

Well, the teacher said "You're sassy. There's ways that things should be.
And you'll paint flowers the way they are. So repeat after me..."

And she said "Flowers are red, young man, green leaves are green.
There's no need to see flowers any other way
Than they way they always have been seen."

But the little boy said again "There are so many colors in the rainbow,
So many colors in the morning sun,
So many colors in the flower, and I see every one."

Well, the teacher put him in a corner. She said "It's for your own good.
And you won't come out 'til you get it right and all responding like you should."
Well, finally he got lonely, frightened thoughts filled his head,
And he went up to the teacher, and this is what he said...

And he said "Flowers are red, and green leaves 'er' green.
There's no need to see flowers any other way
Than they way they always have been seen."

Of course time went by like it always does: they moved to another town.
And the little boy went to another school, this is what he found:
The teacher there was smiling. She said "Painting should be fun.
And there are so many colors in a flower, so let's use every one."
But that little boy painted flowers in neat rows of green and red,
And when the teacher asked him why, this is what he said...

And he said "Flowers are red, and green leaves 'er' green.
There's no need to see flowers any other way
Than they way they always have been seen."

But there still must be a way to have our children say:
"There are so many colors in the rainbow, so many colors in the morning sun,
So many colors in the flower, and I see every one."

SYNTHESIS AND REACTIVITY OF RHENIUM AND TECHNETIUM POLYARYL COMPLEXES

by

Christopher Alan Morse

Submitted to the Department of Chemistry on August 5, 1998 in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

Abstract

Chapter 1. The organometallic chemistry of rhenium includes a variety of σ-aryl complexes. The syntheses and structures for these complexes follow a pattern that relates predominantly to their oxidation states. The high oxidation state compounds all contain oxo or imido ligands. The low oxidation state complexes are mostly carbonyl and phosphine complexes, many of which result from orthometallation of a ligand. The middle oxidation state compounds bridge the motifs seen in the higher and lower oxidation states. A summary of rhenium-carbon bond lengths is presented.

Chapter 2. Several complexes of the form $Re(aryl)_3(PMe_2Ph)_2$ have been synthesized from $ReCl_3(PMe_2Ph)_3$, where aryl is *m*-tolyl, *p*-tolyl, phenyl, or *p*-methoxyphenyl. The complex $Re(p\text{-tolyl})_3(THT)_2$ (THT = tetrahydrothiophene) was synthesized from $ReBr_3(THT)_3$ and was structurally characterized by a single crystal X-ray diffraction study. It was found to have a nearly ideal trigonal bipyramidal structure with a propeller arrangment of aryl rings in the trigonal plane. The average Re-C bond length in $Re(p\text{-tolyl})_3(THT)_2$ was 2.04 Å. Treating *in situ* solutions of $Re(p\text{-tolyl})_3(THT)_2$ with phosphines results in complexes of the form $Re(p\text{-tolyl})_3(PR_3)_2$, where PR_3 is PMe_2Ph, PPh_3 or PMe_3. Several polyaryl rhenium complexes with chelating phosphines are synthesized and examined.

Chapter 3. The complex Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ is used as a probe to study the stability and reactivity of rhenium tris(aryl) complexes. The complexes are stable to temperature and substitution, but decompose in the presence of many oxidants by forming biphenyl as a reductive elimination product and unknown rhenium complexes without coordinated aryl groups. In the presence of carbon monoxide, Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ reductively eliminates biphenyl and forms the rhenium(I) complex *mer*-Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl). An X-ray structural analysis of *mer*-Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) shows a nearly ideal octahedral geometry with a long Re-C aryl bond length of 2.19 Å. The complex Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) can be treated with iodine to form Re(CO)$_3$(PMe$_2$Ph)$_2$I.

Chapter 4. Technetium has a limited number of known organometallic compounds. Most of these complexes have carbonyl or isonitrile ligands. A small number of technetium complexes have anionic or polyhapto organometallic ligands. These include a variety of cyclopentadienyl complexes and η^6-arene complexes. Recently, the organometallic complexes of technetium have come to include η^1-sigma donors as well as multiply bonded alkylidenes and alkylidynes. A summary of technetium-carbon bond lengths is presented.

Chapter 5. The first technetium aryl complexes were synthesized from TcCl$_3$(PMe$_2$Ph)$_3$. They have the general formula Tc(aryl)$_3$(PMe$_2$Ph)$_2$, where aryl is *p*-tolyl, *m*-tolyl, or phenyl. The complex Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ was structurally characterized by a single crystal X-ray diffraction study which found the technetium in a trigonal bipyramidal arrangment with a Tc-C average bond length of 2.037 Å. Both the *m*-tolyl and *p*-tolyl analogs of Tc(aryl)$_3$(PMe$_2$Ph)$_2$ react with carbon monoxide to reductively eliminate biphenyl and benzophenone resulting in technetium(I) complexes of the form Tc(CO)$_3$(PMe$_2$Ph)$_2$(aryl). An X-ray structural analysis of Tc(CO)$_3$(PMe$_2$Ph)$_2$(*m*-tolyl) showed an octahedral coordination around the metal with a long Tc-C bond length of 2.242 Å. The complex Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ also reacts with ^{t}BuNC to form a technetium(I) organometallic oil formulated as Tc(^{t}BuNC)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl). The complex TcCl$_4$(THT)$_2$ (THT = tetrahydrothiophene) was synthesized from TcCl$_6^{2-}$ and was structurally characterized by an X-ray crystallographic analysis. The structure for TcCl$_4$(THT)$_2$ showed a standard octahedral coordination around the technetium(IV) center.

Thesis Supervisor: Alan Davison

Title: Professor of Chemistry

Table of Contents

List of Tables

Chapter 4.

Chapter 5.

List of Figures and Schemes

Chapter 4.

Chapter 5.

Chapter 1

A Review of Rhenium Aryl Complexes

Introduction

In spite of the fact that rhenium was the last of the stable transition metals to be isolated, the field of rhenium chemistry has grown rapidly since its 1925 discovery to equal that of other transition metals. However, rhenium chemistry is hindered by the low natural abundance of the metal, and hence its expense, even though it has been found to be important in catalysis.[1,2] The organometallic chemistry of rhenium is varied and ranges from low oxidation state carbonyls to high oxidation state alkylidenes. One absence in the chemsitry of rhenium is the lack of a ferrocene analog. The bis(cyclopentadienyl)rhenium fragment only exists as a hydride, a dimer, or with an additional η^1-cyclopentadienyl (Cp) ring.[3]

The structure and reactivity of rhenium aryl complexes differ from that of rhenium alkyl complexes. Aryl groups are far more likely to decompose via reductive elimination pathways. Aryl groups do not possess α-hydrogens, and the β-hydrogens do not react as do the β-hydrogens of an alkyl. Occasionally, in the lower oxidation states, phenyl rings on some ligands are orthometallated to form aryl complexes. For rhenium, the majority of aryl complexes exist in the high (VI and VII) and low (I) oxidation states. Only one of these complexes is homoleptic; the rest have ligands ranging from oxos and imidos in the higher oxidation states to carbonyls in the lower states. The following review will detail the chemistry of rhenium aryls from the 1960's through 1997 as organized by decreasing oxidation state for later comparision to the complexes in Chapters 2 and 3. The end of the review features an organized collection of the known rhenium-carbon bond lengths in aryl complexes along with an analysis of the values.

High Oxidation State Aryl Complexes (VI and VII)

All of the σ-aryl complexes in the higher (VI and VII) oxidation states of rhenium have an oxo group, an imido group or a combination of both. The only imido groups found on rhenium aryl complexes are *tert*-butyl imido groups. The majority of these complexes are made by treating rhenium(VII) and (VI) halide complexes or rhenium(VII) oxo complexes with aryl Grignard reagents. All of the imido chemistry comes from the work of Geoffrey Wilkinson, while the oxo complexes come from both Wilkinson and Wolfgang Herrmann.

Several rhenium(VII) imido complexes with one aryl group have been synthesized. By treating $Re(^tBuN)_3OSiMe_3$ (**1**) with the appropriate aryl Grignard reagent, trisimido aryl complexes, $Re(^tBuN)_3Ar$ (**2**) [**2a** Ar = *o*-tolyl, **2b** Ar = mes, **2c** Ar = xylyl] [xylyl = 2,6-dimethylphenyl; mes = 2,4,6-trimethylphenyl], can be isolated.[4] These complexes are air-stable yellow solids. An X-ray structural determination of (**2b**) shows a distorted tetrahedral geometry for rhenium and three bent imido groups indicating an 18-electron complex.[5] The reaction can be done with phenyl or *p*-(^{t}Bu)phenyl Grignard reagents, but the products are oils. If any of the complexes (**2**)[4] or the *in situ* unisolated phenyl derivative[6] are hydrolyzed with hydrochloric acid, aryl dichlorides $Re(^tBuN)_2Cl_2Ar$ (**3**) [**3a** Ar = *o*-tolyl, **3b** Ar = mes, **3c** Ar = xylyl, **3d** Ar = Ph] are afforded. The X-ray structure of (**3a**) was determined and showed a square pyramidal rhenium coordination geometry with both a linear and a bent imido group.[4] However, the X-ray structure of (**3d**) shows the rhenium in a distorted trigonal bipyramidal geometry with both imidos axial; the bent imido in (**3d**) is 10° less bent than in (**3a**).[6] The bent imido group indicates that the

complexes (**3**) are actually 16-electron complexes with only the linear imido group donating four electrons.

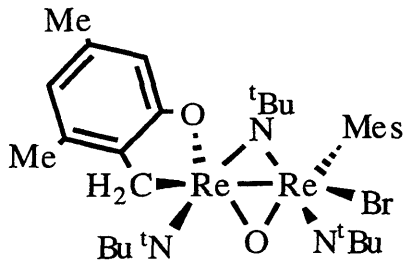
Several bis(aryl) rhenium(VI) and (VII) complexes can be synthesized. Starting from the bisimido complex, $Re(^tBuN)_2Cl_3$ (**4**), treatment with at least three equivalents of the appropriate aryl Grignard reagent affords the reduced rhenium(VI) complexes $Re(^tBuN)_2Ar_2$ (**5**) [**5a** Ar = xylyl, **5b** Ar = mes].[5,6] However, if (**4**) is treated with two equivalents of *o*-tolyl Grignard, non-reduced chloride complex $Re(^tBuN)_2(o\text{-tolyl})_2Cl$ (**6**) results.[5] An electrochemical study shows that (**5b**) can undergo a reversible one-electron reduction or oxidation;[5] both (**5a**) and (**5b**) can be chemically oxidized and isolated as salts $[Re(^tBuN)_2Ar_2]^+$ (**7**) [**7a** Ar = xylyl, **7b** Ar = mes].[5,6] If (**6**) is treated with $AgPF_6$, the analogous cation (**7c**) [Ar = *o*-tolyl] is formed.

While the neutral complexes (**5**) do not undergo insertions with isonitriles, the cationic complexes (**7**) do. The complex (**7a**) reacts with ^{t}BuNC to form an η^2-iminoacyl complex $[Re(^tBuN)_2(xylyl)(^tBuN{=}C(xylyl))]^+$ (**8a**) via insertion into an aryl-rhenium bond.[5] The analogous reaction was also seen with (**7b**) which was found to react with RNC [R = xylyl or ^{t}Bu] to form $[Re(^tBuN)_2(mes)(RN{=}C(mes))]^+$ (**8b**).[6] The complexes (**8**) are formed even in an excess of isonitrile and were characterized by IR and NMR spectroscopies by analogy to the chemistry of Group 6.

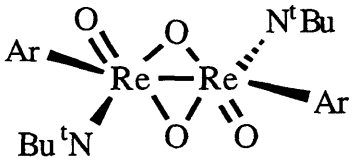
When $Re(^tBuN)_2Cl_3$ (**4**) was treated with 2 equivalents of *o*-tolyl Grignard, $Re(^tBuN)_2(o\text{-tolyl})_2Cl$ (**6**) resulted, *vide supra*. If three equivalents of Grignard are used, $Re(^tBuN)_2(o\text{-tolyl})_3$ (**9**), the only high oxidation state tris(aryl) complex, results.[6] The complex (**9**) is expected to have a trigonal bipyramidal structure with two equatorial imidos because the proton NMR spectrum shows a ratio of 2:1 for the *o*-tolyl resonances.[6]

Unlike any other high oxidation state complexes for rhenium, the synthesis of (**9**) completed a family of complexes such that $Re(^tBuN)_2(o\text{-tolyl})_xCl_{3-x}$ [x = 0, 1, 2 or 3] all exist.

Several aryl complexes share both oxo and imido ligands. The first of these is $Re(^tBuN)_2(O)(mes)$ (**10a**), synthesized by treating $Re(^tBuN)_2Cl(OH)_2$ with mesityl Grignard or by treating $Re(^tBuN)_2Cl_2(mes)$ (**3b**) with moist Ag_2O.[5] The first synthesis for (**10a**) has a byproduct that can be isolated by fractional crystallization; this complex is a rhenium dimer, $Re_2O(^tBuN)_3Br(mes)(C_9H_{10}O)$ (**11**), with one intact aryl ring and one aryl ring that is now bound through its methyl group as well as through a newly formed phenolic oxygen (*vide infra*). The structure of (**11**) was confirmed by X-ray crystallography and shows two different rhenium(VI) centers with a bridging oxo and a bridging imido.[5] In order to make the analogous xylyl complex, $Re(^tBuN)_2(xylyl)_2$ (**10b**), $[Re(^tBuN)_2(xylyl)_2]^+$(**5a**) must be treated with one equivalent of NO to make the rhenium(V) complex $Re(^tBuN)_2(xylyl)_2NO$ (**21**) which can then be treated with another equivalent of NO to make (**10b**).



11



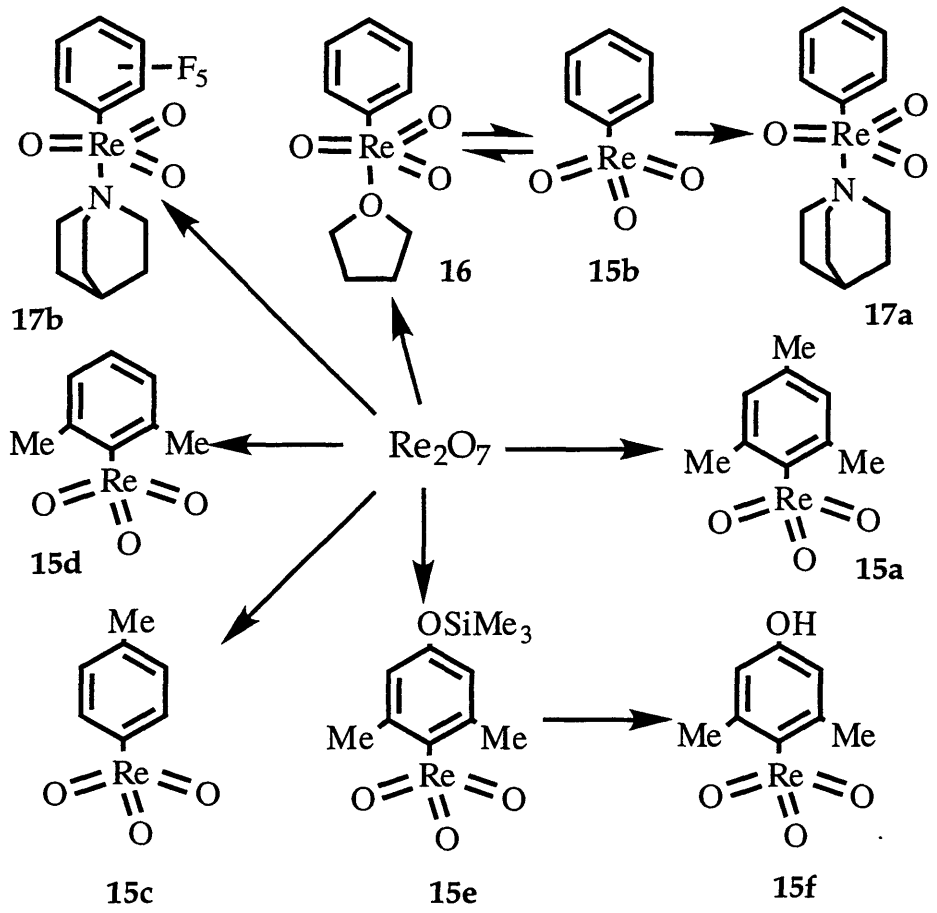
12

If (**5a**) or (**5b**) is treated with an excess of NO, the reaction is much different, forming oxo bridged dimers of the formula $[Re(^tBuN)(O)(\mu\text{-}O)Ar]_2$ [**12a** Ar = xylyl, **12b** Ar = mes].[5] The X-ray structures of (**12a**) and (**12b**)

both show two oxo bridges with a trigonal bipyramidal geometry for each metal with the imido and bridging oxo in the axial positions. The oxo bridges are very asymmetric in (**12b**), differing by 0.57 Å; in the xylyl compound (**12a**) they only differ by 0.21 Å.[5]

Several high oxidation state complexes contain both oxo ligands and multiple σ-aryl ligands. Treatment of $ReOCl_4$ with the appropriate aryl Grignard and subsequent oxidation affords complexes of the form $ReOAr_4$ [**13a** Ar = *o*-methoxyphenyl, **13b** Ar = mes, **13c** Ar = *o*-tolyl].[7] The formation of the stable paramagnetic rhenium(VI) complexes is preceded by the formation of an unstable, unisolable diamagnetic intermediate formulated as $[ReOAr_4]^-$. This reaction only proceeds to form (**13**) when the aryl group has an *ortho* substituent; the products with other aryl groups are not stable to thermal decomposition even below -30 °C. The structure of (**13b**) shows the rhenium in a square pyramidal geometry with the oxo group in the axial site.[7] The structure for (**13c**) shows a similar geometry but with the four identical aryl rings in a propeller arrangement; the Re-C bond lengths in (**13c**) are 0.1 Å shorter on average than those from the mesityl derivative (**13b**).[8]

The other family of rhenium(VI) oxo aryl complexes has the form ReO_2Ar_2 [**14a** Ar = xylyl, **14b** Ar = mes]. The xylyl analog (**14a**) can be formed by the reaction of xylyl Grignard on $ReO_3(OSiMe_3)$,[4] whereas the mesityl analog (**14b**) is formed from ReO_4^- by treatment with mesityl Grignard, followed by bubbling with dioxygen.[7] The structure of (**14b**) shows that the rhenium is almost ideally tetrahedral with a slightly wide O-Re-O angle of 121.5°. The compound is relatively stable to air, most likely due to the protection offered by the *ortho* methyl groups. The structure for (**14a**) is completely analogous to that of (**14b**).



Scheme 1: The chemistry of aryl trioxide complexes

In 1989, Herrmann synthesized the first trioxo rhenium aryl complex. This complex was ReO_3(mes) (**15a**) and was synthesized by treating Re_2O_7 with dimesityl zinc.[9] The X-ray structure of this rhenium complex showed a pyramidal geometry with a short Re-C bond. Three other analogs of ReO_3Ar (**15**) [**15b** Ar = phenyl, **15c** Ar = *p*-tolyl, **15d** Ar = xylyl) were also synthesized by this same route; the colorless (**15b**) and (**15c**), however, were found to be unstable at room temperature, decomposing to biphenyl and rhenium oxides.[10,11] Using the reagent (*p*-Me_3SiO-xylyl)ZnCl, Re_2O_7 can be converted to (**15e**) where the aryl group is transferred from the zinc reagent intact. The X-ray structure for (**15e**)

shows a tetrahedral geometry for rhenium with the aryl ring slightly angled away from the nearest oxo group. Subsequent treatment of (**15e**) with $HCl_{(g)}$ afforded (**15f**), with the replacement of the *p*-Me_3SiO- group by a hydroxyl group.[11]

The rhenium(VII) trioxo aryl compounds have found use in physical inorganic research. Several physical studies on (**15a**) show that the ReO_3 fragment acts as a strong electron withdrawing group on mesitylene; photoelectron spectroscopy, ^{13}C NMR spectroscopy, and cyclic voltammetry were used to support this analysis.[12] More recently, Herrmann has explored the electronics of $RReO_3$ complexes; using many of the preceding complexes, he found that ^{17}O NMR spectroscopic chemical shift was well correlated to the electronic donor properties of R. The phenyl group in (**15a**) was found to be the weakest electronic donor ligand.[13]

These rhenium(VII) trioxo aryl complexes also have the ability to coordinate a fifth ligand. The phenyl complex (**15b**) was first isolated as $ReO_3Ph(THF)$ (**16**). The structure of (**16**) shows that it has a trigonal bipyramidal geometry with the three oxo groups all in the equatorial plane. The THF solvate complex can be converted *in vacuo* to (**15b**), and the reverse reaction merely requires the presence of excess THF.[11] In solution, (**15b**) can be treated with quinuclidine (quin) and can be isolated as the 5-coordinate complex $ReO_3Ph(quin)$ (**17a**). Along similar lines, if $(C_6F_5)_2Zn$ is combined, using a catalytic amount of $ZnCl_2$, with Re_2O_7, $ReO_3(C_6F_5)$ cannot be isolated; however, treatment of the reaction mixture with quinuclidine affords the 5-coordinate $ReO_3(C_6F_5)(quin)$ (**17b**) complex.[11] Herrmann found that the ability to coordinate THF or quinuclidine was related to the sterics interference from the *ortho* position substitutent.

Middle Oxidation State Aryl Complexes (V through II)

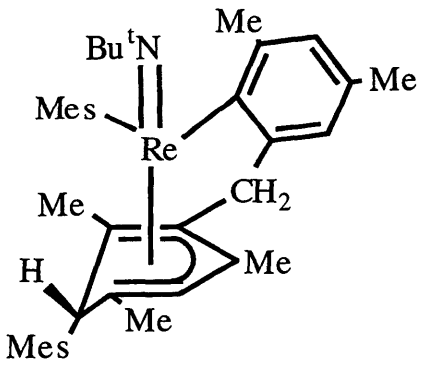
The σ-aryl complexes of rhenium in the middle oxidation states (from V to II) have a larger variety of co-ligands than the higher oxidation state complexes. Several aryl complexes have multiply-bonded ligands, including imidos, oxos, and nitridos; however, the most common ligands in this set of complexes are the phosphine ligands. The complexes in this section will be arranged roughly by decreasing oxidation state and grouped by compounds with similar ligands.

The first few rhenium(V) complexes described here are very similar to those of the higher oxidation state complexes. The following oxo complexes are derived from the same starting materials as the higher oxidation state complexes. The complexes $[ReO_2Ar_2]^-$ (**18**) [**18a** Ar = xylyl, **18b** Ar = mes] are formed by the treatment of Re_2O_7 or ReO_4^- with the appropriate aryl Grignard reagent.[4,5] If the complexes (**18**) are exposed to dioxygen or air, they can be oxidized to ReO_2Ar_2 (**14**) *in situ* or after isolation. These diamagnetic, air-sensitive complexes are isolated as their magnesium salts.

There are also several rhenium(V) imido complexes that are products of the reduction the higher oxidation state imido compounds. While $Re(^tBuN)_2Ar_2$ (**5**) was shown to have both a reversible oxidation and reduction under cyclic voltammetry, only the xylyl analog (**5a**) has an isolable rhenium(V) anion, $[Re(^tBuN)_2(xylyl)_2]^-$ (**19**). Reduction of (**5a**) with sodium/mercury amalgam afforded (**19**); however, the ease with which (**19**) is oxidized back to (**5a**) only allowed for characterization by proton NMR spectroscopy.[5] If (**5a**) is treated with one equivalent of NO, $Re(^tBuN)_2(xyl)_2NO$ (**20**), formally a rhenium(V) complex, is isolated;

however, if an excess of NO is used, the aforementioned rhenium(VI) dimers (**12**) are formed. Based on proton NMR and IR spectroscopies, (**20**) is predicted to be trigonal bipyramidal with two imidos and a bent nitrosyl in the equatorial plane.[5]

Another rhenium(V) complex results from some of the high oxidation state chemistry. As mentioned earlier, when $Re(^tBuN)_2Cl_3$ (**4**) is treated with mesityl Grignard in ether, $Re(^tBuN)_2(mes)_2$ (**5b**) is formed; however, if the reaction is performed in THF a rhenium(V) product $Re(^tBuN)(mes)(C_{17}H_{32})$ (**21**) results. The complex (**21**) has a ligand that is the result of the coupling of two mesityl ligands; one of the two mesityl fragments is coordinated to rhenium in a η^5-fashion. The structure was determined by X-ray crystallography, and the configuration of the chiral carbon was determined;[5] this is the only published X-ray structure of a rhenium(V) aryl complex. The mechanism for the formation of (**21**) is unknown. One hypothesis for the formation of (**21**) requires the rearrangement of an undetected, previously unknown rhenium(V) tris(aryl) complex, $Re(^tBuN)(mes)_3$.



21

In addition to rhenium(V) imido complexes, there are also several nitrido complexes. To form the nitrido aryl compounds, the complex $ReNCl_2(PPh_3)_3$ can be treated with the appropriate aryl lithium salt to

afford $ReNAr_2(PPh_3)_2$ (**22**) [**22a** Ar = phenyl, **22b** Ar = *o*-tolyl, **22c** Ar = *p*-tolyl]. The nitrido remains intact and the phosphines remain *trans*.[14] The geometry of this family of compounds (**22**) was originally theorized, by dipole measurements and analogy, to be square pyramidal with the nitrido at the apex. However, more recently, the crystal structure of $ReNMe_2(PPh_3)_2$ was discovered to have a distorted trigonal bipyramidal geometry with the phosphines in the axial positions; the authors expect (**22**) to be similar in geometry.[15]

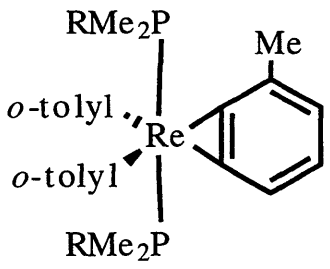
The last of the rhenium(V) complexes all involve the hydrotris(1-pyrazolyl)borate ($HBpz_3$) ligand. The only polyaryl among this family of complexes is $(HBpz_3)ReOPh_2$ (**23**); this can be synthesized from $(HBpz_3)ReOCl_2$ with phenyllithium[16] or by photolyzing $(HBpz_3)ReOI_2$ in benzene.[17] The structure of (**23**) was determined but has not yet been published. The bis(aryl) complex (**23**) can be treated with I_2 to afford $(HBpz_3)ReO(Ph)X$ (**24a**) [X = I].[16] The complex (**24a**), along with (**23**), results from the photolysis of $(HBpz_3)ReOI_2$ in benzene[17] and can be converted to the triflate (**24b**) [X = triflate] by treatment with silver triflate.[16] The triflate (**24b**) can be subsequently treated with a variety of neutral ligands to isolate salts of the form $[(HBpz_3)ReO(Ph)L]^-$ (**25**), where L can be dimethylsulfide, pyridine, or dimethylsulfoxide. Oxo-transfer reagents, such as pyridine-*N*-oxide, react with (**24b**) to produce $[(HBpz_3)ReO_2(Ph)]^-$ as a reactive intermediate.[16]

An entire family of rhenium aryl complexes was synthesized by photolysis of $(HBpz_3)ReO(Cl)I$. By choosing an aromatic solvent in the presence of pyridine, good yields of $(HBpz_3)ReO(Ar)Cl$ (**26**) are obtained; the aryl group for (**26**) can be phenyl, mesityl, *p*-methoxyphenyl, or any of several isomers of xylyl.[16,17] When toluene and fluorobenzene are used as

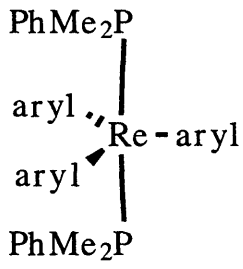
the solvent, mixtures of the *ortho*, *meta*, and *para* substitution are seen for the aryl group in (**26**).[17] These complexes were all synthesized as part of a study examining how aryl groups migrate to oxo groups resulting in phenoxide ligands; the full results of this study are forthcoming.

Only one rhenium(IV) aryl complex has been synthesized. It also happens to be the only homoleptic aryl complex of rhenium. Wilkinson *et al.* synthesized Re(*o*-tolyl)$_4$ (**27**) by treating $ReCl_4(THF)_2$ with *o*-tolyl Grignard.[8] Upon exposure to oxygen, (**27**) is quickly converted to ReO(*o*-tolyl)$_4$ (**13a**). The deep red complex (**27**) was found to have only one unpaired electron and thus a low-spin d^3 configuration. An X-ray structural analysis of (**27**) shows that the rhenium has a distorted tetrahedral geometry with an average Re-C bond length of 2.03 Å.[8]

Upon treatment of (**27**) with two equivalents of either PMe_3 or PMe_2Ph, a rhenium(II) η^2-benzyne complex Re(η^2-$C_6H_3CH_3$)(*o*-tolyl)$_2$($PRMe_2$)$_2$ (**28**) [**28a** R = Me, **28b** R = Ph] is formed.[18] The resulting paramagnetic complexes (**28**) are air stable and were formed by *ortho* hydrogen abstraction and elimination of toluene. A crystal structure of (**28b**) shows that the benzyne takes up approximately one coordination site, and the rhenium is at the center of a distorted trigonal bipyramid.[18] The benzyne complexes (**28**) are relatively unreactive but they can be oxidized under mild conditions to the cations [Re(η^2-$C_6H_3CH_3$)(*o*-tolyl)$_2$($PRMe_2$)$_2$]$^+$ (**29**) [**29a** R = Me, **29b** R = Ph]. An X-ray analysis of (**29a**) shows that the cation is structurally analogous to the neutral benzyne complex.[19]



28

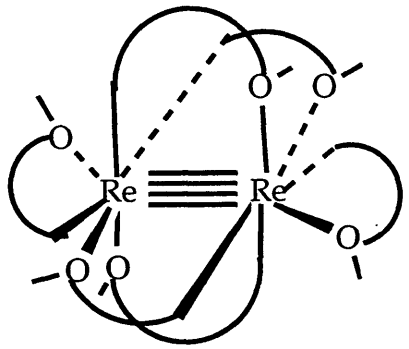


30

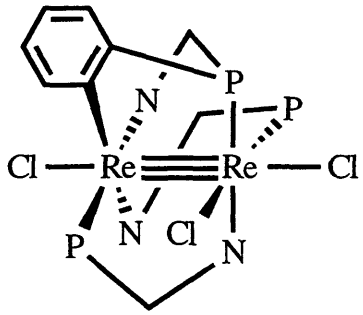
In the same report as the rhenium(V) nitrido complexes, two tris(aryl) complexes were synthesized from $ReCl_3(PEt_2Ph)_3$. Treatment of $ReCl_3(PEt_2Ph)_3$ with aryl lithium salts afforded blue complexes $ReAr_3(PEt_2Ph)_2$ (**30**) [**30a** Ar = phenyl, **30b** Ar = *p*-tolyl].[14] However, when $ReOCl_3(PPh_3)_2$ was treated with phenyllithium, a blue polymer of the formula $[RePh_2(PPh_3)_2]_n$ (**31**) resulted;[14] the insolubility of the polymer allowed for characterization only by elemental analysis and IR spectroscopy. Years later, a structure for (**30a**) was determined (see Figure 2, Chapter 2); the geometry of the rhenium was found to be trigonal bipyramidal with the phosphines occupying the axial positions.[20]

Two dimeric aryl complexes exist, both with an aryl group that is polydentate. Starting from the dimer $Re_2(acetate)_4Cl_2$, treatment with three equivalents of *o*-methoxyphenyl Grignard results in the formation of the dimer, Re_2(*o*-methoxyphenyl)$_6$ (**32**). The proposed structure (*vide infra*), based on carbon and proton NMR spectroscopy, has a quadruple Re-Re bond, and its bridging and terminal ligands interchange on the NMR timescale.[21] Another rhenium dimer with an aryl group results from the orthometallation of diphenylpyridylphosphine (PPh_2pyr); the dimer, $Re_2Cl_3(PPh_2pyr)_2[(C_6H_5)(C_6H_4)Ppyr]$ (**33**), is the result of heating $Re_2Cl_6(PBu_3)_4$ in the presence of excess PPh_2pyr.[22] The structure was determined by X-ray crystallography and it showed two eclipsed

octahedrally bound rheniums in different chemical enviroments. Each rhenium is formally rhenium(II); one metal has two chloride ligands, while the other has the aryl ring and the remaining chloride.



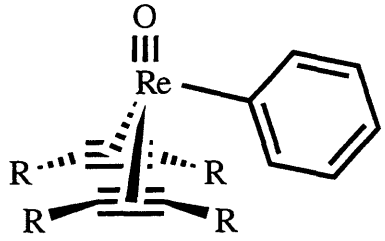
32



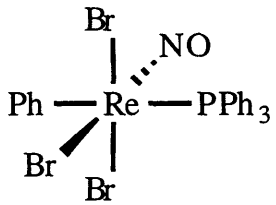
33

P^N = PPh_2pyr

The last few complexes from middle oxidation states of rhenium are all derived from very different sources. The first complex, $Re(O)Ph(RC{\equiv}CR)_2$ (**34**) [**34a** R = Me, **34b** = R = Et], can be synthesized by treating $[Re(O)(RC{\equiv}CR)_2]^+$ with iodobenzene or by alkylating $Re(O)I(RC{\equiv}CR)_2$ with diphenylzinc.[23] Both complexes (**34**) feature two η^2-coordinated alkyne ligands. Lastly, during the reductive nitrosylation of $ReOBr_3(PPh_3)_2$ with NO gas, $ReNO(Ph)Br_3(PPh_3)$ (**35**) was formed as a byproduct. The X-ray crystal structure for this complex shows an octahedral coordination for rhenium with the phosphine *trans* to the phenyl group and a linear nitrosyl ligand.[24]



34



35

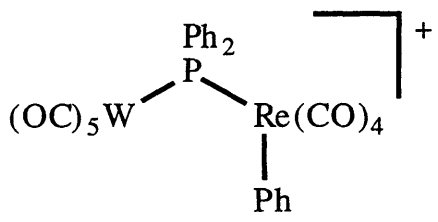
Low Oxidation State Aryl Complexes (I)

The σ-aryl complexes of rhenium(I) have come from a large variety of research groups made by a variety of methods. The majority of the co-ligands accompanying the lone aryl group on these complexes are phosphines and carbonyl ligands. The sources of the aryl group in these complexes include standard metalloaryl reagents such as lithium salts, halogenated reactive aryl rings, and aryl acyl ligands that lose carbon monoxide. Many of these complexes are the results of orthometallation or involve heterobimetallic dimers. The complexes in this section will be arranged by similar ligand motifs.

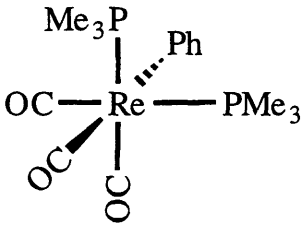
The earliest work concerning rhenium(I) aryl complexes involved a family of polycarbonyl complexes first made by Anisimov in the 1960's. This family of complexes, $Re(CO)_5Ar$ (**36**) [**36a** Ar = *m*-tolyl, **36b** Ar = *p*-tolyl, **36c** Ar = phenyl, **36d**,**e**,**f** Ar = *o*,*m*,*p*-chlorophenyl], were synthesized by heating the associated aryl acyl complexes, $Re(CO)_5C(=O)Ar$, to drive off carbon monoxide.[25,26] The related complex, $Re(CO)_5(C_6F_5)$ (**36g**), was synthesized by a different reaction, the treatment of $ReCl(CO)_5$ with LiC_6F_5.[27] Ellis tried to make (**36c**) using $[Re(CO)_5]^-$ with either $AsPh_4^-$ or PPh_4^- but only $Re_2(CO)_{10}$ was found as a product.[28] In similar work to that of Anisimov, Casey found that [*cis*-$(CO)_5Re(C(=O)Me)(C(=O)Ph)]^-$ could be decarbonylated to yield $[Re(CO)_4(C(=O)Me)Ph]^-$ (**37**).[29] Later studies using ^{13}C labeling of the acylic carbon on the benzoyl ligand showed that the ^{13}C was always incorporated into a CO ligand in the resulting (**37**), thus supporting a dissociative process.[30]

Several carbonyl phosphine complexes can be made by routes similar to that for (**36**). If either $Re(CO)_5$(*p*-chlorophenyl) or $Re(CO)_5$(*m*-

chlorophenyl) is heated in the presence of PPh_3, the complex does not transfer an aryl group to a carbonyl, but it loses a CO to form $Re(CO)_4(PPh_3)Ar$ (**38**) [**38a** Ar = *p*-chlorophenyl, **38b** Ar = *m*-chlorophenyl]. The complexes (**38a**) and (**38b**) also result if the appropriate aryl acyl complexes $Re(CO)_5C(=O)Ar$ are treated initially with PPh_3.[31] A closely related dimeric complex $[(CO)_5W(\mu\text{-}PPh_2)RePh(CO)_4]^-$ (**39**) can be made by the reaction of $(CO)_5W(\mu\text{-}PPh_2)RePh(CO)_4$ (with a Re-W bond) with PhLi.[32]



39

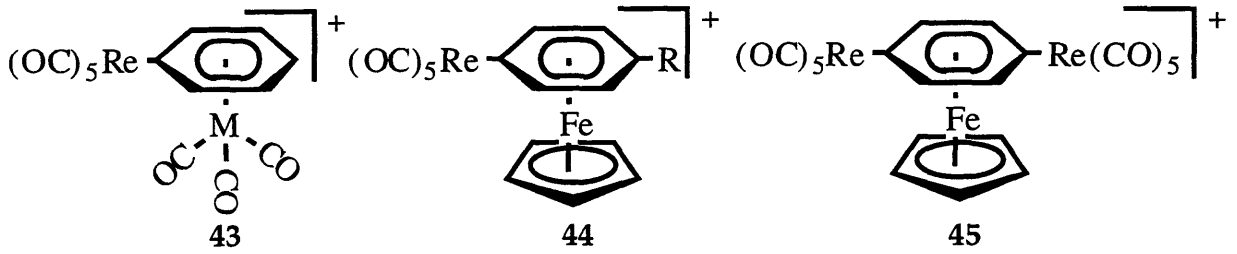


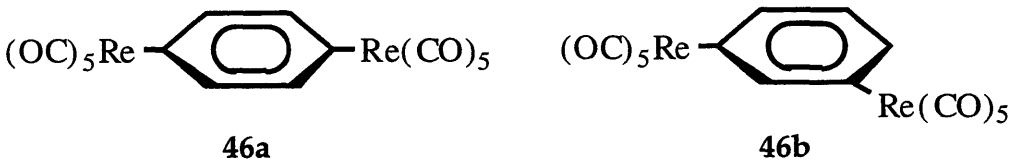
42

If the aforementioned $Re(CO)_5Ph$ (**36c**) is refluxed for several days in THF with $P(OMe)_3$ present, both the *cis* and *trans* isomers of $RePh(CO)_4P(OMe)_3$ (**40**) are formed; the *cis* isomer is the major isomer.[33] However, in order to form the PMe_3 analog of (**40**), *cis*-$ReBr(CO)_4PMe_3$ must be treated with CuPh to yield *cis*-$RePh(CO)_4PMe_3$ (**41**). By analogy, if *fac*-$ReBr(CO)_3(PMe_3)_2$ is treated with CuPh, *fac*-$RePh(CO)_3(PMe_3)_2$ (**42**) is obtained in good yield.[33] These complexes were all synthesized to study the acidolysis of the aryl-metal bonds in Group 7.

The $Re(CO)_5$ fragment can be attached to aryl groups on homometallic and hetereometallic clusters. The complex $Re(CO)_5Ph$ (**36c**) reacts with either $[M(CO)_5]^-$ [M = Re or Mn] anion; the product is a dimer, $[(CO)_5Re(\mu\text{-}\eta^1\text{:}\eta^6\text{-}C_6H_5)M(CO)_3]^+$ (**43**) [M = Re or Mn], where the anion has attacked the phenyl ring yielding an η^6-benzene, which also binds in an η^1-fashion to the other metal center.[34] Similarly, if $[Fe(\eta^6\text{-}p\text{-}RClC_6H_4)Cp]^+$ [Cp =

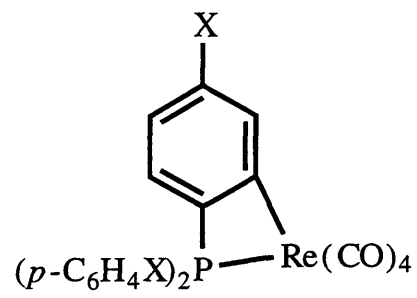
cyclopentadienyl; R = H or Me] is treated with $[Re(CO)_5]^-$, the result is a dimer, $[(CO)_5Re(\mu\text{-}\eta^1\text{:}\eta^6\text{-}p\text{-}RC_6H_4)FeCp]^+$ (**44**) (R = H, Me) where the rhenium anion has replaced the chlorine of the η^6-benzene ring on the iron fragment. If $Fe(\eta^6\text{-}p\text{-}Cl_2C_6H_4)Cp]^+$ is used instead, a 50/50 mixture of products is obtained; (**44**) [R = Cl] as well as the trimer, $[((CO)_5Re)_2(\mu\text{-}\eta^1,\eta^1\text{:}\eta^6\text{-}p\text{-}C_6H_4)FeCp]^+$ (**45**), where both chlorines are replaced by the rhenium anion.[34] A similar arrangement of rhenium atoms on a phenyl ring was obtained by decarbonylation; heating of the biacyl complex $[(CO)_5Re]_2(\mu\text{-}(C{=}O)_2\text{-}C_6H_4)$, either the *meta* or the *para* isomer, yields the dimers $[(CO)_5Re]_2(\mu\text{-}\eta^1,\eta^1\text{-}p\text{-}C_6H_4)$ (**46a**) and $[(CO)_5Re]_2(\mu\text{-}\eta^1,\eta^1\text{-}m\text{-}C_6H_4)$ (**46b**), via the loss of both CO groups from the biacyl bridge.[35]



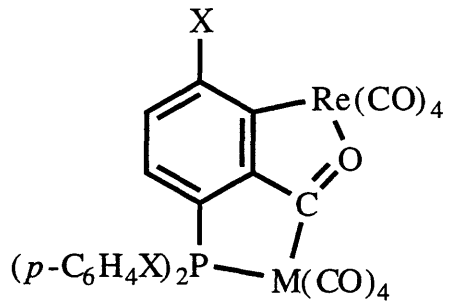


Several of the rhenium(I) aryl complexes result from orthometallation of ligands either present in solution or already coordinated to the metal. Kaesz was able to synthesize $CH_3Re(CO)_4(PR_3)$ [R = phenyl or *p*-fluorophenyl], which loses methane upon heating, forming the orthometallated product $Re(CO)_4(R'PR_2)$ (**47**) [**47a** R = phenyl, **47b** R = *p*-fluorophenyl] (*vide infra*).[36] Either orthometallated product (**47**) can then be treated with $CH_3M(CO)_5$ [M = Re or Mn] at elevated temperatures, resulting in the loss of another methane molecule and the coupling of one

CO to the aryl ring to form the bridged dimers $ReM(CO)_8(COR'PR_2)$ (**48**) [M = Re or Mn] (*vide infra*).[36]

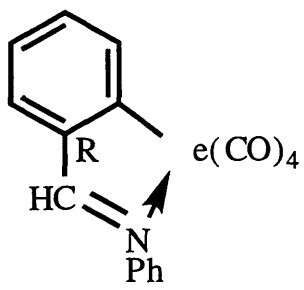


47

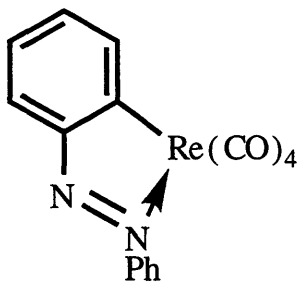


48

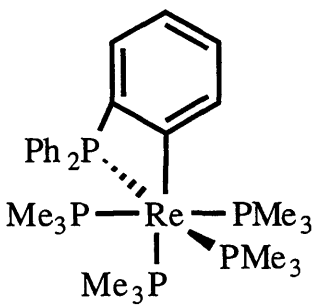
A second route to orthometallated products starts directly from $Re_2(CO)_{10}$; if $Re_2(CO)_{10}$ is stirred with azobenzene, then the product is $(CO)_4Re(\eta^1\text{-}o\text{-}C_6H_4N{=}NPh)$ (**49**). In complex (**49**), the rhenium is coordinated through both the aryl ring and the β-nitrogen atom.[37] A similar reaction can be performed by treating $Re(CO)_5Me$ with benzylideneaniline; the result is $(CO)_4Re(\eta^1\text{-}o\text{-}C_6H_4C(H){=}NPh)$ (**50**), an analog of (**49**) with a -CH- fragment replacing the α-nitrogen.[38] Another type orthometallation reaction occurs when $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$ is heated in benzene in the presence of PMe_3; the orthometallated product, $Re(PPh_2(\eta^1\text{-}o\text{-}C_6H_4))(PMe_3)_4$ (**51**), results after loss of THT and PPh_3.[39] An X-ray structure of (**51**) shows the rhenium in an octahedral coordination with a 65.1° strained angle in the ring of the 4-membered metallacycle.



49



50



51

The remaining complexes of rhenium(I) aryls are loosely related by the presence of π-bonded rings. If rhenium atoms, benzene, and PMe_3 are co-condensed at low temperature, the main product is the $[Re(\eta^6\text{-benzene})(PMe_3)_2]_2$ dimer; however, 2% of the yield is the aryl complex $Re(\eta^6\text{-benzene})(PMe_3)_2Ph$ (**52**).[40] The complex CpReNO(CO)Cl can be treated with a variety of arylcopper(I) reagents to afford CpReCO(NO)Ar (**53**) (Ar = phenyl, *o*,*m*,*p*-tolyl, *m*,*p*-$CF_3C_6H_4$). These complexes (**53**) were only attainable in low yields or not at all from the treatment of CpReNO(CO)X [X = Cl, Br or I] with aryl Grignards.[41] These complexes (**53**) were used in a study of the equilibrium of converting η^1-aryls to η^2-arenes under protic conditions; for these complexes, this reaction resulted in mixtures of isomers of (**53**) when deprotonated.[42] A slightly different aryl complex was made in a similar method starting from $CpReNO(PPh_3)Cl$; treatment with CuPh afforded the chiral $CpReNO(PPh_3)Ph$ (**54**) as a racemic mixture. The complex resolves itself upon crystallization; the structure shows a piano stool formation with the aryl ring twisted such that its *ipso* carbon is between the nitrosyl and phosphine ligands.[43]

Rhenium-Carbon Bonds in Aryl Complexes

There are a limited number of rhenium aryl complexes for which there is available X-ray crystallographic structural data. The twenty-three known structures contain forty-one unique rhenium-carbon bond distances to the *ipso* carbon on the aryl ring. These lengths are summarized in Table 1 at the end of this section. These values range from a low of 2.006 Å in ReO_3(mes) (**15a**) to a high of 2.216 Å for one of the bonds in $ReO(mes)_4$ (**13b**). It is more appropriate to designate 2.205 Å

from $ReNO(Ph)Br_3(PPh_3)$ (**35**) as the high end value for the range; the bond length value from (**13b**) is clouded by an occupancy disorder in the structure which yields eight different bond distances averaging 2.17 Å. The average value for the lengths in all twenty-three complexes is 2.11 Å with a standard deviation of 0.0592 Å.

There appears to be no correlation between oxidation state and the length of the rhenium-carbon bond length. While some of the bonds in complexes fall at the low end of the range because of π-backbonding between filled d orbitals and the π* of the aryl group as in $RePh_3(PEt_2Ph)_2$ (**30a**), the complex ReO_3(*p*-Me_3SiO-xylyl) (**15e**) also shows a very short Re-C bond but cannot backbond because it is d^0. Also, complexes with and without *ortho* substitutents on the aryl rings fall at both ends of the range for the Re-C bond lengths, ruling out a steric effect.

Conclusion

This review has shown the wide variety of σ-aryl complexes ranging from the high to the low oxidation states of rhenium. Many of these compounds were synthesized as logical partner to the known related alkyl complexes such as for the high oxidation state complexes of Herrmann and Wilkinson. Many of the others were serendipitous results of non-σ-aryl chemistry. The majority of these complexes are stable to air and other harsher conditions, which is contrary to the relative instability of the related alkyl complexes. Thus, due to their stabilty, σ-aryl complexes of rhenium often do not undergo many reactions to transform them into novel complexes, but they have found use in several physical inorganic and mechanistic studies.

Table 1: Rhenium-carbon(aryl) bond lengths from crystal structures

Molecular Formula	Complex Number	Oxidation State	Re-C (aryl) Length (Å)
$Re(^tBuN)_3mes$[5]	**2 b**	VII	2.097(36)
$Re(^tBuN)_2Cl_2(o\text{-tolyl})$[4]	**3 a**	VII	2.148(8)
$Re(^tBuN)_2Cl_2Ph$[6]	**3 d**	VII	2.125(12)
$Re(^tBuN)_2(mes)_2$[5]	**5 b**	VI	2.105(13)
			2.096(14)
$Re_2O(^tBuN)_3Br(mes)(C_9H_{10}O)$[5]	**1 1**	VI	2.149(16)
$[Re(^tBuN)(O)(\mu\text{-}O)xylyl]_2$[5]	**1 2 a**	VII	2.147(10)
$[Re(^tBuN)(O)(\mu\text{-}O)mes]_2$[5]	**1 2 b**	VII	2.090(10)
$ReO(mes)_4$[7]	**1 3 b**	VI	2.146(8)*
			2.173(9)
			2.194(8)
			2.089(8)
			2.141(8)
			2.191(8)
			2.197(8)
			2.216(8)
$ReO(o\text{-tolyl})_4$[8]	**1 3 c**	VI	2.063(6)
$ReO_2(xylyl)_2$[4]	**1 4 a**	VI	2.065(7)
			2.069(7)
$ReO_2(mes)_2$[7]	**1 4 b**	VI	2.062(6)
$ReO_3(mes)$[11]	**1 5 a**	VII	2.063(7)**
			2.006(9)
			2.075(8)

Molecular Formula	Complex Number	Oxidation State	Re-C (aryl) Length (Å)
ReO_3(*p*-Me_3SiO-xylyl)[11]	**15e**	VII	2.04(1)
$ReO_3Ph(THF)$[11]	**16**	VII	2.071(3)
Re(^tBuN)(mes)($C_{17}H_{32}$)[5]	**21**	V	2.191(8)
			2.159(7)
Re(*o*-tolyl)$_4$[8]	**27**	IV	2.020(9)
			2.033(8)
			2.038(9)
			2.028(9)
Re(η^2-$C_6H_3CH_3$)(*o*-tolyl)$_2$(PMe_2Ph)$_2$[18]	**28b**	II	2.120(7)
			2.115(7)
[Re(η^2-$C_6H_3CH_3$)(*o*-tolyl)$_2$(PMe_3)$_2$]$^{+}$[19]	**29a**	III	2.08(1)
			2.09(1)
$RePh_3(PEt_2Ph)_2$[20]	**30a**	III	2.029(10)
			2.024(11)
$ReNO(Ph)Br_3(PPh_3)$[24]	**35**	III	2.205(9)
Re(PPh_2(η^1-*o*-C_6H_4))(PMe_3)$_4$[39]	**51**	I	2.17(1)
$CpReNO(PPh_3)Ph$[43]	**54**	I	2.139(6)

* There are two sets of lengths due to a disorder in the crystal of (**13b**).[7]

** The first report of (**15a**) shows lengths of 2.00(1) and 2.06(1). The second report has the values above which are for the three unique distances from two different lattice types. [9]

References

(1) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189-90.

(2) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127-137.

(3) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1955**, *77*, 3421-3422.

(4) Longley, C. J.; Savage, P. D.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1079-1088.

(5) Gutierrez, A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 2081-2096.

(6) Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1989**, *8*, 2657-2670.

(7) Stravropoulos, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc. Dalton Trans.* **1987**, 169-175.

(8) Savage, P. D.; WIlkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc. Dalton Trans.* **1988**, 669-673.

(9) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13-C17.

(10) Herrmann, W. A.; Romao, C. C.; Fischer, R. W.; Kiprof, P.; de Meric de Bellefon, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185-187.

(11) de Meric de Bellefon, C.; Herrmann, W. A.; Kiprof, P.; Whitaker, C. R. *Organometallics* **1992**, *11*, 1072-1081.

(12) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527-6537.

(13) Herrmann, W. A.; Kuhn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1995**, *485*, 243-251.

(14) Chatt, J.; Garforth, J. D.; Rowe, G. A. *J. Chem. Soc. (A)* **1966**, 1834-1836.

(15) Yam, V. W.-W.; Tam, K.-K.; Lai, T.-F. *J. Chem. Soc. Dalton Trans.* **1993**, 651-652.

(16) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119-12133.

(17) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 2219-2220.

(18) Arnold, J.; WIlkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1988**, 704-705.

(19) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Organometallics* **1989**, *8*, 415-420.

(20) Carroll, W. E.; Bau, R. *J. Chem. Soc. Chem. Comm.* **1978**, 825-826.

(21) Jones, R. A.; Wilkinson, G. *J. Chem. Soc. Dalton Trans.* **1979**, 472-477.

(22) Barder, T. J.; Tetrick, S. M.; Walton, R. A.; Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 4090-4091.

(23) Conry, R. R.; Mayer, J. M. *Organometallics* **1991**, *10*, 3160-3166.

(24) Dziegielewski, J. O.; Machura, B.; Marek, J. *Polyhedron* **1996**, *15*, 3713-3716.

(25) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Ioganson, A. A. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1968**, *8*, 1801-1803.

(26) Denisovich, L. I.; Ioganson, A. A.; Gubin, S. P.; Kolobova, N. E.; Anisimov, K. N. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1969**, *9*, 218-222.

(27) Jolly, P. W.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5831.

(28) Ellis, J. E. *J. Organomet. Chem.* **1976**, *111*, 331-337.

(29) Casey, C. P.; Scheck, D. M. *J. Organomet. Chem.* **1977**, *142*, C12-C14.

(30) Casey, C. P.; Baltusis, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6347-6353.

(31) Anisimov, K. N.; Kolobova, N. E.; Ioganson, A. A. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1969**, *9*, 1620-1623.

(32) Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68-74.

(33) Fronko, R. M. Ph.D. Thesis, University of Wisconsin - Madison, 1984.

(34) Niemer, B.; Weidmann, T.; Beck, W. *Z. Naurforsch.* **1992**, *47b*, 509-516.

(35) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Ioganson, A. A. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 358-360.

(36) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066-3072.

(37) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. (A)* **1970**, 3204-3209.

(38) Bennett, R. L.; Bruce, M. I.; Goodall, B. L.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* **1972**, 1787-1791.

(39) Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10767-10775.

(40) Green, M. L. H.; O'Hare, D.; Wallis, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 233-234.

(41) Sweet, J. R.; Graham, W. A. G. *J. Organometal. Chem.* **1983**, *241*, 45-51.

(42) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305-6.

(43) Agbossou, S. K.; Bodner, G. S.; Patton, A. T.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1184-1191.

Chapter 2

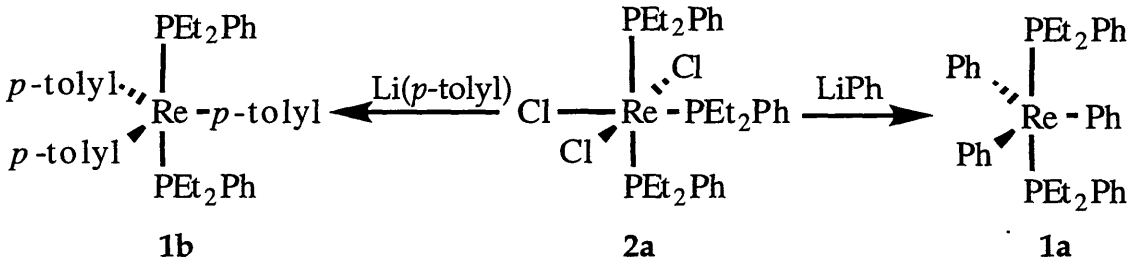
The Synthesis of Rhenium Polyaryl Complexes

Introduction

This research is an investigation into the synthesis of polyaryl rhenium species, specifically compounds of the form $Re(aryl)_3L_2$. The majority of rhenium complexes with η^1-aryl ligands either have only one aryl group or have several aryl groups with oxo or imido functionalities present. These complexes also tend to be of the highest (V though VII) and lowest (I) oxidation states for rhenium. Previously, there were only two known complexes of the form $Re(aryl)_3L_2$ (where L was PEt_2Ph) and no work had been done concerning their reactivity.

Discussion

Chatt made Re(*p*-tolyl)$_3$(PEt$_2$Ph)$_2$ (**1a**) and RePh$_3$(PEt$_2$Ph)$_2$ (**1b**) in the early 1960's by the reaction of ReCl$_3$(PEt$_2$Ph)$_3$ (**2a**) with an excess of *p*-tolyllithium or phenyllithium, respectively (Scheme 1).[1] The compounds were characterized but the chemistry of these compounds was not studied at this time; the crystal structure of RePh$_3$(PEt$_2$Ph)$_2$ (**1b**) was not solved until sixteen years later.[2] Afterward, no work on or related to these complexes was reported in the literature.



1b **2a** **1a**

Scheme 1: Chemistry of Chatt *et al.*

In the chemistry of rhenium(III), a very useful correlation between the common geometric structures and electron structure accounts for the magnetism of these molecules (including (**1**) and (**2**)). Since rhenium(III) has four d-electrons to place into its appropriate ligand field theory derived diagram, it can be seen in Figure 1 that both trigonal bipyramidal and 7-coordinate geometries should exhibit diamagnetic characteristics, as the lowest doubly-degenerate E set should be completely filled. Consequently, an octahedral complex should have two unpaired electrons in its lowest energy configuration (assuming a low-spin complex). This electronic configuration, in complexes such as (**2a**) and ReCl$_3$(PMe$_2$Ph)$_3$ (**2b**), yields hyperfine contact shifts of the resonances in NMR spectroscopy

due to interaction between the nuclei and the unpaired electrons. Rhenium(III) exhibits relatively narrow line widths as compared to other contact shifted species such as those of ruthenium(III).[3]

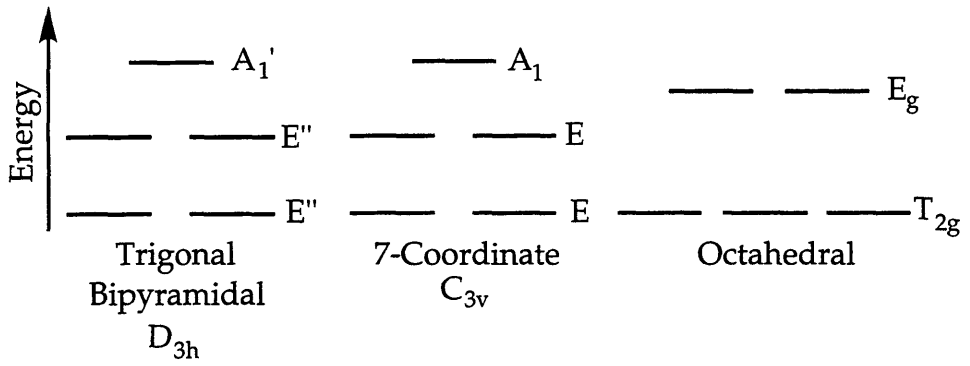
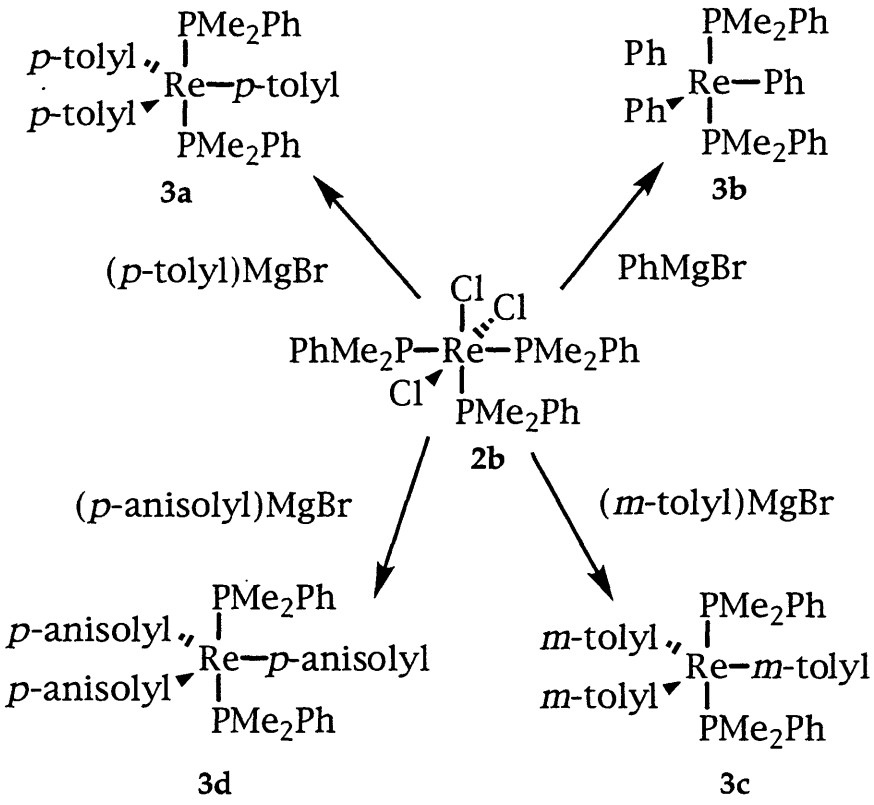


Figure 1: d orbital diagrams common for Group 7

Using $ReCl_3(PMe_2Ph)_3$ (**2b**) and the appropriate Grignard reagents in place of the lithium salts, several analogs of the Chatt compounds were synthesized (Scheme 2); the reaction is nearly complete within twenty minutes. These include Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3a**), $RePh_3(PMe_2Ph)_2$ (**3b**), and Re(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3c**). One benefit of using (**2b**) as the starting synthon is that dimethylphenyl phosphine is considerably cheaper and easier to obtain commercially than the ethyl analog. Aryl Grignard reagents were used because a greater variety of commercially available Grignard reagents exists compared to the aryl lithium reagents, and aryl Grignard reagents are simpler to make than the analogous lithium reagents. These complexes (**3**) are stable in aqueous solution, and so can be separated by extraction with water to eliminate any excess Grignard reagent and remove the magnesium halide salt into the aqueous layer. If there is still a residual salt, the compounds are all easily recrystallized from cold hydrocarbon solutions or from toluene/acetonitrile.



Scheme 2: Trigonal bipyramidal rhenium(III) aryl complexes

While extracting the toluene solutions into water, the complexes (**3**) are exposed to air. Fortunately, although these compounds are slightly air sensitive, they are stable in solution for at least a day in the presence of air. These compounds are stable in the solid state indefinitely under an inert atmosphere and for weeks in air. The stability of these complexes will be discussed in Chapter 3. These reactions are not quantitative; the yields range from 50% up to 80%. Washing the reaction mixtures with methanol removes an orange-brown solution, which contains some unreacted (**2b**), even if large excesses of Grignard reagents are used, along with a brown non-homogenous oil. It is fortunate that (**2b**) reacts with aryl Grignard reagents and lithium salts; as a general rule, it is a relatively unreactive complex.[4]

All of these compounds, (**1**) and (**3**), are highly colored; the colors range from blue to purple. The colors of these complexes are intense and due to symmetry and parity allowed d-d transitions. A YAeHMOP[5] calculation using the coordinates from the Cambridge Crystallographic Database for (**1b**) showed that the HOMO is a degenerate set of orbitals that are almost entirely d_{xz} and d_{yz} in character. The LUMO, comprised of the d_{xy} and d_{x2-y2} set, is also a degenerate set of orbitals exhibiting very little mixing with the ligand orbitals. Since these frontier orbitals show almost no mixing with the π-systems of the aryl rings, the electronic transition that leads to the colors of these complexes should not be due to a ligand-metal interaction.

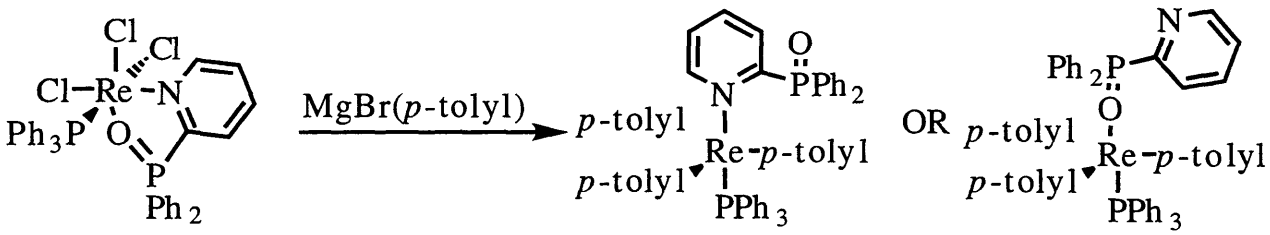
One of the initial goals of this project was to use rhenium precursors to achieve low coordinate (three and four) aryl complexes. If $ReCl_3(PMe_2Ph)_3$ were to react with an aryl Grignard reagent with a large steric presence, *i.e.*, groups in the *ortho* position, rather than adopting the trigonal bipyramidal geometry seen in (**1**) and (**3**), one or both of the phosphines might be lost and the low coordinate species would result. The resulting three-coordinate rhenium(III) product would join Wilkinson's Re(*o*-tolyl)$_4$ as the sole representatives of homoleptic rhenium aryl complexes.[6] The Re(*o*-tolyl)$_4$ complex is quite interesting in its own right; it reacts readily with PMe_3 to eliminate toluene and results in an η^2-benzyne complex of rhenium(II) which is geometrically similar to the family of trigonal bipyramidal compounds (**1**) and (**3**).[7,8] These complexes all contain phosphine ligands in the two axial positions and aryl rings in the three equatorial positions; the neutral η^2-benzyne takes the place of an anionic η^1-aryl ring.

Variation in the aryl substituent can be obtained by following the synthetic route from $ReCl_3(PMe_2Ph)_3$ using different Grignard reagents, although the phosphine ligands cannot be varied. During the reaction, one equivalent of phosphine is lost and complexes of the general formula $Re(aryl)_3(PMe_2Ph)_2$ are formed when phenyl, *p*-tolyl, or *m*-tolyl Grignard reagents are used. However, 2,4,6-mesityl and *o*-tolyl Grignard do not react with $ReCl_3(PMe_2Ph)_3$, even if the ether that the Grignard is dissolved in is removed and the solutions are heated; the starting material (**2b**) can be recovered nearly quantitatively from the reaction mixtures. As both these unreactive reagents have at least one methyl group *ortho* to the reactive carbon, the mechanism of attack of the Grignard reagent on the rhenium center must be hindered by substitution in the *ortho* position on the ring. This result was unexpected, but molecular models suggest a steric crowding would exist. Using 2,4,6-mesityllithium in place of the Grignard reagent also results in no reactivity. Additionally, the 3,5-xylyl Grignard also shows no reactivity with (**2b**). As 3,5-xylyl has no *ortho* substituents but instead two *meta* substituents, the steric requirements for reactivity can be more narrowly defined. The *m*-tolyl reacts but the 3,5-xylyl does not; therefore, even substitution of two methyl groups in the *meta* position must provide enough steric encumbrance to prevent approach to the rhenium center.

The *p*-tolyl Grignard reagent has been used for these reactivity studies for several reasons. The *p*-tolyl groups present excellent proton NMR characteristics. The two sets of doublets in the aryl region (roughly between 7 and 8 ppm) of the proton NMR spectrum are very distinctive. The singlet for the methyl peak in the *para* position is in an area (around 2 ppm) where other resonances seldom occur. When there are mixtures, the

number of methyl peaks is indicative of the number of aryl groups in the mixture; the coupling constants for the doublets can be used to match the sets of doublets. In addition, the doublet for the *ortho* protons tends to be shifted upfield out of the usual aryl range when it is coordinated to a metal center. Most of the *ortho* proton resonances for the different aryl complexes in this chapter (phenyl, *m*-tolyl, and *p*-tolyl) can be found between 6.07 and 6.50 ppm, with the remaining resonance just slightly out of the range at 6.70 ppm. A further advantage is that the *p*-tolyl Grignard seems to have the best reactivity with different starting materials. Also, the decomposition of many of the aryl complexes results in the formation of biphenyls; the 4,4'-dimethylbiphenyl formed from the *p*-tolyl groups is very easy to detect by NMR spectroscopy or even by aroma.

The complex $Re(PPh_3)(O{=}PPh_2pyr)Cl_3$ (**4**) is also rhenium(III), but unlike (**2b**) it has one phosphine ligand and one chelating nitrogen-oxygen ligand. When (**4**) is suspended in toluene and exposed to greater than three equivalents of *p*-tolyl Grignard, a reaction slowly occurs, creating a brown solution. A small amount (under 20%) of the solid isolated from this solution is pale blue; the remainder is a mixture of 4,4'-dimethylbiphenyl, magnesium halide, and a brown residue containing no *p*-tolyl groups. This blue complex (**5**) was found, via mass spectral analysis, to have a molecular formula and fragmentation pattern corresponding to $Re(p\text{-tolyl})_3(PPh_3)(O{=}PPh_2pyr)$, although it analyzes low for carbon. However, its proton NMR spectrum shows a ratio for the chemically equivalent, coordinated *p*-tolyl resonances to the pyridyldiphenylphosphine pyridyl ring resonances of three to one. The *p*-tolyl resonances appear as two sets of doublets at 6.0 and 6.8 ppm, with a resonance for the methyl around 2.3 ppm.



Scheme 3: Possible geometries for (**5**)

An important observation is that the NMR spectrum is not contact shifted; this indicates that the complex is rhenium(III) but diamagnetic, and thus must be 7 or 5 coordinate. However, if the three *p*-tolyl rings are equivalent, they must be in a trigonal plane of a 5-coordinate trigonal bipyramidal complex. The triphenylphosphine and the pyridylphosphine oxide must be axial. Since the pyridylphosphine can bind through either the pyridyl nitrogen or the oxygen, there are two possible coordination geometries (Scheme 3). The IR spectrum for (**5**) shows stretches between 1000 and 1100 cm^{-1}, which is generally indicative of coordinated phosphine oxides;[9,10] however, these absorbances are too weak to be conclusively attributed to phosphine oxide stretches. Another factor supporting the 5-coordinate geometry is the stability of (**5**). In the solid state, (**5**) is stable indefinitely; however, in solution, unless kept at -40 °C, it decomposes to a pale brown oil and 4,4'-dimethylbiphenyl. While the family of rhenium(III) tris(aryl) complexes is susceptible to the reductive elimination of biphenyl, it usually takes an external ligand or reactant to do so; complex (**5**) has an internal source of a "sixth ligand" in its uncoordinated portion of the pyridyl phosphine ligand that can promote this decomposition.

The complex $ReBr_3(THT)_3$ (**6**), (THT = tetrahydrothiophene) was chosen as an alternative starting material since the phosphine complex

(**2b**) only allows for the synthesis of aryl complexes having basic phosphine ligands (PMe_2Ph and PEt_2Ph). Thus, other rhenium(III) synthons with non-phosphine ligands were sought. The hope was that the THT ligands might allow for more sterically hindered Grignard reagents to react with a Re(III) center. Unfortunately, neither the 2,4,6-mesityl Grignard nor its lithium salt reacts with $ReBr_3(THT)_3$ (**6**) nor does the 3,5-xylyllithium reagent. However, when the reaction mixture from 2,4,6-mesityllithium and $ReBr_3(THT)_3$ (**6**) was allowed to sit in air for an extended period of time, the rhenium(V) oxo bridged dimer, $[Re(=O)Br_2(THT)_2]_2O$, formed as green crystals. A preliminary structure was determined via X-ray crystallography showing the above dimeric formula, and thus no coordinated aryl rings present. This dimeric oxo bridged structure is a very common motif in rhenium(V) chemistry.[11]

The *p*-tolyl Grignard does react with $ReBr_3(THT)_3$ (**6**) but only if all the ether is removed from the Grignard reagent. If ether is removed from the Grignard reagent *in vacuo*, it can be redissolved in toluene and $ReBr_3(THT)_3$ (**6**) can be added. Once (**6**) begins to dissolve in the toluene, the Grignard reacts and a blue air-sensitive intermediate complex is formed. This compound, Re(*p*-tolyl)$_3$(THT)$_2$ (**7**), is analogous to complex (**3a**) with an equatorial arrangement of three *p*-tolyl rings and two THT ligands occupy the axial sites of a trigonal bipyramid, in lieu of the phosphine of (**3a**).

The existence of an unbroadened, non-contact shifted proton NMR spectrum for (**7**) supports the trigonal bipyramidal structure and the diamagnetic electron configuration for a d^4 system. With a ratio of three equivalent aryl rings to two equivalent THT rings, the proton NMR spectrum further supports the trigonal bipyramidal geometry of (**7**). The

high air sensitivity of (**7**) makes purification and crystallization difficult; this was compounded by a short life span in both solid state and solution. The formulation of (**7**) as Re(*p*-tolyl)$_3$(THT)$_2$ was later confirmed by both reactivity studies as well as an eventual X-ray structural analysis which will be subsequently discussed.

One hindrance to the isolation of (**7**) is its solubility. It is readily soluble in benzene, toluene, pentane, diethyl ether, hexane, and heptane; the family of phosphine complexes (**3**) are much less soluble and are easily crystallized from toluene/hydrocarbon systems. Under rigorous air-free conditions, a concentrated solution of (**7**) in pentane produced small purple crystals when chilled to -10 °C. The molecular structure of Re(*p*-tolyl)$_3$(THT)$_2$ (**7**) was investigated by a single crystal X-ray diffraction study.

Before discussing the structure of (**7**), it would be fruitful to look at the structure for RePh$_3$(PEt$_2$Ph)$_2$ (**1b**). The structure for (**1b**) was determined by Carroll and Bau in 1978 (Figure 2). It shows a nearly planar array of equatorial aryl rings and a nearly ideal trigonal bipyramidal geometry. By analogy, the complexes of the family (**3**) are expected to be very similar in structure. The Re-C bonds are shorter than expected [2.027(3) Å average][2] for (**1b**); Bau rationalizes this by invoking strong π bonding between the filled d_{xz} and d_{yz} orbitals on rhenium and the π^* systems of the aryl rings. The structure shows the C_2 axis of symmetry running through one of the aryl rings. The rings of (**1b**) are found to be in a propeller arrangement with torsional angles of 4.5°, 4.5°, and 18.6°;[2] Bau claims this is a compromise arrangement that the rings adopt to balance the π overlap with the steric interaction between *ortho* hydrogens that would result in complete coplanarity of the rings. Bau

calculated that if the rings were planar the hydrogen contacts would be an intolerable 1.63 Å rather than the 2.16 Å that they are after the small tilting of the rings.[2] However, the aforementioned YAeHMOP results show that there are no energetically accessible π orbtials from the aryl rings that can have bonding interactions with the valence d orbitals. The reason for the short bond length can be best explained by the difference in radii between a rhenium(III) five-coordinate structure and one of higher coordination geometry (Shannon-Prewitt radii).

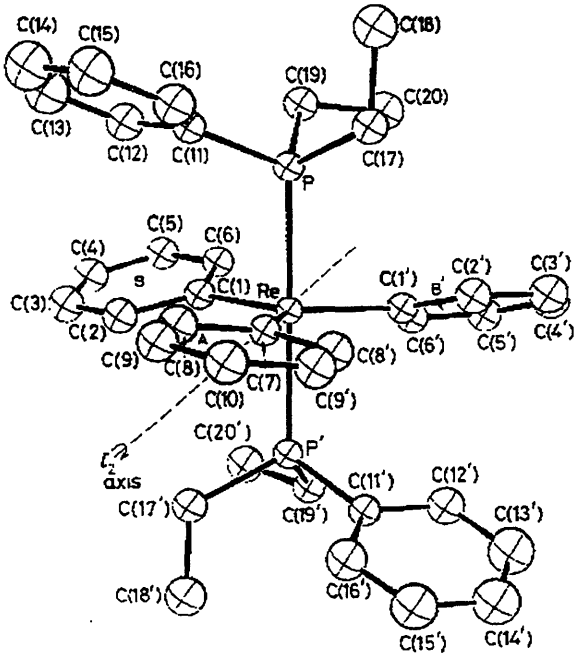


Figure 2: Structure of (**1b**) $RePh_3(PEt_2Ph)_2$[2]

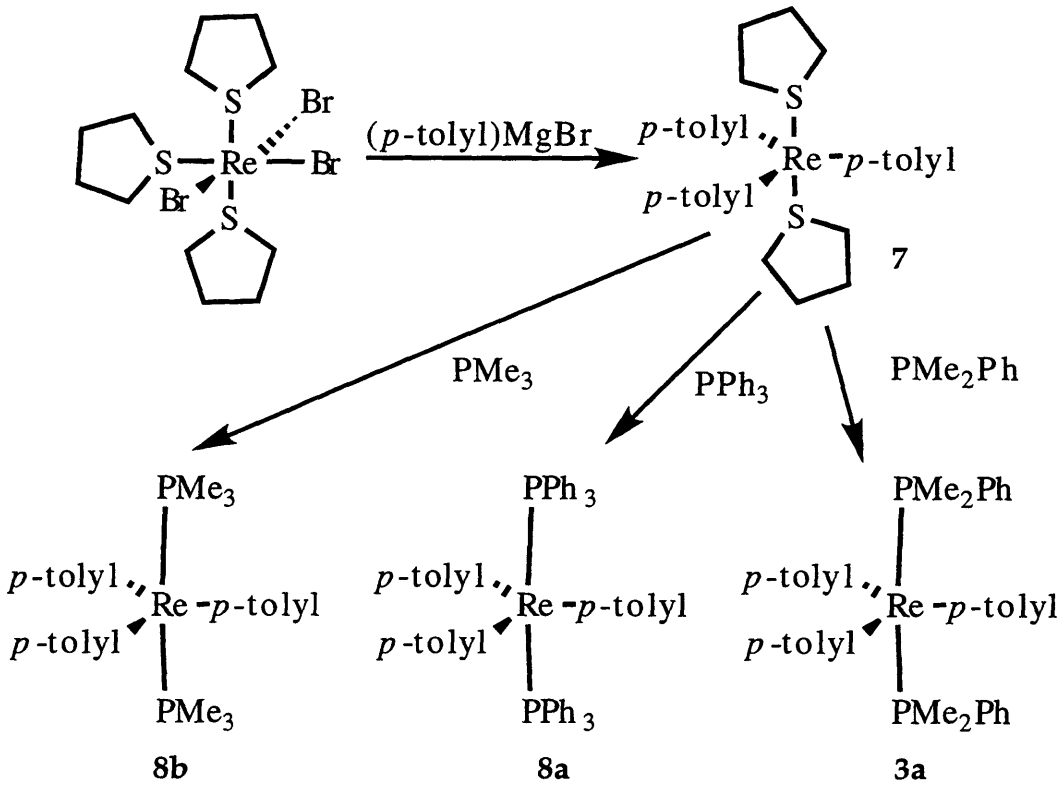
Crystals of Re(*p*-tolyl)$_3$(THT)$_2$ (**7**), grown from cold heptane, were suitable for an X-ray diffraction analysis. Data collection parameters are given in Table 1 and the experimental section. A full set of bond lengths, angles, and positional parameters is given in Tables 2, 3, and 4 at the end of the chapter along with the ORTEP diagram (Figure 4). The ORTEP shows a side-on view of the trigonal bipyramidal geometry. The S-Re-S bond is

nearly linear at 174°, and the three angles formed by the ring *ipso* carbons and rhenium are between 119° and 121°, forming a well-spaced equatorial plane. At 2.37 Å, the rhenium-sulfur bond lengths are standard and not very different from the length of 2.39 Å for the rhenium-phosphorus distance in (**1b**).

In the structure of (**7**), the three unique Re-C bonds range from 2.03 to 2.06 Å, all being on the short end of the range of rhenium-carbon bonds for aryl complexes (see Chapter 1). Complex (**1b**) shows a similar range for its Re-C bonds from 2.02 to 2.03 Å. This shorter bond is expected because the smaller metal radius of a five-coordinate metal center allows for the five ligands to have a closer approach to the formally 14-electron complex. However, the aryl rings are not flat in the equatorial plane, but canted as in a propeller with torsional angles from that plane of 13°, 6°, and 6°; this is the same result seen in the structure for (**1b**). Thus, by analogy to (**1b**), the rings adopt this conformation avoid steric problems with the *ortho* hydrogens, not to balance the π-d ligand to metal orbital overlap with the steric constraints of the ligands as thought by Bau.[2]

Despite the fact that Re(*p*-tolyl)$_3$(THT)$_2$ (**7**) itself is quite unstable to oxygen and decomposes over time in solution, it serves as a convenient synthon when used *in situ*. Solutions of (**7**) can be filtered (to removed magnesium bromide salts) or can be used directly in this manner. This intermediate can be reacted with a variety of phosphines to make compounds of the formula Re(*p*-tolyl)$_3$(PR$_3$)$_2$ (**8**). Even though both phosphines and thioethers are soft ligands that bond well to a soft metal such as rhenium(III), phosphine ligands form much more stable complexes. If dimethylphenyl phosphine is added to (**7**) *in situ*, Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3a**) can be isolated in comparable yield (>50%) to the

synthesis from (**2b**). Both the triphenyl phosphine (**8a**) and trimethyl phosphine (**8b**) analogs of (**3a**) can be synthesized via this method (Scheme 4). These complexes are not accessible via direct reaction of aryl Grignard reagents on rhenium phosphine complexes because $ReX_3(PPh_3)_3$ does not exist and $ReCl_3(PMe_3)_3$ is very difficult to synthesize.[12]



Scheme 4: Reactions with tetrahydrothiophene (THT) complexes

If a solution of $Re(p\text{-tolyl})_3(THT)_2$ (**7**) is treated with bis(diphenylphosphino)ethane (DIPHOS) *in situ*, a color change to a lighter blue is observed and a blue powder precipitates out of solution. This solid is insoluble in all solvents investigated, includling polar, non-polar, and aromatic solvents. The original purpose for this reaction was to try to alter the positions that the phosphines and aryl rings adopt in the 5-coordinate species by eliminating possible *trans*-phosphines with a bidentate

chelating phosphine. It was hypothesized that d^4 low-spin five-coordinate complexes might expect a large barrier for the interconversion of trigonal bipyramids;[2,13] this would allow for possible isolation of different isomers with the monodentate phosphines. However, rather than making monomeric species, a polymeric structure is probable, even with only one equivalent of DIPHOS. The insolubility of the product, as well as its similarity in color to other trigonal bipyramidal aryl species, leads to the formulation of a polymer of bis(phosphine)-tris(aryl) rhenium centers linked via DIPHOS in their axial positions (Figure 3).

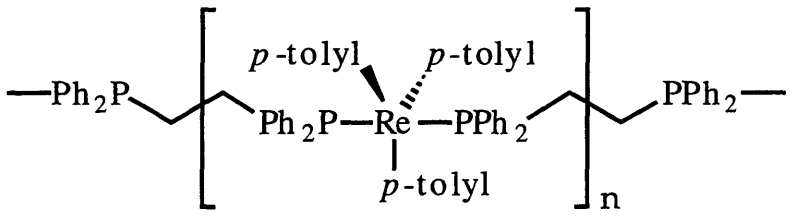


Figure 3: Hypothetical structure of DIPHOS polymer

If bis(diphenylphosphino)methane (dppm) is used instead of DIPHOS, the result is slightly different. Since the dppm has only one methylene linker between the two phosphine portions of the chelate, it has less of an ability to span two metal centers. When the reaction between dppm and a solution of Re(*p*-tolyl)$_3$(THT)$_2$ (**7**) takes place, the color first becomes a lighter shade of blue. If the solvent is removed *in vacuo*, a blue residue results. This residue is soluble in a variety of solvents, but a proton NMR spectrum shows that it is a mixture of complexes. If the residue is redissolved, over time it precipitates out of solution as a blue insoluble solid, similar in color and character to the DIPHOS product. Thus, the ultimate dppm product is probably polymeric in structure as well, as in Figure 3.

Using *p*-tolyl Grignard as a probe of reactivity, a variety of rhenium synthons, ranging from (I) to (V) in oxidation state, were tested to see if they could yield aryl complexes. Intractable mixtures resulted from reactions with rhenium complexes, such as $[Bu_4N]ReOBr_4$,[14,15] $Re(NPh)Cl_3(PPh_3)_2$,[16] and $ReCl_3$(2,2'-bipyridine)(PPh_3),[17] when treated with *p*-tolyl Grignard. Reactions with $ReCl_3(CH_3CN)(PPh_3)_2$[17] and $[Re(CO)_3Br_3]^{2-}$ both showed no reaction with the starting rhenium complex.[18] The former is a rhenium(I) complex that loses its halides in solution to become a tris(solvento) complex;it has been found to be useful for some recent low oxidation state chemistry.[18] From the latter, one can synthesize $ReCl_3$(benzil)PPh_3 (**9**) [benzil = Ph(C=O)(C=O)Ph];[17] the benzil ligand in this complex occupies two of the coordination sites in this paramagnetic octahedral complex. While (**9**) reacts with *p*-tolyl Grignard, it gives different products depending on the number of equivalents and the products were uncharacterizable under all the different stoichiometries.

From an early publication that reports the benzil complex (**9**), there is a claim that refluxing it in pyridine will afford $ReCl_3(pyridine)_3$.[17] However, if the preparation in the literature is followed, the complex $ReCl_3(pyridine)_2(PPh_3)$ is formed. This result was confirmed by proton NMR and mass spectroscopies and elemental analysis. This is a known complex that can be made directly from $ReCl_3(CH_3CN)(PPh_3)_2$ without going through complex (**9**) as an intermediate step.[17] Recently, a legitimate preparation for $ReBr_3(pyridine)_3$ has appeared in the literature; however, this has only a low yield after separation from several complexes of a mixture of $[ReBr_x(pyridine)_{6-x}]^{3-x}$ (x = 3, 4, or 5).[19] A pure sample of $ReCl_3(pyridine)_3$ was synthesized, but it does not react with *p*-tolyl Grignard to form isolatable aryl products.

In an effort to alter the electron donating ablity of the aryl ring, several variations of substituted aryl groups were employed. Electron withdrawing aryl groups such as *p*-trifluoromethylphenyl and *m*-trifluoromethylphenyl Grignard do not react with either $ReCl_3(PMe_2Ph)_3$ (**2b**) or $ReBr_3(THT)_3$ (**6**) even if the ethers are removed from the Grignard reagents *in vacuo*. The *p*-methoxyphenyl Grignard was used as an electron rich aryl group. The *p*-methoxyphenyl reagent does not react with (**6**) but it does react with (**2b**) to afford Re(*p*-methoxyphenyl)$_3$(PMe_2Ph)$_2$ (**3d**). The stablity of (**3d**) is simliar to that of the family of (**3**) complexes; however, isolation and purification were hindered by its high solublity in most sovents, including high solubility in heptane at -40 °C.

The electronic donation from the aryl rings in the Re(aryl)$_3$(PMe_2Ph)$_2$ (**3**) family of complexes can be directly correlated to the stability of the compounds. Stability, as measured by sensitivity to dioxygen, for the *p*-anisolyl complex (**3d**) was the lowest whereby it began decomposition in a few hours. The phenyl derivative (**3b**) was the most robust, surviving for years in the solid state with little decomposition. Both tolyl derivatives, (**3a**) and (**3c**) showed similar stabilities, but mid-way between that found for (**3d**) and (**3b**). Thus, it seems that electron donating groups like the *p*-methoxy and, to a lesser extent, methyl lead to a lowering of the stabilty of the tris(aryl) complex. At the other end of the spectrum, would be a derivative with a *p*-trifluoromethyl group; however, while the electronics of the aryl group might favor a stable tris(aryl) complex, it did not allow for a reactive enough Grignard reagent to form a complex initially.

The final venture into aryl derivatives involved the 2,2'-biphenyldiyl ligand used as its dilithium salt, made from the 2,2'-dibromobiphenyl.[20] If both aryl groups were to bind to the metal center, a metallafluorene

(Figure 3) would result. These complexes have been found to be stable as well as robust for both early and late transition metals. All rhenium compounds investigated, including $ReCl_3(PMe_2Ph)_3$, $ReBr_3(THT)_3$, $HB(pyrazole)_3ReOCl_2$,[21] Re(2,2'-bipyridine)$(PMe_2Ph)Cl_3$,[22] $ReCl_3(CH_3CN)(PPh_3)_2$, and $[Re(CO)_3Br_3]^{2-}$, showed no reactivity with the 2,2'-biphenyldiyl ligand under a variety of conditions. Since metallafluorenes exist for almost every group on the periodic table except for Group 7, by casting a wider net the proper rhenium synthon most likely can be found.

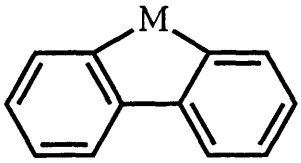


Figure 4: A metallafluorene

Conclusion

This chapter details the synthesis of a family of trigonal bipyramidal rhenium aryl complexes. The complexes with phosphorus based neutral ligands were much more stable than those with sulfur based ligands. However, the sulfur ligands could be replaced in solution by a variety of phosphine ligands to make complexes that were not accessible from the known rhenium starting materials. The structure of Re(*p*-tolyl)$_3$(THT)$_2$ confirmed that these complexes are analogous to the phosphine complexes (**1**) and (**3**). The chemistry of these complexes will be explored in the next chapter.

Experimental

All chemistry was performed either on a Schlenk line under an argon atmosphere or in a dry box under a dinitrogen atmosphere with dried, deoxygenated solvents unless otherwise specified. The solvents were either purchased dry or distilled from a sodium-benzophenone ketyl pot. The Grignard reagents were purchased from Aldrich with the exception of the phenyl Grignard, which was purchased from Strem. The 4-bromoanisole (99% purity), bis(diphenylphosphino)ethane (DIPHOS), and bis(diphenylphosphino)methane (dppm) were purchased from Aldrich; the Celite545® is non-acid-washed diatomaceous earth from Fischer. ^{1}H and ^{31}P NMR spectra were recorded on a Varian XL-300, a Varian Unity-300 or a Varian 500-VXR spectrometer. The chemical shifts were referenced to the residual proton impurity in the deuterated solvents obtained from Cambridge Isotopes Laboratory. ^{31}P chemical shifts are reported relative to an external standard of 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 series spectrophotometer as KBr pellets. Fast atom bombardment mass spectra of samples dissolved in 3-nitrobenzylalcohol (NBA) matrix were recorded with a Finnigan MAT 8200 mass spectrometer equipped with an Ion Tech FAB gun operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6-8 keV xenon neutrals.

Carbon, hydrogen, and nitrogen elemental analyses were carried out by Atlantic Microlab, Norcross, GA. However, the results of these analyses has been problematic. Five of the complexes in this chapter, as well as two from Chapter 5, have received poor analytical results out of the 0.4% range for carbon. These complexes were shown to be pure by proton NMR

spectroscopy and have, in several cases, yielded poor analytical results on crystals that X-ray analysis was satisfactorily completed for. The most likely explanation for these discrepancies is the possibility of formation of refractory rhenium carbides during combustion. A test sample, from the same vial of complex (**3b**) that analyzed poorly from Atlantic, was sent to H. Kolbe Mikroanalytisches Laboratorium in Germany; the carbon percentages for calculated, Atlantic, and Kolbe are 58.86%, 57.94%, and 58.74%, respectively. Since complex (**3b**) analyzes well only from Kolbe, and all the complexes that analyzed poorly from Atlantic also exhibit clean proton NMR spectra (as well as several having X-ray structures), the remaining complexes must also have allowable purities. Figure 5 (*vide infra*) shows the proton NMR spectrum of the analyzed sample of (**3b**).

The complexes $ReCl_3(PMe_2Ph)_3$[23] and $ReBr_3(THT)_3$[24] were both prepared by previously published methods. The complex $ReCl_3(PPh_3)(O{=}PPh_2pyr)$ was synthesized from $ReOCl_3(PPh_3)_2$[23] and PPh_2pyr using method of Davison and Shellenbarger-Jones.[25]

$Re(PMe_2Ph)_2(p\text{-tolyl})_3$ (3a) - Method I:

A solution of $ReCl_3(PMe_2Ph)_3$ (1.92 g, 2.72 mmol) in toluene (200 mL) was placed in a Schlenk flask, and a seven-fold excess of *p*-tolylmagnesium bromide (19.0 mL, 19.0 mmol) was added as a 1.0 M ether solution. The orange-yellow solution instantly became a deep blue and was stirred for 30 minutes. The blue solution was extracted in air with 5 x 100 mL of water and dried with sodium sulfate. The solvent was removed under reduced pressure leaving a purple-blue solid. Rinsing with

methanol afforded a purple-blue powder isolated by filtration onto a fritted glass funnel (E). Yield 1.24 g (1.68 mmol, 62% yield).

Anal. Calcd. for $C_{37}H_{43}P_2Re$: C, 60.39%; H, 5.89%. Found: C, 60.18%; H, 6.00%. ^1H NMR (C_6D_6, 300 MHz) δ: 1.15 (t, 12H), 2.51 (s, 9H), 6.18 (d, 6H), 6.72 (m, 4H), 7.01 (m, 6H), 7.01 (d, 6H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 9.80 (s).

$Re(PMe_2Ph)_2(p\text{-tolyl})_3$ (3a) - Method II:

A solution of 1.0 M p-tolylmagnesium bromide (0.44 mL, 0.44 mmol) in ether was placed under reduced pressure and evaporated to dryness. Toluene (35 mL) and $ReBr_3(THT)_3$[24] (101.5 mg, 0.14 mmol) (THT = tetrahydrothiophene) were added to the solution. The orange solution became deep blue. Addition of PMe_2Ph (0.40 mL, 0.28 mmol) yielded a purple-blue solution and subsequent removal of solvent under reduced pressure left a purple-blue solid. Addition of methanol (5 mL) in air followed by filtration yielded (**3a**). Yield 52.8 mg (0.071 mmol, >50% yield). It was found to be identical to a sample of (**3a**) from Method I by ^1H NMR spectroscopy.

$Re(PMe_2Ph)_2(phenyl)_3$ (3b):

Compound (**3b**) is made by the analogous route used in Method I for compound (**3a**). The $ReCl_3(PMe_2Ph)_3$ (1.01g, 1.43 mmol) was used with a 3.0 M solution of phenylmagnesium bromide (4.77 mL, 14.3 mmol) in ether. However, after extraction with water, the residue was dissolved in hexanes, the solvent was removed under reduced pressure, and the residue was rinsed with methanol leaving an isolable blue solid that could be collected on a fritted glass funnel. Yield 0.49 g (0.71 mmol, 50%).

Unfortunately, complex (**3b**) is slightly methanol soluble whereas (**3a**) is not. Thus (**3b**) can also be obtained by taking the residue from the water extraction and dissolving it in heptane; crystals can be grown from a minimum amount of heptane at -40 °C. The impurities that the methanol would rinse away remain in the heptane solution.

Anal. Calcd. for $C_{34}H_{37}P_2Re$: C, 58.86%; H, 5.37%. Found: C, 57.94; H, 5.45%. ^1H NMR (C_6D_6, 300 MHz) δ: 1.08 (s, 12H), 6.21 (d, 6H), 6.42 (t, 3H), 6.63 (m, 4H), 6.95 (m, 6H), 7.08 (t, 6H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 11.16 (s).

$Re(PMe_2Ph)_2(m\text{-tolyl})_3$ (3c):

A solution of 1.0 M *m*-tolylmagnesium bromide (4.25 mL, 4.3 mmol) in THF was added to a Schlenk flask and evaporated to dryness under reduced pressure. Subsequently, $ReCl_3(PMe_2Ph)_3$ (500 mg, 0.71 mmol) and toluene (40 mL) were added, and the solution became dark purple. After 30 minutes, the solution was extracted with 4 x 35 mL of water in air and dried with sodium sulfate. The solvent was removed under reduced pressure yielding a dark blue, sticky solid, which became a purple-blue powder after stirring in methanol and filtering. Yield 142 mg (0.19 mmol, 28%).

Anal. Calcd. for $C_{37}H_{43}P_2Re$: C, 60.39%; H, 5.89%. Found: C, 60.15%; H, 5.97%. ^1H NMR (C_6D_6, 300 MHz) δ: 1.24 (t, 12H), 2.17 (s, 9H), 6.07 (s, 3H), 6.31 (d, 3H), 6.38 (d, 3H), 6.76 (m, 4H), 7.07 (m, 6H), 7.18 (t, 3H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 11.30 (s).

$Re(PPh_3)(O{=}PPh_2pyr)(p\text{-tolyl})_3$ (5):

The black powder of $Re(PPh_3)(O{=}PPh_2pyr)Cl_3$ (56.2 mg, 0.0673) was suspended in toluene (17 mL). An excess of a solution of 1.0 M *p*-tolylmagnesium bromide (0.32 mL, 0.32 mmol) was added. After 5 minutes, the solid began dissolving and forming a brownish-purple solution. After an hour, the solvent was removed *in vacuo*, and the residue was scraped and rinsed with methanol (20 mL). Using a fritted glass funnel, the brown methanol solution could be separated from a pale blue solid. This must be done quickly because the blue solid is slightly soluble in methanol. Rather than filtering from methanol, a rinse with methanol followed by tituration and filtering in acetone will work equally well. Yield 6.5 mg (0.0065 mmol, 9.6%). The yield varies considerably from reaction to reaction.

Anal. Calcd. for $C_{56}H_{50}NOP_2Re$: C, 67.18%; H, 5.03%; N, 1.40%. Found: C, 64.86; H, 5.31%; N, 1.43%. ^1H NMR (C_6D_6, 300 MHz) δ: 2.3 (t, 9H), 6.0 (d, 6H), 6.8 (d, 6H), 7.0 (m, 25H), 7.7 (m, 1H), 8.2 (m, 1H), 8.3 (d, 1H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 28.735 (s), 30.557 (s), 30.870 (s), 32.445 (s). FABMS(+) (p-nitrobenzylalcohol): $[Re(PPh_3)(p\text{-tolyl})_3(OPPh_2(C_6H_4N))]^+$, 1001 *m/z*; $[Re(PPh_3)(p\text{-tolyl})_3(PPh_2(C_6H_4N))]^+$, 985 *m/z*; $[Re(PPh_3)(p\text{-tolyl})_3]^+$, 722 m/z; $[Re(PPh_3)(p\text{-tolyl})_2]^+$, 631 *m/z*.

$Re(THT)_2(p\text{-tolyl})_3$ (7):

NMR tube scale: A solution of 1.0 M *p*-tolyl magnesium bromide (0.047 mL, 0.047 mmol) in ether was placed in an NMR tube. The ether was removed under reduced pressure. The orange-yellow colored $ReBr_3(THT)_3$ (10.7 mg, 0.016 mmol) and d_6-benzene (1 mL) were added, and the solution became deep blue after 30 seconds. The reaction mixture

was then observed by ^1H NMR spectroscopy. While the ^1H NMR spectrum is complex, all resonances can be assigned. Resonances due to ether, 4,4'-biphenyl, toluene, and tetrahydrothiophene are observed. The remaining resonances correspond to one type of *p*-tolyl group and one type of coordinated tetrahydrothiophene.

^1H NMR (C_6D_6, 300 MHz) δ: 1.20 (m, 8H), 2.40 (m, 8H) 2.45 (s, 9H), 6.70 (d, 6H), 7.15 (d, 6H).

Large scale reaction: A solution of 1.0M *p*-tolyl magnesium bromide (0.50 mL, 0.50 mmol) in ether was placed in a round-bottomed flask, and the ether was removed under reduced pressure. Toluene (10 mL) was added to the flask and followed by $ReBr_3(THT)_3$ (97.2 mg, 0.141 mmol). The solution slowly became blue as the rhenium dissolved. After stirring for 30 minutes, the reaction solution was reduced to dryness *in vacuo*. The dark blue and whitish-green mixture of solid residues were titurated into 15 mL of pentane. This solution was then filtered through Celite leaving a whitish-green consisting mostly of magnesium bromide. Subsequently, the pentane was removed *in vacuo*, and the residue was redissolved in a minimum amount of heptane. X-ray quality crystals could be grown from this solution at -10 °C. The solutions from this reaction are generally used *in situ* and not isolated. Due to the solubility of (7), recyrstallized yields are low. Recrystallized yield 26 mg (0.041 mmol, 29%).

Anal. Calcd. for $C_{29}H_{37}ReS_2$: C, 54.77%; H, 5.86%, S, 10.08%. Found: C, 52.74%; H, 5.62%; S, 9.63%.

X-Ray Crystallographic Data Collection Parameters for (7)

The data for (**7**) were collected using a Siemens platform goniometer with a CCD detector using a molybdenum Kα radiation (λ = 0.71073 Å). The data for (**7**) were collected using a crystal having dimensions 0.20 x 0.10 x 0.10 mm. The crystal system was orthorhombic (α = β = γ = 90°) with a = 11.210(3) Å, b = 14.271(3) Å, and c = 16.734(4) Å; this leads to a cell volume V = 2677.1(11) Å^3 with Z = 4. The space group was found to be $P2_12_12_1$. The absorption coefficient was 4.710 mm^{-1}, the calculated density ρ = 1.578 g/cm^3, and F(000) = 1272. The data were obtained at 183(2) K in the θ range 1.88 to 23.27° with limiting indices $-10 \leq h \leq 12$, $-9 \leq k \leq 15$, and $-17 \leq l \leq 18$. Of the 11012 reflections collected, 3852 were independent (R_{int} = 0.0957). The structure was solved by direct methods (SHELXTL v5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Least squares refinement based upon F^2 with 3850 data, no restraints and 284 parameters converged with final residuals: R_1 = 0.0330, wR_2 = 0.0775, and GOF = 1.126 based upon $I > 2\sigma(I)$; the absolute structure parameter was 0.001(13).

$Re(PPh_3)_2(p\text{-tolyl})_3$ (8a) - Method I:

A solution of 1.0 M *p*-tolylmagnesium bromide (0.33 mL, 0.33 mmol) in ether was added to a Schlenk flask. The ether was removed under reduced pressure. Toluene (30 mL) and $ReBr_3(THT)_3$ (74.0 mg, 0.108 mmol) were added to the flask, and a deep blue solution resulted. After 30 minutes, triphenylphosphine (70 mg, 0.27 mmol) was added. The solution was stirred overnight, and the solvent was removed under pressure. The residue was dissolved in methanol and filtered in air, yielding a blue solid. Yield 45.1 mg (0.048 mmol, 44%).

Anal. Calcd. for $C_{57}H_{51}P_2Re$: C, 69.56%; H, 5.22%. Found: C, 66.99%; H, 5.04%. ^1H NMR (C_6D_6, 300 MHz) δ: 2.35 (s, 9H), 6.05 (d, 6H), 6.85 (d, 6H), 7.0-7.6 (m, 30H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 MHz) δ: 24.34 (s).

Re(PPh$_3$)$_2$(*p*-tolyl)$_3$ (8a) - Method II:

A solution of 1.0 M *p*-tolylmagnesium bromide (1.0 mL, 1.0 mmol) in ether was added to a Schlenk flask. The ether was removed under reduced pressure. Toluene (10 mL) and $ReBr_3(THT)_3$ (93.5 mg, 0.135 mmol) were added to the flask, and a deep blue solution resulted. After 30 minutes, just over two equivalents of triphenylphosphine (75 mg, 0.286 mmol) were added. The solution was stirred for two hours during which the solution became more turquoise than blue. The toluene solution was extracted with 5 x 10 mL of water and then dried over Na_2SO_4. The residue was dried *in vacuo* and taken up into a large volume (20 mL) of toluene. Upon cooling this solution at -10 °C, a blue powder precipitates out. The blue powder was found to be identical to the product form Method I by proton NMR spectroscopy. Yield 34 mg (0.035 mmol, 25%).

Re(PMe$_3$)$_2$(*p*-tolyl)$_3$ (8b) - Method I:

$Re(PMe_3)_2$(*p*-tolyl)$_3$ was prepared according to the procedure for (**8a**). PMe_3 (0.10 mL, 0.97 mmol) was added to a solution of $ReBr_3(THT)_3$ (76 mg, 0.11 mmol) and Grignard (0.45 mL, 0.45 mmol) was stirred for 30 minutes. Yield 13.5 mg (0.024 mmol, 22%).

Anal. Calcd. for $C_{27}H_{39}P_2Re$: C, 53.01%; H, 6.43%. Found: C, 51.55%; H, 6.24%. ^1H NMR (C_6D_6, 300 MHz) δ: 0.85 (t, 18H), 2.45 (s, 9H), 6.50 (d, 6H), 7.10 (d, 6H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 0.38 (s).

$Re(PMe_3)_2(p\text{-tolyl})_3$ (8b) - Method I:

A solution of 1.0 M *p*-tolylmagnesium bromide (1.0 mL, 1.0 mmol) in ether was added to a Schlenk flask. The ether was removed under reduced pressure. Toluene (10 mL) and $ReBr_3(THT)_3$ (97.9 mg, 0.142 mmol) were added to the flask, and a deep blue solution resulted. After 30 minutes, an excess of triphenylphosphine (0.10 mL, 0.97 mmol) was added. The solution was stirred for six hours during which the solution became more purple. The toluene solution was extracted with 5 x 30 mL of water and then dried over Na_2SO_4. The residue was dried *in vacuo* and taken up into a small volume of heptane. This solution was filtered through cotton to remove any residual solids. Upon cooling this solution to -10 °C, small purple crystals formed. The purple crystals were found to be identical to the product from Method I by proton NMR spectroscopy. Recrystallized yield 20 mg (0.033 mmol, 23%).

$Re(PMe_2Ph)_2(p\text{-methoxyphenyl})_3$ (3d):

To 20 mL of THF was added 4-bromoanisole (0.50 mL, 0.40 mmol) and magnesium turnings (100.3 mg, 0.413 mmol); the reaction was initiated by heating, and a nearly clear solution of *p*-methoxyphenyl Grignard resulted (0.020 M). A solution of $ReCl_3(PMe_2Ph)_3$ (100.0 mg, 0.141 mmol) in toluene (10 mL) was placed in a Schlenk flask, and an excess of *p*-methoxyphenylmagnesium bromide (3.5 mL, 0.70 mmol) was added from the above solution. The orange-yellow solution darkened slowly and after 10 hours appeared blue-green. The solvent was removed *in vacuo* and the residue was redissolved in 10 mL of toluene. The blue solution was extracted in air with 3 x 10 mL of water and dried over sodium sulfate. The solvent was removed under reduced pressure leaving

a blue residue which can be extracted into either pentane or heptane. A solid can be isolate by cooling the heptane solution in a -40 °C freezer. Recrystallized yield 22 mg (0.028 mmol, 20% yield).

^{1}H NMR (C_6D_6, 300 MHz) δ: 0.90 (t, 12H), 3.52 (s,9H), 6.02 (d,6H), 6.73 (d, 6H), 6.9-7.1 (m, 10H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 30.334 (s).

Reaction of Re(*p*-tolyl)$_3$(THT)$_2$ with DIPHOS:

A solution of 1.0 M *p*-tolylmagnesium bromide (0.50 mL, 0.50 mmol) in ether was added to a Schlenk flask. The ether was removed under reduced pressure. Toluene (20 mL) and $ReBr_3(THT)_3$ (97.0 mg, 0.140 mmol) were added to the flask, and a deep blue solution resulted. After 20 minutes, DIPHOS (58 mg, 0.146 mmol) was added with another 10 mL of toluene. The solution became a darker blue and was allowed to stir. After several hours, a blue solid precipitated, and the solvent was removed *in vacuo*. The blue solid did not redissolve in any of the following solvents: acetone, benzene, toluene, chloroform, methanol, or methylene chloride. The solid could be isolated on a fritted glass funnel and separated from a pale brown solution.

Reaction of Re(*p*-tolyl)$_3$(THT)$_2$ with dppm:

A solution of 1.0 M *p*-tolylmagnesium bromide (0.27 mL, 0.27 mmol) in ether was added to a Schlenk flask. The ether was removed under reduced pressure. Toluene (10 mL) and $ReBr_3(THT)_3$ (62.6 mg, 0.0907 mmol) were added to the flask, and a deep blue solution resulted. After 20 minutes, dppm (32.7 mg, 0.0851 mmol) was added with another 10 mL of toluene. The solution became a darker blue and was allowed to stir for several hours. The solvent was removed *in vacuo* and the residue was

filtered through Celite. After filtering, the solvent was again removed leaving a blue residue. This residue was soluble in ether, acetone, benzene, toluene, heptane and slightly soluble in pentane. A solid could be precipitated out of cold heptane, but it did not appear to be a homogenous complex as shown by proton NMR spectroscopy. However, after prolonged time in solution, an insoluble blue powder precipitated, which could not be redissolved.

Anal. Calcd. for $C_{46}H_{43}P_2Re$: C, 65.46%; H, 5.14%. Found: C, 65.40%; H, 5.05%. IR (KBr) ν 1473.2(m), 1436.4(m), 1094.2(s) cm^{-1}.

Reaction of $ReCl_3$(benzil)PPh_3 with pyridine:

After following the standard preparation for $ReCl_3(pyridine)_3$[17] from the complex $ReCl_3(benzil)(PPh_3)$ (0.40g, 0.523 mmol), dark orange crystals appeared over time. These crystals were determined by proton NMR spectroscopy, mass spectrometry, and elemental analysis to be $ReCl_3(PPh_3)(pyridine)_2$. Anal. Calcd. for $C_{28}H_{25}Cl_3N_2PRe$: C, 47.16%; H, 3.53%; Cl, 14.92%. Found: C, 47.17; H, 3.55%; Cl, 15.04%. EI shows no peak at 529.8, corresponding to the $ReCl_3(pyridine)_3$ complex.

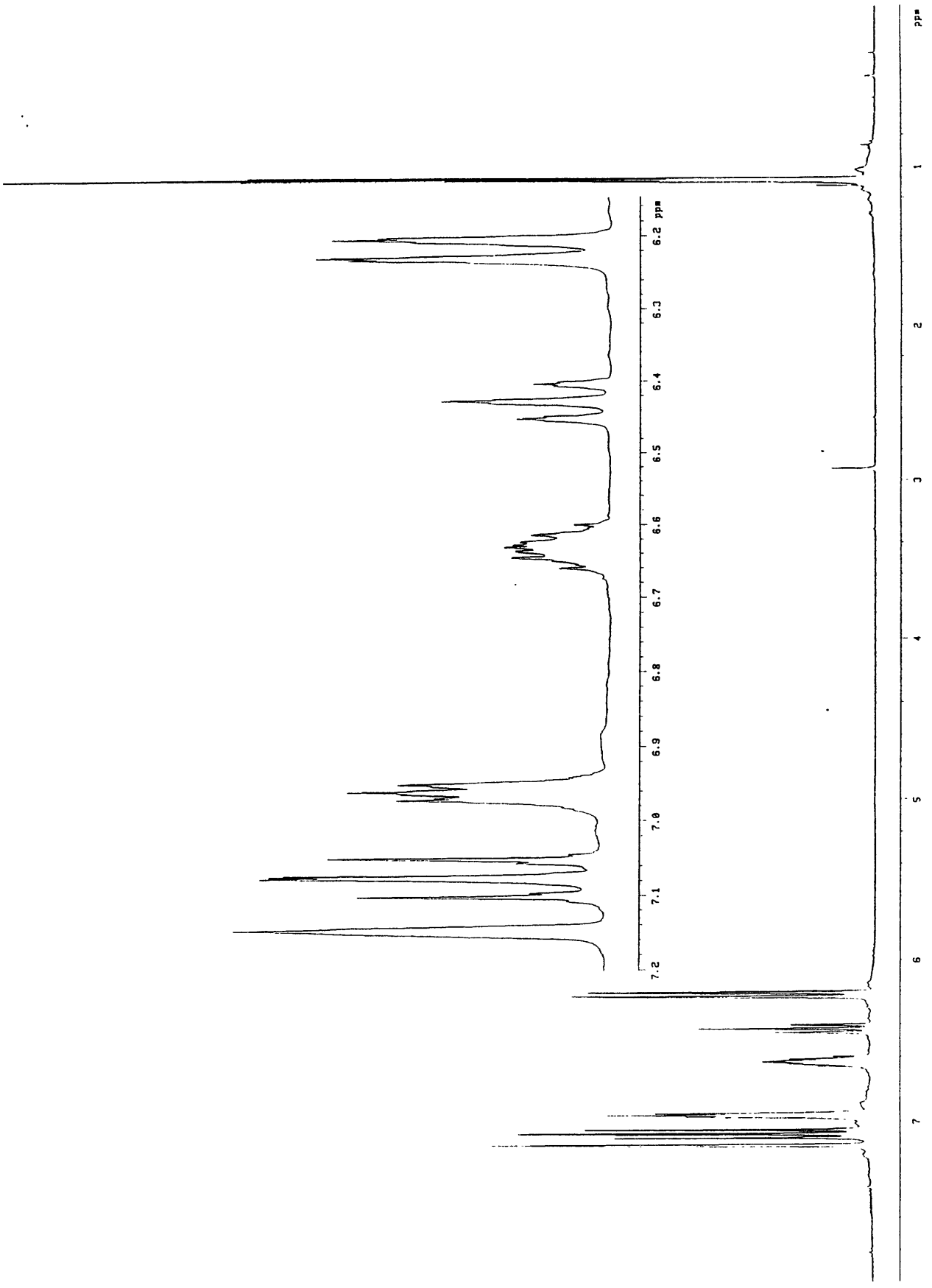


Figure 5: Proton NMR spectrum of $Re(phenyl)_3(PMe_2Ph)_2$ (**3b**)

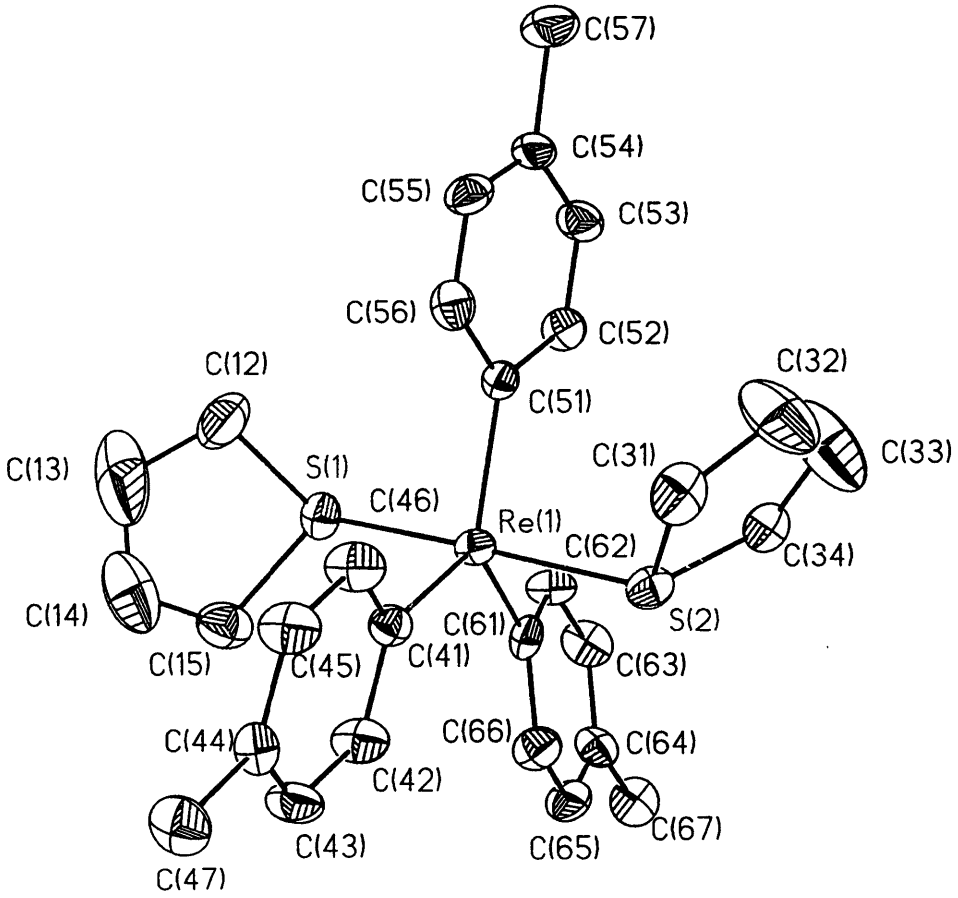


Figure 5: ORTEP of Re(*p*-tolyl)$_3$(THT)$_2$ (**7**) with 35% ellipsoids.

Table 1. Crystal and Data Collection Parameters for Re(*p*-tolyl)$_3$(THT)$_2$

Empirical formula	$C_{29}H_{37}ReS_2$
Formula weight	635.91 g/mol
Temperature	183(2) K
Radiation	MoKα
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 11.210(3) Å $\quad \alpha = \beta = \gamma = 90°$
	b = 14.271(3) Å
	c = 16.734(4) Å
Volume	2667.1(11) Å^3
Z	4
Density (calculated)	1.578 g/cm^3
Absorption coefficient	4.710 mm^{-1}
F(000)	1272
θ range for data collection	1.88 to 23.27 °
Limiting indices	$-10 \le h \le 12$, $-9 \le k \le 15$, $-17 \le l \le 18$
Reflections collected	11012
Independent reflections	3852 (R_{int} = 0.0957)
Diffractometer	Siemens SMART/CCD
Scan Type	ω scans
Refinement method	Full-matrix least-squares on F^2
Structure solution	Direct methods
Data / restraints / parameters	3850 / 0 / 284
Goodness-of-fit on F^2	1.126
Final R indices [I>2σ(I)]	R1 = 0.0330, wR2 = 0.0775
R indices (all data)	R1 = 0.0375, wR2 = 0.0819
Absolute structure parameter	0.001(13)
Largest diff. peak and hole	0.775 and -0.907 eÅ^{-3}

Table 2: Bond Lengths for Re(*p*-tolyl)$_3$(THT)$_2$ (**7**)

Atoms	Length (Å)	Atoms	Length (Å)
Re(1)-C(51)	2.026(7)	Re(1)-C(41)	2.038(7)
Re(1)-C(61)	2.055(7)	Re(1)-S(2)	2.372(2)
Re(1)-S(1)	2.375(2)	S(1)-C(15)	1.812(10)
S(1)-C(12)	1.821(9)	S(2)-C(34)	1.829(9)
S(2)-C(31)	1.862(9)	C(41)-C(42)	1.373(11)
C(41)-C(46)	1.435(11)	C(42)-C(43)	1.385(11)
C(43)-C(44)	1.393(11)	C(44)-C(45)	1.354(12)
C(44)-C(47)	1.516(10)	C(45)-C(46)	1.370(11)
C(51)-C(52)	1.394(11)	C(51)-C(56)	1.445(11)
C(52)-C(53)	1.383(11)	C(53)-C(54)	1.412(12)
C(54)-C(55)	1.365(13)	C(54)-C(57)	1.542(12)
C(55)-C(56)	1.361(12)	C(12)-C(13)	1.42(2)
C(61)-C(66)	1.393(11)	C(61)-C(62)	1.395(11)
C(15)-C(14)	1.50(2)	C(14)-C(13)	1.39(2)
C(64)-C(65)	1.338(11)	C(64)-C(63)	1.369(12)
C(64)-C(67)	1.520(12)	C(66)-C(65)	1.383(12)
C(34)-C(33)	1.436(13)	C(63)-C(62)	1.411(11)
C(31)-C(32)	1.49(2)	C(33)-C(32)	1.37(2)

Table 3: Bond Angles for Re(*p*-tolyl)$_3$(THT)$_2$ (**7**)

Atoms	Angle (°)	Atoms	Angle (°)
C(51)-Re(1)-C(41)	120.9(3)	C(51)-Re(1)-C(61)	120.3(3)
C(41)-Re(1)-C(61)	118.8(3)	C(51)-Re(1)-S(2)	94.1(2)
C(41)-Re(1)-S(2)	88.5(2)	C(61)-Re(1)-S(2)	88.7(2)
C(51)-Re(1)-S(1)	87.7(2)	C(41)-Re(1)-S(1)	95.3(2)
C(61)-Re(1)-S(1)	85.6(2)	S(2)-Re(1)-S(1)	174.17(7)
C(15)-S(1)-C(12)	92.5(5)	C(15)-S(1)-Re(1)	113.7(4)
C(12)-S(1)-Re(1)	112.4(3)	C(34)-S(2)-C(31)	93.5(4)
C(34)-S(2)-Re(1)	111.7(3)	C(31)-S(2)-Re(1)	112.0(3)
C(42)-C(41)-C(46)	115.4(7)	C(42)-C(41)-Re(1)	122.2(6)
C(46)-C(41)-Re(1)	122.3(6)	C(41)-C(42)-C(43)	122.7(8)
C(42)-C(43)-C(44)	121.7(8)	C(45)-C(44)-C(43)	115.4(7)
C(45)-C(44)-C(47)	124.2(7)	C(43)-C(44)-C(47)	120.4(7)
C(44)-C(45)-C(46)	125.0(8)	C(45)-C(46)-C(41)	119.7(8)
C(52)-C(51)-C(56)	114.7(7)	C(52)-C(51)-Re(1)	124.3(6)
C(56)-C(51)-Re(1)	121.0(6)	C(53)-C(52)-C(51)	123.3(9)
C(52)-C(53)-C(54)	120.1(8)	C(55)-C(54)-C(53)	117.6(8)
C(55)-C(54)-C(57)	121.6(9)	C(53)-C(54)-C(57)	120.7(8)
C(56)-C(55)-C(54)	122.8(9)	C(55)-C(56)-C(51)	121.4(8)
C(13)-C(12)-S(1)	108.3(9)	C(66)-C(61)-C(62)	115.5(7)
C(66)-C(61)-Re(1)	124.7(6)	C(62)-C(61)-Re(1)	119.8(6)
C(14)-C(15)-S(1)	105.7(8)	C(13)-C(14)-C(15)	111.4(11)
C(14)-C(13)-C(12)	114.6(12)	C(65)-C(64)-C(63)	118.8(7)
C(65)-C(64)-C(67)	120.8(8)	C(63)-C(64)-C(67)	120.4(8)
C(65)-C(66)-C(61)	122.8(8)	C(33)-C(34)-S(2)	108.1(7)
C(64)-C(63)-C(62)	121.1(7)	C(64)-C(65)-C(66)	121.0(8)
C(61)-C(62)-C(63)	120.5(8)	C(32)-C(31)-S(2)	104.6(7)
C(32)-C(33)-C(34)	116.2(11)	C(33)-C(32)-C(31)	116.7(10)

Table 4: Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Re(1)	186(1)	4998(1)	8432(1)	32(1)
S(1)	718(2)	5931(1)	7312(1)	42(1)
S(2)	-378(2)	4211(1)	9622(1)	43(1)
C(41)	1658(7)	4162(5)	8380(5)	37(2)
C(42)	2732(8)	4424(6)	8706(6)	48(2)
C(43)	3744(7)	3870(6)	8660(6)	51(2)
C(44)	3722(7)	2987(5)	8306(5)	36(2)
C(45)	2659(8)	2725(6)	7994(6)	51(2)
C(46)	1637(8)	3251(6)	8018(6)	52(2)
C(47)	4838(8)	2387(6)	8285(6)	56(2)
C(51)	-1326(7)	4649(5)	7838(5)	34(2)
C(52)	-2405(6)	5127(7)	7912(5)	41(2)
C(53)	-3429(7)	4872(7)	7505(5)	46(2)
C(54)	-3422(7)	4082(7)	6997(5)	49(2)
C(55)	-2371(8)	3608(6)	6911(5)	47(2)
C(56)	-1360(7)	3845(6)	7313(5)	46(2)
C(12)	747(11)	5260(7)	6386(6)	75(3)
C(61)	274(7)	6224(5)	9073(4)	37(2)
C(57)	-4550(9)	3800(7)	6528(6)	68(3)
C(15)	2298(9)	6189(7)	7254(7)	63(3)
C(14)	2795(12)	5529(10)	6636(11)	109(5)
C(13)	1930(16)	5271(11)	6083(12)	161(10)
C(64)	312(7)	7907(5)	9965(5)	42(2)
C(66)	1135(7)	6424(6)	9648(5)	48(2)
C(34)	-1824(8)	4617(6)	9990(6)	54(2)
C(63)	-552(8)	7755(5)	9402(5)	47(2)
C(65)	1169(8)	7263(6)	10061(5)	50(2)
C(62)	-571(8)	6925(5)	8944(5)	44(2)
C(31)	-927(10)	3002(6)	9420(6)	58(3)
C(33)	-2631(11)	3836(8)	9984(12)	122(7)
C(32)	-2223(11)	3033(8)	9624(11)	104(5)
C(67)	310(9)	8799(6)	10461(6)	65(3)

References

(1) Chatt, J.; Garforth, J. D.; Rowe, G. A. *J. Chem. Soc. A* **1966**, 1834-1836.

(2) Carroll, W. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 825-826.

(3) Shaw, D.; Randall, E. W. *Chem. Commun.* **1965**, 82-83.

(4) Abram, U., personal communication.

(5) Landrum, G. In http://overlap.chem.cornell.edu:8080/yaehmop.html: 1997.

(6) Savage, P. D.; WIlkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc. Dalton Trans.* **1988**, 669-673.

(7) Arnold, J. W., G.; Hussain, B.; Hursthouse, M.B. *J. Chem. Soc., Chem. Commun.* **1988**, 704-705.

(8) Arnold, J. W., G.; Hussain, B.; Hursthouse, M.B. *Organometallics* **1989**, *8*, 415-420.

(9) Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 403-404.

(10) Guillaume, P.; Postel, M. *Inorg. Chim. Acta* **1995**, *233*, 190-112.

(11) Conner, K. A.; Walton, R. A. In *Middle Transition Elements*; Permagon Press: London, 1986; Vol. 4; pp 187.

(12) Wenzel; Bergman, R. *J. Am. Chem. Soc.* **1986**, *108*, 4682.

(13) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(14) Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1964**, *4*, 1621.

(15) Dilworth, J. R.; Hussain, W.; Hutson, A. J.; Jones, C. J.; McQuillan, F. S. *Inorg. Syn.* **1997**, *31*, 257.

(16) Chatt, J.; Garforth, J. D.; Johnson, N. P.; Rowe, G. A. *J. Chem. Soc.* **1964**, 1012.

(17) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993-1000.

(18) Alberto, R.; Schibli, R.; Schubiger, P. A.; Abram, U.; Kaden, T. A. *Polyhedron* **1996**, *15*, 1079-1089.

(19) Arp, O.; Preetz, W. *Z. anorg. allg. Chem.* **1996**, *622*, 219-224.

(20) Gilman, H.; Gaj, B. J. *J. Org. Chem.* **1957**, *22*, 447-449.

(21) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.

(22) Casper, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104.

(23) Parshall, G. W. *Inorg. Syn.* **1977**, *17*, 110-112.

(24) Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3688-3695.

(25) Shellenbarger-Jones, A.; Davison, A., personal communication.

Chapter 3

The Reactivity of Rhenium Polyaryl Complexes

Introduction

This chapter will explore rhenium(III) trigonal bipyramidal complexes. These complexes include those with both phosphine and tetrahydrothiophene (THT) axial ligands. While Chatt first made complexes of the general form $Re(aryl)_3(PR_3)_2$ in the early 1960's, only their synthesis and characterization were published at that time. In the late 1970's the structure of $RePh_3(PEt_2Ph)_2$ was published; however, there were still no reports about the reactivity or the stability of complexes in this family. A discussion of the chemistry of rhenium(I) complexes resulting from reductive elimination from the rhenium(III) complexes will follow.

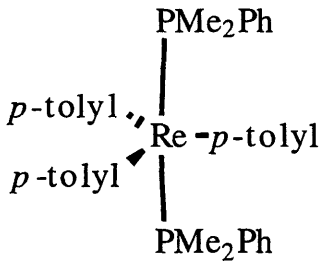
Discussion

Several basic patterns govern the structure and reactivity of complexes of rhenium(III). First, rhenium(III) complexes are almost exclusively five, six and seven-coordinate compounds. Trigonal bipyramidal, octahedral, and seven-coordinate complexes in Group 7 tend to be 14, 16 and 18-electron complexes respectively since the majority of rhenium(III) complexes are neutral and have monoanionic ligands. In general, rhenium(III) is a very stable oxidation state; rhenium(III) complexes are often formed from a simple reduction of the available rhenium(V) complexes such as $ReOCl_3(PPh_3)_2$. Octahedral rhenium(III) complexes tend to be air stable and to react only under more rigorous conditions or with more reactive reagents. On the other hand, trigonal bipyramidal complexes of rhenium(III), such as the family of complexes $Re(aryl)_3L_2$ (where L = neutral ligand), are coordinatively unsaturated as well as being formally 14-electron complexes. What follows will use the complexes, $Re(aryl)_3L_2$, as a probe for the stability and reactivity of trigonal bipyramidal complexes of rhenium(III).

The complexes of the form $Re(aryl)_3(PR_3)_2$, originally made by Chatt and expanded to include the complexes discussed in Chapter 1, are more robust than might be expected for a complex with three anionic organometallic ligands. Hydrolysis of the organometallic ligands might be expected if they were to come in contact with water. However, while they are formed under inert atmosphere to prevent decomposition of the Grignard reagents, a toluene solution of $Re(aryl)_3(PR_3)_2$ is then extracted with water in air to consume any extra equivalents of Grignard as well as to remove the magnesium salts and some residual phosphine lost during

the reaction. The complex, Re(p-tolyl)$_3$(PMe_2Ph)$_2$, does not decompose in wet deoxygenated toluene either at room temperature or in refluxing toluene. Recently, work by Mayer *et al.* has shown that the rhenium-aryl bond in several rhenium(V) complexes is rather inert.[1]

The complex Re(p-tolyl)$_3$(PMe_2Ph)$_2$ is the main focus of this chapter for several reasons. First, the p-tolyl groups in the complex make a perfect NMR probe for following reactivity and decomposition. Also, when two aryl groups on Re(p-tolyl)$_3$(PMe_2Ph)$_2$ reductively eliminate to form a biphenyl, the result is 4,4'-dimethylbiphenyl (p-biph); p-biph has a distinctive proton NMR spectrum, exhibits an easily identifiable aroma, and is crystalline. Lastly, it has the cheapest and simplest synthetic procedure as well as the highest yield for the complexes of the form Re(aryl)$_3$(PR_3)$_2$. At the end of the discussion section, Table 2 gives a selected overview of the results of the stabilty and reactivity studies on Re(p-tolyl)$_3$(PMe_2Ph)$_2$.



The Re(aryl)$_3$(PR_3)$_2$ compounds are stable in the solid state indefinitely under an inert atmosphere and for weeks in air. In air, they decompose over time to a non-homogeneous brown oil and the appropriate substituted biphenyl derived from the aryl groups on the tris(aryl) complex. The formation of biphenyl requires a two electron reduction of the metal; dioxygen appears to promote the reductive elimination of the biphenyl, but dioxygen can also oxidize the remaining rhenium fragment

back up to (III) or (V). By proton NMR spectroscopy, aryl groups do not remain coordinated to the metal center after the decomposition to the brown oil; however, many aryl and many methyl proton resonances, corresponding to metal complexes with PMe_2Ph, are observable in the spectra. The proton NMR spectra of the decomposition products do not show any resonances that are paramagnetically contact-shifted, as octahedral rhenium(III) complexes might exhibit. The IR spectra of the brown oil show one strong stretch at 912 cm^{-1} which is indicative of a rhenium oxo group.[2] There may also be another IR stretch a few wavenumbers higher than the one at 912 cm^{-1} possibly indicating a mixture of oxo species. These results suggest that the brown oil probably contains rhenium(III) or (V) oxo complexes, with the possibility of dimers.

In deoxygenated solutions, the $Re(aryl)_3(PR_3)_2$ compounds are stable for weeks; however, the presence of oxygen causes the solutions to decompose in hours to the same products observed in the solid state decomposition. Heated solutions of $Re(aryl)_3(PR_3)_2$ decompose to biphenyl and the unidentifiable brown oil in under a minute unless dioxygen is excluded. Yet, a solution of $Re(p\text{-tolyl})_3(PMe_2Ph)_2$ can be refluxed in deoxygenated toluene for a week without decomposition. The first step of this dioxygen-dependent decomposition of $Re(aryl)_3(PR_3)_2$ appears to be unimolecular. A controlled crossover reaction between $Re(p\text{-tolyl})_3(PMe_2Ph)_2$ and $Re(m\text{-tolyl})_3(PMe_2Ph)_2$ in toluene with dioxygen was performed. Only formation of 4,4'-dimethylbiphenyl and 3,3'-dimethylbiphenyl was obsevered, with none of the mixed 3,4'-dimethylbiphenyl being formed. This result supports the unimolecular decomposition pathway for $Re(aryl)_3(PR_3)_2$ since the coupled aryl groups came from the same rhenium center

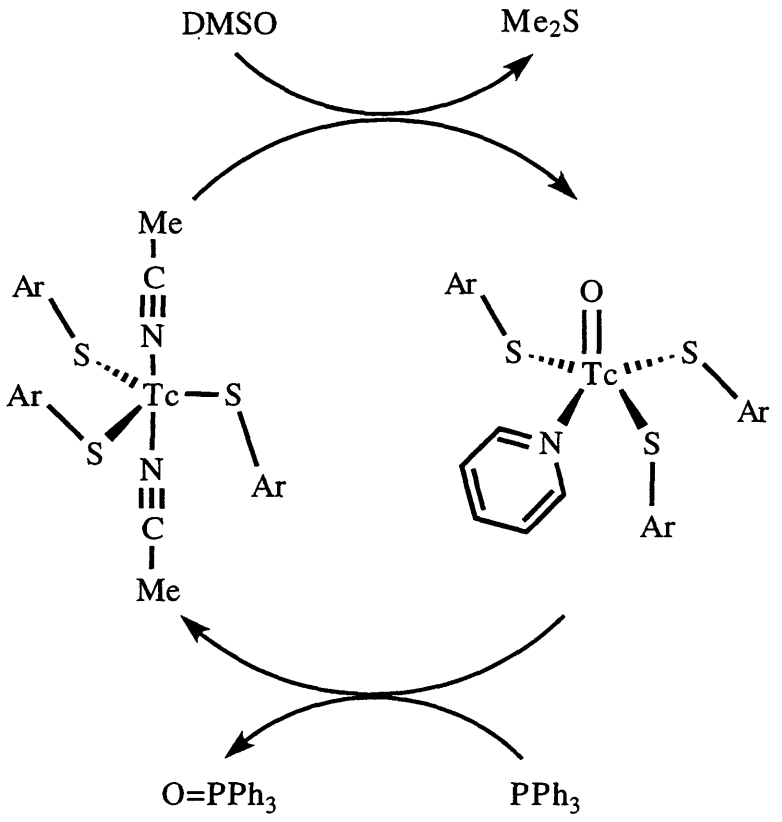
Further evidence for the stability of the tris(aryl) fragment is the absence of any ligand exchange of the aryl groups with the solvent. Stirring Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ in C_6D_6 does not show incorporation of a deuterophenyl group even with heating: Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ does not activate the C-D bond in the solvent and eliminate *p*-deuterotoluene. In addition to the core of stable aryl groups, the axial phosphine ligands of Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ are unreactive and non-labile. In the presence of phosphines, Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ shows neither decomposition nor substitution. Even when a basic phosphine such as PMe$_3$ is used, no reaction is observed. Despite the unsaturated coordination sphere of the rhenium and the small relative cone angle of PMe$_3$, the PMe$_3$ ligand is sterically hindered from approach to the metal center. Formation of an octahedral complex, substitution of a PMe$_2$Ph, or decomposition by reductive elimination of *p*-biph appear to be reasonable results of PMe$_3$ addition, but none of these results is observed.

Other reagents show varied reactivity with Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$. Methyl iodide shows no reactivity with Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ even at elevated temperatures; aided by its small size, it could have oxidatively added to the rhenium center. At room temperature, pyridine and Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ do not react; however, at elevated temperatures, the pyridine promotes Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ to decompose to a brown tacky multi-component solid, containing no coordinated *p*-tolyl groups. The pyridine might have promoted reductive elimination or possibly substituted for a phosphine; however, no products can be identified.

Suitable oxidants for controlled oxidation of Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ were sought. Amine-*N*-oxides, including trimethylamine-*N*-oxide, pyridine-*N*-oxide, and 4-methylmorpholine-*N*-oxide, do not react with

$Re(p\text{-tolyl})_3(PMe_2Ph)_2$ even at elevated temperatures. Triphenylphosphine sulfide is inert to $Re(p\text{-tolyl})_3(PMe_2Ph)_2$ as well; however, S_8 promotes a very fast conversion of $Re(p\text{-tolyl})_3(PMe_2Ph)_2$ upon heating to an intractable black sticky residue. The ideal oxidant is more controllable than dioxygen or S_8, but more reactive than triphenyl phosphine sulfide or amine-*N*-oxides; dimethylsulfoxide (DMSO) appeared to be a favorable choice of oxidant.

Dimethylsulfoxide has been shown to transfer oxygen atoms to transition metal fragments; the formation of dimethylsulfide (DMS) by the abstraction of an oxygen atom from DMSO is a thermodynamically favored process.[3] Structurally related complexes on technetium have utilized DMSO for oxidation. The complexes $Tc(tmbt)_3L_2$ (tmbt = 2,3,5,6-tetramethylthiophenoxide) (*e.g.*, L = acetonitrile, pyridine) were found by de Vries to oxidize in the presence of hot DMSO.[4] The $Tc(tmbt)_3L_2$ complexes are similar to $Re(p\text{-tolyl})_3(PMe_2Ph)_2$; both are trigonal bipyramidal complexes with neutral axial ligands and anionic ligands in the equatorial plane. However, the tmbt ligands in $Tc(tmbt)_3L_2$ are much more flexible and encompass a larger steric volume; they are also less likely to reductively eliminate, as a disulfide would form. From $Tc(tmbt)_3(pyridine)_2$, $TcO(tmbt)_3(pyridine)$ can be isolated; when $TcO(tmbt)_3(pyridine)$ is placed in solution with DMSO and PPh_3, it acts as a catalyst for the oxo transfer that results in DMS and $O{=}PPh_3$ (Scheme 1).[4]



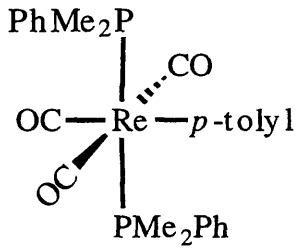
Scheme 1: Catalytic oxidation of PPh_3 by DMSO with $Tc(tmbt)_3L_2$

In contrast to other mild oxidants, DMSO does not react with Re(*p*-tolyl)$_3$(PMe_2Ph)$_2$. Upon heating with DMSO, the deep blue solution of Re(*p*-tolyl)$_3$(PMe_2Ph)$_2$ fades to a pale blue in a few minutes; there are several intermediate colors. However, the reaction is not analogous to those of complexes $Tc(tmbt)_3L_2$. An excess or a stoichiometric amount of DMSO reacts with Re(*p*-tolyl)$_3$(PMe_2Ph)$_2$ to form one equivalent of biphenyl and about one equivalent of DMS, with its unmistakable odor. The amount of DMS can be quantified by isolation of its complex with $HgCl_2$.[5] The rhenium containing products take the form of a pale bluish oil; this oil is a mixture as shown by proton NMR spectroscopy and has so far eluded purification. The inclusion of chelating ligands such as bipyridine in order to possibly stabilize intermediates after the loss of the *p*-biph offered no

improvement for the isolation of a pure product. Since the reaction between Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ and DMSO is accompanied by concomitant loss of *p*-biph, it is unlikely that Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ could be made a part of a catalytic oxo transfer cycle.

Since reactions with σ-donor ligands yielded no isolatable complexes, ligands with good π-accepting abilities were employed. Reaction of Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ with isonitriles affords *p*-biph and a reddish mixture of uncharacterizable rhenium complexes. The reaction takes place in less than one minute and yields similar mixtures whether small isonitriles, such as ^{t}BuNC, or larger isonitriles, such as 2,6-disubstituted aryl isonitriles, are used. The Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ complex is unreactive to thiocyanate anion, but it reacts quickly with NOBF$_4$ to form uncharacterizable dark-colored products.

Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ reacts cleanly with carbon monoxide to form exclusively one rhenium containing complex and *p*-biph. Carbon monoxide promotes the reductive elimination of a biphenyl as well as the coordination of two additional CO ligands to afford an octahedral rhenium(I) complex, Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl), that retains the *trans*-phosphine coordination. The reaction to form Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) is facile and clean, but separation of *p*-biph from Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) is problematic due to the high solubility of both in the same solvents. Most of the *p*-biph can be separated on a column and the "enriched" mixture of Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) can be recrystallized from hot methanol to yield pale red-orange crystals.

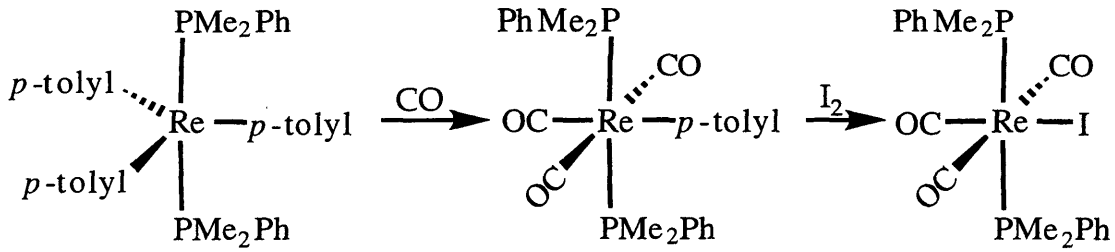


The experimental data for the reaction of carbon monoxide with Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ supports an associative mechanism. This requires carbon monoxide to approach the complex in the equatorial plane, which then promotes the reductive elimination of biphenyl. The coordination number is then increased with more CO ligands, also in the equatorial plane, resulting in a diamagnetic 18-electron octahedral complex with retention of *trans* phosphines. A crossover reaction between Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ and Re(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ shows that the reaction with carbon monoxide is unimolecular with respect to rhenium, as no mixing of *para* and *meta* substitution is seen in the biphenyl products.

The crystals of Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl), grown from hot methanol, were suitable for an X-ray diffraction analysis. Data collection parameters are given in Table 2 and the experimental section. A full set of bond lengths, angles, and positional parameters are given in Tables 3, 4, and 5 at the end of the chapter along with the ORTEP diagram (Figure 1). The crystal structure of Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) shows no major deviations from octahedral geometry; the X-Re-Y angles range from 85.3° to 94.7° and the *trans* angles range between 179.0° and 171.9°. The ORTEP of Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) shows the octahedral geometry of the molecule; one of the phenyl rings on one of the phosphine ligands does not have a very good derived geometry after refinement.

The crystal structure can be used to look at the bonding in the two different types of organometallic ligands. The average rhenium-carbon bond length for the carbonyl carbons is 1.85 Å; this value is short and shows the multiple bonding character of the metal-carbonyl bond. The average carbon-oxygen length in $Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl) is 1.21 Å. This bond length is longer than that of free carbon monoxide (1.13 Å) as would be expected, as the filled metal orbitals donate into the π^* orbital of the ligand.[6] The IR spectrum for $Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl) supports the bond length data by showing a shift of the carbonyl stretching frequency from 2143 cm^{-1} in free carbon monoxide to 1912 cm^{-1} . The bond length for the rhenium-carbon bond of the *ipso* carbon from the aryl ring is 2.19 Å, at the high end of the range for rhenium-carbon aryl bonds (2.006 to 2.216 Å, see Chapter 1). The analogous bond length in $RePh_3(PEt_2Ph)_2$, a complex closely related to the starting material, had an average length of 2.027 Å, near the lower limit of the range.[7] This difference of 0.2 Å is due to the geometric constraints of six-coordination versus five-coordination where there is more space for the ligands to be closer to the metal center, i.e., five-coordinate metals have lower Shannon-Prewitt radii.

This X-ray structure is the first for a complex of the form $Re(CO)_3(PR_3)_2R$ with meridional CO ligands. Other complexes of this form do exist, although they have not been structurally characterized. A similar compound, *fac*-$Re(CO)_3(Ph)(PMe_3)_2$, was made by the addition of CuPh to *fac*-$Re(CO)_3Br(PMe_3)_2$.[8] Other compounds of the form $Re(CO)_3(PR_3)_2R$ have been synthesized by different routes.[9] These include the addition of methyllithium to *trans*-$Re(PPh_3)_2(CO)_3Cl$[10] and the addition of phosphines to $Re(CO)_3L$ (L = indenyl, cyclopentadienyl, etc.) complexes, where L becomes an η^1-sigma bound ligand.[11,12]



Scheme 2: Pathway for rhenium carbonyl formation

If it were possible to oxidatively add a reagent to $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$, there might be a possibility of cycling the rhenium between (III) and (I) oxidation states. However, $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$ does not react with methyl iodide, a good oxidative addition reagent, even under refluxing conditions. When $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$ is treated with I_2 in solution, a reaction quickly takes place (Scheme 1). Rather than undergoing an oxidative addition, $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$ substitutes its aryl group for an iodide. The product, *trans*-$Re(PMe_2Ph)_2(CO)_3I$, retains the geometry of the starting material $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$ as evidenced by the appearance of a virtual triplet for the methyl groups of the phosphine in the proton NMR spectrum. Colorless needles of the iodide can be isolated after removal of excess iodine. The rectivity with iodine indicates that in order to make a stable complex via oxidative addition to $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$, the two resulting anionic ligands should be good π-donors. The π-donors could then stabilize the resultant formally 14-electron rhenium(III) center that would result.

The reactivity of the tetrahydrothiophene (THT) analog $Re(p\text{-tolyl})_3(THT)_2$ was also explored. This complex is less stable and displays greater reactivity. While $Re(p\text{-tolyl})_3(THT)_2$ reacts instantly with carbon

monoxide in solution, no homogeneous rhenium product can be isolated, although an equivalent of *p*-biph formed. The same is true for reactions of Re(*p*-tolyl)$_3$(THT)$_2$ with isonitriles; *p*-biph is formed, but no rhenium complexes could be isolated. This increased reactivity is due to the fact that tetrahydrothiophene is not as strong of an electron donor ligand as dimethylphenyl phosphine. The smaller ligand size of THT also allows more room for other ligands to approach, or for bimolecular decomposition pathways to occur.

Table 1: Selected reactions with Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$

Reagent	With Heating or Without	Biphenyl Produced	Reaction
O_2	either	yes	forms Re oxo complex(es)
water	either	no	none
toluene	either	no	none
PMe_3	either	no	none
MeI	either	no	none
pyridine	with	N/A	intractable
amine-N-oxides	either	no	none
$S{=}PPh_3$	either	no	none
S_8	with	N/A	intractable
DMSO	with	yes	unknown oil
^{t}BuNC	without	yes	unknown mixture
SCN^-	either	no	none
NO^+	without	N/A	intractable
CO	without	yes	Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl)

Conclusion

The 14-electron rhenium(III) complexes $Re(aryl)_3(PR_3)_2$, even though they are coordinatively unsaturated and contain anionic organometallic ligands, are quite stable. When the axial ligands are phosphines, the complexes are more stable and less reactive than the analogous bis(thioether) compound. All of these complexes are susceptible to reductive elimination of substituted biphenyl which can result in both isolable and non-isolable rhenium end products. While carbon monoxide provides a clean rhenium(I) product, molecules such as isonitriles and dioxygen yield intractable mixtures of rhenium containing complexes.

Experimental

All chemistry was performed either on a Schlenk line under an argon atmosphere or in a dry box under a dinitrogen atmosphere with dried, deoxygenated solvents unless otherwise specified. The solvents were either purchased dry or distilled from a sodium-benzophenone ketyl pot. The methyl iodide was purchased from Aldrich. ^{1}H and ^{31}P NMR spectra were recorded on a Varian XL-300, a Varian Unity-300 or a Varian 500-VXR spectrometer. The chemical shifts were referenced to the residual proton impurity in the deuterated solvents obtained from Cambridge Isotopes Laboratory. ^{31}P chemical shifts are reported relative to an external standard of 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 series spectrophotometer as KBr pellets. Fast atom bombardment mass spectra of samples dissolved in 3-nitrobenzylalcohol (NBA) matrix were recorded with a Finnigan MAT 8200 mass spectrometer equipped with an Ion Tech FAB gun operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6-8 keV xenon neutrals. Carbon, hydrogen, and nitrogen elemental analyses were carried out by Atlantic Microlab, Norcross, GA.

The complexes Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ and Re(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ were prepared by the method outlined in Chapter 2.

mer-Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl):

Carbon monoxide was bubbled through a toluene (20 mL) solution of Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (300 mg, 0.408 mmol) for an hour. The solution went from purple-blue to pale red. The solvent was removed under

reduced pressure, and the residue was dissolved in pentane. The pentane solution was loaded onto an alumina/pentane column, and the column was eluted with pentane and then with acetone. The 4,4'-dimethylbiphenyl eluted with the pentane and $Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl), with acetone. The acetone was removed by evaporation, and $Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl) was recrystallized from hot methanol and was isolated as pale red-orange crystals. The biphenyl was identified by ^1H NMR spectroscopy and GC-mass spectrometry. Recrystallized yield 109.2 g (0.171 mmol, 41% yield).

Anal. Calcd. for $C_{26}H_{29}O_3P_2Re$: C, 48.97%; H, 4.58%. Found: C, 49.08%; H, 4.65%. ^1H NMR (C_6D_6) δ: 1.41 (t, 12H), 2.32 (s, 3H), 6.98 (d, 4H), 7.06 (t, 6H), 7.2 (d, 2H), 7.78 (d, 2H). ^{31}P NMR (C_6D_6) δ: -26.60(s). IR (KBr) ν(C≡O) 1912.7(s), 1882.9(s), 2016.5(w) cm^{-1}.

***mer*-$Re(CO)_3(PMe_2Ph)_2I$:**

The pale orange complex *mer*-$Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl) (109.2 mg, 0.171 mmol) was dissolved in THF (10 mL). Subsequently, I_2 crystals (50.0 mg, 0.197 mmol) were added to the solution. As they dissolved, the solution became greenish, then brown. The solution was allowed to stir for 6 hours after which the THF was removed *in vacuo*. The resulting black residue was dissolved in toluene (15 mL) affording a green-brown solution. The excess iodine was extracted into a saturated aqueous solution of sodium thiosulfate. The toluene was then removed in vacuo. The residue was dissolved in a minimum amount of boiling methanol; colorless needles of *mer*-$Re(CO)_3(PMe_2Ph)_2I$ crystallized from this solution. Recrystallized yield 55 mg (0.082 mmol, 42% yield).

Anal. Calcd. for $C_{19}H_{22}IO_3P_2Re$: C, 33.89%; H, 3.29%. Found: C, 34.30%; H, 3.41%. ^1H NMR (d_6-acetone, 300 MHz) δ: 2.20 (t, 12H), 7.41 (t, 2H), 7.49

(m, 4H), 7.64 (m, 4H). ^{31}P NMR (d_6-acetone, 300 MHz) δ: -35.49 (s). IR (KBr) ν(C≡O) 1892.0(s), 1952.1(s) cm^{-1}. FABMS(+) (p-nitrobenzylalcohol): $[Re(PMe_2Ph)_2(CO)_3I]^+$, 674 *m/z*; $[Re(PMe_2Ph)_2(CO)_2I]^+$, 646 *m/z*; $[Re(PMe_2Ph)_2(CO)I]^+$, 618 *m/z*; $[Re(PMe_2Ph)_2I]^+$, 590 *m/z*; $[Re(PMe_2Ph)_2(CO)_3]^+$, 547 *m/z*; $[Re(PMe_2Ph)_2(CO)_2]^+$, 519 *m/z*; $[Re(PMe_2Ph)I]^+$, 452 *m/z*.

Crossover Reaction of Re(tolyl)$_3$(PMe$_2$Ph)$_2$ with Dioxygen:

To a round-bottomed flask containing toluene (15 mL) were added both Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (18.4 mg, 0.0250 mmol) and Re(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ (18.4 mg, 0.0250 mmol). The reaction was stirred overnight (20 h) while exposed to the atmosphere. The initially deep blue solution had become pale yellow after 4 h. The solvent was removed *in vacuo* leaving a brownish residue. The organic portion of the residue was extracted into pentane. After removal of the pentane *in vacuo*, the proton NMR spectrum was taken, in d_6-acetone, of the organic products extracted into pentane. The proton NMR had resonances corresponding to 3,3'-dimethylbiphenyl and 4,4'-dimethylbiphenyl with an integration of 1:1; there was also some dimethylphenylphosphine in the NMR; no resonances corresponding to the m,p'-dimethylbiphenyl were present.

^1H NMR (CD_3COCD_3, 300 MHz) δ: 2.35 (s, 6H), 7.25 (d, 4H), 7.51 (d, 4H). ^1H NMR (CD_3COCD_3, 300 MHz) δ: 2.39 (s, 6H), 7.17 (d, 2H), 7.44 (s, d, 4H), 7.18 (m, 2H).

Crossover Reaction of $Re(tolyl)_3(PMe_2Ph)_2$ with Carbon Monoxide:

To a round-bottomed flask containing toluene (20 mL) were added both Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (30.9 mg, 0.0420 mmol) and Re(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ (33.1 mg, 0.0449 mmol). Carbon monoxide was slowly bubbled through the solution. The solution became darker over the first five minutes; then the solution paled to brown then yellowish over the course of the next 15 minutes. The solvent was removed *in vacuo*. Separation by column chromatography was unsuccessful; a proton NMR was taken of the mixture. The spectrum has resonances corresponding to Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) (**7**) and its *m*-tolyl analog, as well as both 3,3'-dimethylbiphenyl and 4,4'-dimethylbiphenyl. The integration of the *meta* versus *para* rhenium(I) complexes and biphenyls gave ratios of 1.1 which corresponds to the ratio of the two isomers of the starting material.

X-Ray Crystallographic Data Collection Parameters for *mer*-$Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl):

The data for Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) were collected on a Rigaku AFC6R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12kW rotating anode generator. The data for Re(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) were collected using an orange prismatic crystal having dimensions 0.280 x 0.140 x 0.280 mm. The crystal system was monoclinic ($\alpha = \gamma = 90°$) with a = 16.097(4) Å, b = 8.794(4) Å, and c = 19.80(1) Å, and β = 107.64(3)°; this leads to a cell volume V = 2672(2) Å^3 with Z = 4. The space group was found to be $P2_1/c$. The absorption coefficient was 4.75 mm^{-1}, the calculated density ρ = 1.585 g/cm^3, and F(000) = 1272. The data were obtained at 296 K with 2θ being 50°. Of the

4545 reflections collected, 4354 were independent (R_{int} = 0.086). The structure was solved by a combination of Patterson method and direct methods. Least squares refinement based upon F^2 with 2503 data, no restraints and 274 parameters converged with final residuals: R = 0.058, R_w= 0.046, and GOF = 1.88 based upon $I > 3\sigma(I)$.

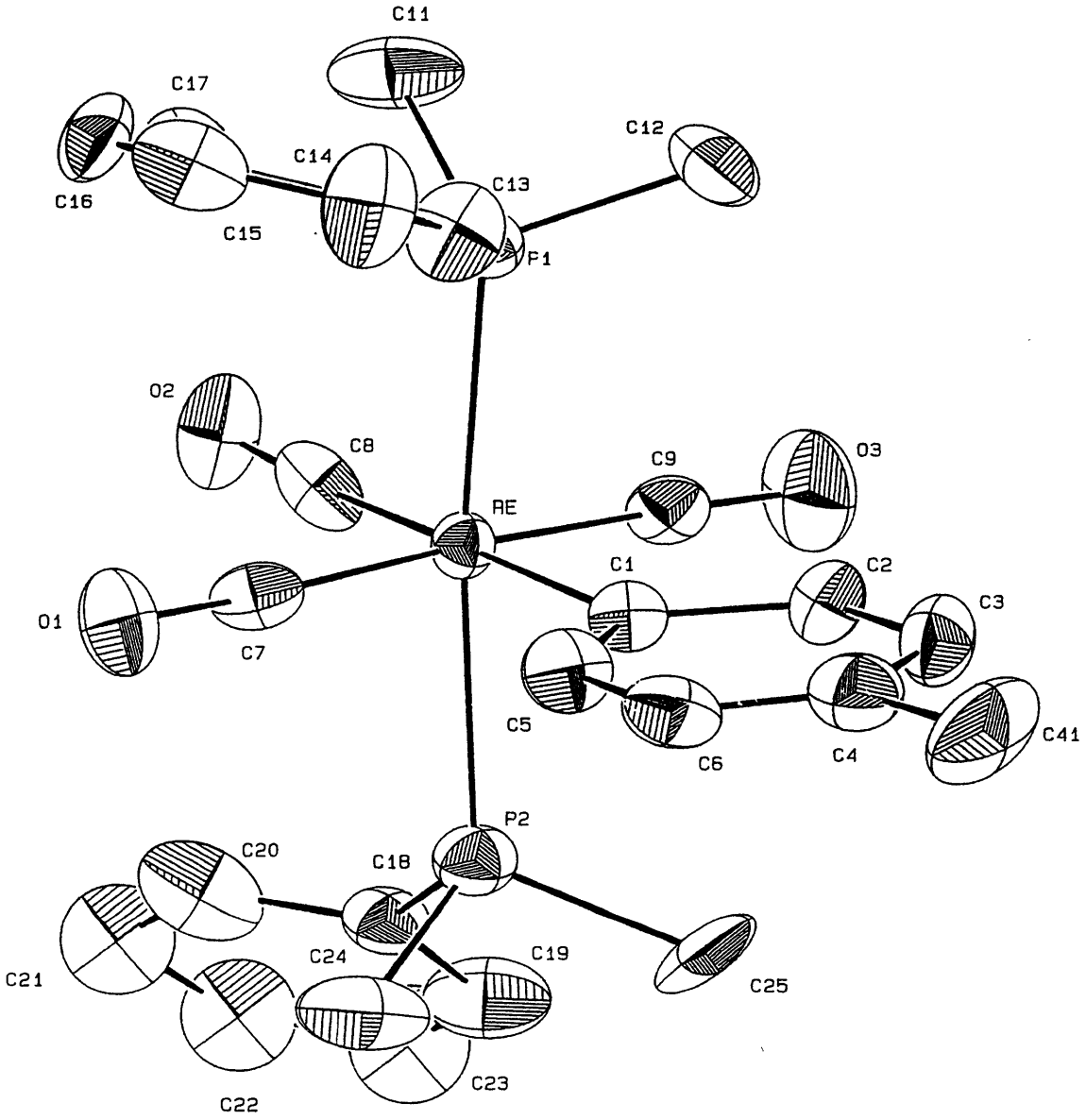


Figure 1: ORTEP of $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})_3$ with 35% ellipsoids

Table 2. Data Collection Parameters for $Re(CO)_3(p\text{-tolyl})(PMe_2Ph)_2$

Empirical formula	$C_{26}H_{29}O_3P_2Re$	
Formula weight	637.67 g/mol	
Temperature	296 K	
Radiation	MoKα	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.097(4) Å	α = γ = 90°
	b = 8.794(4) Å	β = 107.64(3)°
	c = 19.80(1) Å	
Volume	2672(2) Å^3	
Z	4	
Density (calculated)	1.585 g/cm^3	
Absorption coefficient	4.75 mm^{-1}	
F(000)	1256	
2θ	50.0°	
Reflections collected	4545	
Independent reflections	4354 (R_{int} = 0.086)	
Diffractometer	Rigaku AFC6R	
Scan Type	ω - 2θ	
Refinement method	Full-matrix least-squares on F^2	
Structure solution	Patterson Method	
Data / restraints / parameters	2503 / 0 / 274	
Goodness-of-fit on F^2	1.88	
Final R indices [I>3σ(I)]	R = 0.058, R_w= 0.046	
Largest diff. peak and hole	1.20 and -1.09 eÅ^{-3}	

Table 3: Bond Lengths for $Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl)

Atoms	Length (Å)	Atoms	Length (Å)
Re-P(1)	2.409(5)	Re-P(2)	2.405(5)
Re-C(1)	2.19(2)	Re-C(7)	1.89(2)
Re-C(8)	1.85(2)	Re-C(9)	1.87(2)
P(1)-C(10)	1.81(2)	P(1)-C(11)	1.83(2)
P(1)-C(12)	1.83(2)	P(2)-C(18)	1.77(2)
P(2)-C(24)	1.81(2)	P(2)-C(25)	1.83(2)
O(1)-C(7)	1.21(2)	O(2)-C(8)	1.21(2)
O(3)-C(9)	1.22(2)	C(1)-C(2)	1.46(2)
C(1)-C(5)	1.36(2)	C(2)-C(3)	1.45(2)
C(3)-C(4)	1.37(2)	C(4)-C(6)	1.35(2)
C(4)-C(41)	1.51(2)	C(5)-C(6)	1.43(2)
C(10)-C(13)	1.37(2)	C(10)-C(17)	1.41(2)
C(13)-C(14)	1.36(2)	C(14)-C(15)	1.34(2)
C(15)-C(16)	1.38(2)	C(16)-C(17)	1.42(2)
C(18)-C(19)	1.37(2)	C(18)-C(20)	1.39(2)
C(19)-C(23)	1.44(3)	C(20)-C(21)	1.46(3)
C(21)-C(22)	1.38(3)	C(22)-C(23)	1.28(3)

Table 4: Bond Angles for $Re(CO)_3(PMe_2Ph)_2(p\text{-tolyl})$

Atoms	Angle (°)	Atoms	Angle (°)
P(1)-Re-P(2)	171.9(2)	P(1)-Re-C(1)	85.3(4)
P(1)-Re-C(7)	92.4(5)	P(1)-Re-C(8)	94.7(6)
P(1)-Re-C(9)	90.6(5)	P(2)-Re-C(1)	86.7(4)
P(2)-Re-C(7)	89.0(5)	P(2)-Re-C(8)	93.3(6)
P(2)-Re-C(9)	87.8(5)	C(1)-Re-C(7)	87.0(7)
C(1)-Re-C(8)	179.0(7)	C(1)-Re-C(9)	92.3(7)
C(7)-Re-C(8)	92.0(7)	C(7)-Re-C(9)	176.8(7)
C(8)-Re-C(9)	88.8(7)	Re-P(1)-C(10)	115.2(6)
Re-P(1)-C(11)	115.7(7)	Re-P(1)-C(12)	115.6(6)
C(10)-P(1)-C(11)	104.4(8)	C(10)-P(1)-C(12)	101.1(9)
C(11)-P(1)-C(12)	102.9(9)	Re-P(2)-C(18)	116.9(6)
Re-P(2)-C(24)	116.2(6)	Re-P(2)-C(25)	113.9(7)
C(18)-P(2)-C(24)	103.2(9)	C(18)-P(2)-C(25)	104(1)
C(24)-P(2)-C(25)	100.8(9)	Re-C(1)-C(2)	123(1)
Re-C(1)-C(5)	127(1)	C(2)-C(1)-C(5)	110(2)
C(1)-C(2)-C(3)	123(2)	C(2)-C(3)-C(4)	121(2)
C(3)-C(4)-C(6)	118(2)	C(3)-C(4)-C(41)	117(2)
C(6)-C(4)-C(41)	125(2)	C(1)-C(5)-C(6)	128(2)
C(4)-C(6)-C(5)	120(2)	Re-C(7)-O(1)	177(2)
Re-C(8)-O(2)	173(2)	Re-C(9)-O(3)	177(2)
P(1)-C(10)-C(13)	122(1)	P(1)-C(10)-C(17)	119(1)
C(13)-C(10)-C(17)	119(2)	C(10)-C(13)-C(14)	122(2)
C(13)-C(14)-C(15)	121(2)	C(14)-C(15)-C(16)	120(2)
C(15)-C(16)-C(17)	120(2)	C(10)-C(17)-C(16)	118(2)
P(2)-C(18)-C(19)	124(2)	P(2)-C(18)-C(20)	117(2)
C(19)-C(18)-C(20)	119(2)	C(18)-C(19)-C(23)	122(2)
C(18)-C(20)-C(21)	120(2)	C(20)-C(21)-C(22)	114(2)
C(21)-C(22)-C(23)	129(3)	C(19)-C(23)-C(22)	116(2)

Table 5: Positional parameters and estimated standard deviations ($Å^2$) for $Re(CO)_3(PMe_2Ph)_2$(*p*-tolyl)

atom	x	y	z	B(eq)
Re	0.28112(5)	0.16184(9)	0.08809(4)	2.91(3)
P(1)	0.3727(3)	0.3384(7)	0.0506(2)	4.1(2)
P(2)	0.1725(3)	0.0041(6)	0.1140(3)	4.3(2)
O(1)	0.3166(9)	0.093(1)	0.0080(7)	6.1(8)
O(2)	0.4339(8)	0.048(2)	0.2108(6)	5.9(7)
O(3)	0.237(1)	0.408(2)	0.1834(7)	7.4(9)
C(1)	0.177(1)	0.244(2)	0.0037(9)	3.4(9)
C(2)	0.127(1)	0.381(2)	0.0019(9)	4(1)
C(3)	0.061(1)	0.439(2)	0.064(1)	5(1)
C(4)	0.042(1)	0.366(3)	0.128(1)	6(1)
C(5)	0.151(1)	0.182(2)	0.070(1)	5(1)
C(6)	0.085(1)	0.236(2)	0.131(1)	5(1)
C(7)	0.300(1)	0.007(2)	0.0284(8)	4(1)
C(8)	0.370(1)	0.090(2)	0.1647(9)	4(1)
C(9)	0.257(1)	0.309(2)	0.1476(8)	3.7(9)
C(10)	0.390(1)	0.295(2)	0.033(1)	3.4(9)
C(11)	0.483(1)	0.364(2)	0.112(1)	7(1)
C(12)	0.332(1)	0.533(2)	0.035(1)	6(1)
C(13)	0.333(1)	0.341(3)	0.097(1)	6(1)
C(14)	0.346(1)	0.303(3)	0.159(1)	7(1)
C(15)	0.410(1)	0.209(2)	0.162(1)	6(1)
C(16)	0.469(1)	0.156(2)	0.100(1)	5(1)
C(17)	0.459(1)	0.197(2)	0.0340(8)	5(1)
C(18)	0.204(1)	0.095(2)	0.196(1)	4(1)
C(19)	0.166(1)	0.074(2)	0.248(1)	7(1)
C(20)	0.271(1)	0.201(3)	0.206(1)	7(1)
C(21)	0.299(1)	0.288(3)	0.272(1)	8.5(7)
C(22)	0.254(2)	0.254(3)	0.320(1)	8.7(7)
C(23)	0.194(2)	0.157(3)	0.314(1)	9.7(7)
C(24)	0.126(1)	0.144(3)	0.050(1)	8(1)
C(25)	0.074(1)	0.107(2)	0.115(1)	8(1)
C(41)	0.028(1)	0.434(3)	0.189(1)	9(1)

References

(1) Brown, S. N.; Myers, A. W.; Fulton, R. J.; Mayer, J. M. *Organometallics* **1998**, *17*, 3364-3374.

(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

(3) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(4) de Vries, N. H. C. Ph.D. Thesis, M.I.T., 1988.

(5) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728.

(6) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*; VCH: New York, 1992.

(7) Carroll, W. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 825-826.

(8) Fronko, R. M. Ph.D. Thesis, University of Wisconsin-Madison, 1984.

(9) Winter, M. *Organorhenium Compounds - Part I*; Spinger-Verlag: New York, 1989.

(10) Chatt, J.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Organomet. Chem.* **1980**, *184*, C64-C66.

(11) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384-388.

(12) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535-538.

Chapter 4

A Review of Technetium Organometallic Complexes

Introduction

Since the discovery and isolation of technetium in 1937, many research groups have worked toward understanding its chemistry and reactivity. Much of the early chemistry focused on basic inorganic coordination chemistry. However, in 1984, the discovery of Cardiolite, a powerful heart imaging agent, served a two-fold purpose in refocusing the research on technetium.[1] First, what had initially appeared to be a relatively abundant but inconveniently radioactive element was shown to be an important component of a very powerful bioimaging agent. Second, as Cardiolite is a homoleptic isonitrile complex, the field of technetium organometallics saw a resurgence as a possible basis for future imaging agents.

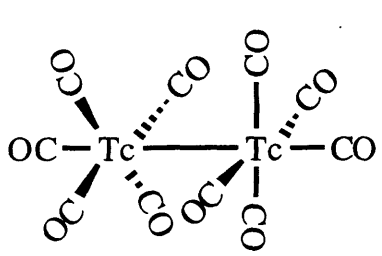
While the total number of technetium organometallic complexes is relatively small, it follows a chronological progression similar to the development of organometallic chemistry as a whole. Around 1960, the earliest organometallics of technetium were synthesized, specifically carbonyl complexes including $Tc_2(CO)_{10}$ (**1**). These were shortly joined by some cyclopentadienyl complexes, as well as η^6-arene complexes. For about 20 years, until the revitalization of the field by Cardiolite, there were few new technetium organometallics synthesized. Currently, there are examples of several classes of organometallics present in the canon of technetium chemistry, including Fischer carbenes, alkylidenes, alkylidynes, and metallacycles.

The following review is a detailed look at technetium organometallic chemistry from the perspectives of both synthesis and reactivity. For the most part, carbonyl complexes and isonitrile complexes will be excluded, as

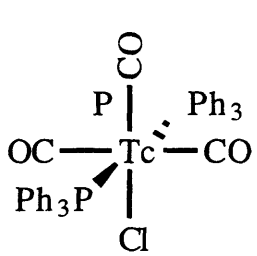
these are well covered in other reviews.[2,3] The main focus will be polyhapto organometallic ligands and anionic organometallic ligands.

Basic Organometallics

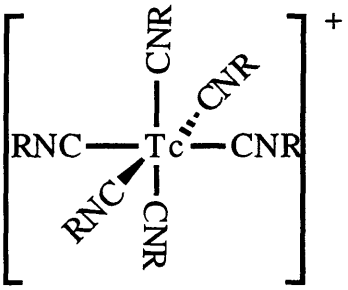
As nickeltetracarbonyl pushed twentieth-century chemistry toward organometallics and the role of the "18-electron rule," it is fitting that the first organometallic complex of technetium, synthesized in 1961, was the homoleptic carbonyl dimer (**1**).[4] It is a volatile complex with a structure that matches that of the other two Group 7 decacarbonyl complexes.[5] After thirty years, there has been much improvement over the original synthesis of (**1**) as well as the discovery of many more carbonyl complexes of technetium. Currently, these carbonyls are, by far, the largest portion of the known organometallic technetium complexes.



1



2



3

Most carbonyl complexes of technetium are in the low oxidation state of +1. These complexes roughly parallel the known complexes for rhenium carbonyls. There exist several monomeric charged homoleptic carbonyls, as well as a number of halide bridged dimers. However, in terms of synthetic utility, the three most commonly used carbonyl complexes are $Tc(CO)_5Br$,[6] *trans-mer*-$Tc(CO)_3(PPh_3)_2Cl$ (**2**), and *fac*-$[Tc(CO)_3X_3]^{2-}$ (where X = halide).[7] These three complexes readily accept new ligands; *fac*-

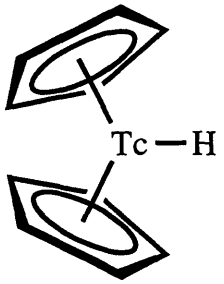
$[Tc(CO)_3X_3]^{2-}$ readily accepts new ligands by becoming a versatile tris-solvento complex in solution via replacement of the halides.

Another large portion of technetium organometallic compounds consist of complexes containing isonitriles. The breadth of this subfield is directly related to the utility of the family of hexakis(isonitrile)technetium cations $[Tc(CNR)_6]^+$ (**3**), especially Cardiolite (**3a**, where R = 2-methoxy-isobutyl), as biological imaging agents.[1] This family of complexes were first reported by Abrams *et. al.* as synthesized from pertechnetate via sodium dithionite reduction in the presence of isonitriles.[8] There are also a variety of other technetium isonitrile complexes, mostly in low oxidation states, which have other ligands including halides, phosphines, and carbonyls.[3,9]

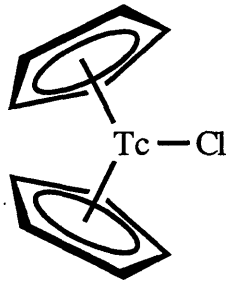
Cyclopentadienyl Complexes

The same year that saw the discovery of the first carbonyl complex of technetium (**1**), saw the synthesis of the first η^5-cyclopentadienide (Cp) ligand complex, $[Cp_2Tc]_2$ (**4**).[10] The original preparation of (**4**) involved the treatment of $TcCl_4$ with NaCp followed by $NaBH_4$ in THF and produced the golden-yellow diamagnetic solid. Molecular weight determination and elemental analysis combined with no proton NMR resonance for a hydride nor a M-H stretch in the infrared spectrum all supported the dimer formation. However, when Fischer repeated the preparation several years later, he obtained Cp_2TcH (**5**) as golden-yellow crystals.[11] He found both the proton NMR resonance for the hydride at -17.8 ppm and the M-H stretch in the infrared spectrum at 1930 cm^{-1}. These results were not reconciled until 1990, when Ziegler found that both the dimer (**4**) and the

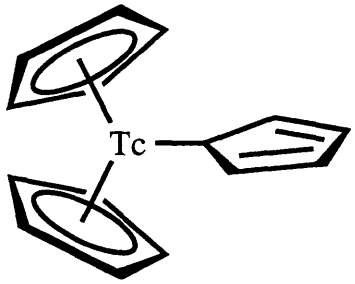
hydride (**5**) were found as golden-yellow crystals by subliming the products of the reaction of sodium naphthalenide with Cp_2TcCl (**6**).[12]



5



6



8

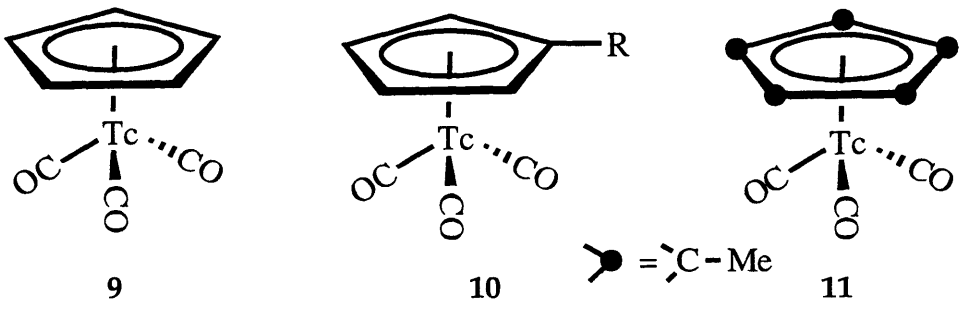
Along with the discovery of the hydride (**5**), an interesting reversible reaction was revealed. If (**5**) is treated with hydrochloric acid, the complex becomes protonated, and the cation $[Cp_2TcH_2]^+$ (**7**) can be isolated as the PF_6^- salt. This complex (**7**) shows a different proton NMR spectrum from (**5**), now having a very broad resonance at -9.7 ppm, corresponding to the metal bound hydrides. Treatment with sodium hydroxide easily returns the technetium complex back to the monohydride (**5**).

$$\underset{\mathbf{5}}{Tc(C_5H_5)_2H} \underset{NaOH}{\overset{HCl}{\rightleftharpoons}} \underset{\mathbf{7}}{[Tc(C_5H_5)_2H_2]^+}$$

The chloride (**6**), mentioned earlier as a source of both the hydride (**5**) and the dimer (**4**), is isolated in 38% yield from the reaction of KCp and $TcCl_4$.[12] The X-ray crystallographic analysis of (**6**) shows a standard bent metallocene structure with a short ring-metal distance indicating high covalent bonding character. The chloride (**6**) can be easily converted to the mixed pentahapto-monohapto complex, Cp_3Tc (**8**) with an equivalent of

KCp. The complex Cp_3Tc (**8**) can also be afforded by treating $TcCl_4$ with an excess of KCp, though in lower yields. Treatment with NH_4Cl or HCl converts (**8**) back to the chloride (**6**). The solid state crystal structure of (**8**) shows a metallocene portion that is bent about 10° and an η^1-Cp roughly in the equatorial gap.[13] Ziegler reports evidence for the existence of Cp_4Tc; however, the only supporting evidence is the shifting of the molecular ion peak from Cp_3Tc^+ to Cp_4Tc^+ in the mass spectrum of (**8**) as the temperature is increased from 50 °C to 80 °C.[12]

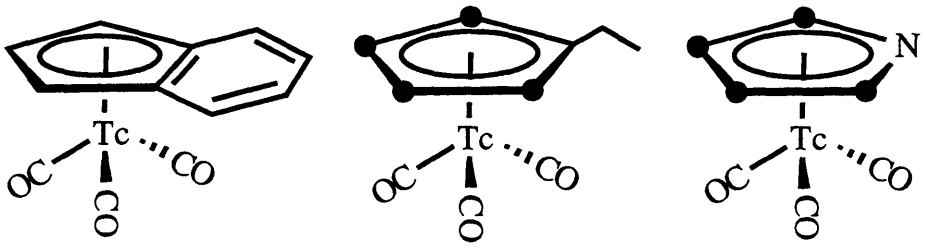
The next major motif seen in technetium cyclopentadienyl chemistry is the family of three-legged piano stool complexes based on $CpTc(CO)_3$ (**9**), a close relative of the prevalent cymantrene, the manganese analog of (**9**). The complex (**9**) was first detected in a thermal neutron nuclear transmutation of the molybdenum in $[CpMo(CO)_3]_2$[14] and later synthesized on a large scale by reacting $TcCl_4$, copper, CO, and NaCp under high pressure.[15] Fischer also performed a Friedel-Crafts acylation on (**9**) to make $(CpR)Tc(CO)_3$ (**10a**) where R = C(O)Ph.[16]



9 **10** **11**

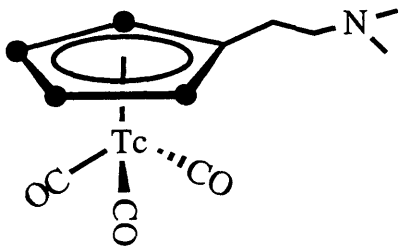
In 1991, Ziegler expanded the family of compounds based on (**9**) to include $Cp^*Tc(CO)_3$ ($Cp^* = C_5Me_5$) (**11**), $(C_5Me_4Et)Tc(CO)_3$ (**12**), and $(indenyl)Tc(CO)_3$ (**13**).[17] The synthesis has now been streamlined to start with $Tc_2(CO)_{10}$ and the appropriate cyclopentadiene. The X-ray crystal

structures have been determined for each of (**11**)-(**13**), and they all show standard piano stool geometries.[17] If $Tc(CO)_5Br$ is combined with tetramethylpyrrolyl potassium $(Me_4C_4N)K$, $(Me_4C_4N)Tc(CO)_3$ (**14**) is isolated.[18] This complex (**14**) has an η^5-pyrrole ring on the technetium, but there is always another Me_4C_4NH hydrogen-bound to the N on the coordinated ring.

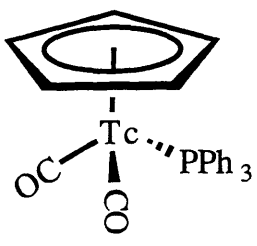


12 **13** **14**

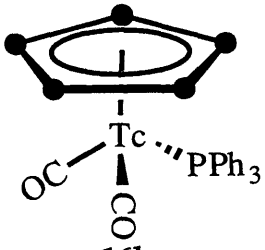
In addition to the use of $Tc_2(CO)_{10}$ as a precursor for (**9**) and its analogs, it was found that (**9**) and (**11**) can both be synthesized from $Tc(CO)_5I$ and the appropriate lithium cyclopentadienide at room temperature in THF.[19] This route allows for much milder conditions than any of the previous methods. As a result, the complex $[C_5Me_{4(}(CH_2)_3NMe_2)]Tc(CO)_3$ (**15**) was also synthesized by this method where the ring has a dangling alkyl amine chain. By treating (**15**) with methyl iodide, its quaternary salt (**15a**) was isolated, and an X-ray crystal structure was determined. The complex (**15a**) was found to have a symmetrically bound ring, with standard piano stool geometry, with the side chain pointing away in open space. Herrmann also synthesized (**11**) by reacting Cp*H with the cluster complex, $NaTc_3(CO)_9(OCH_3)_4$.[20]



15

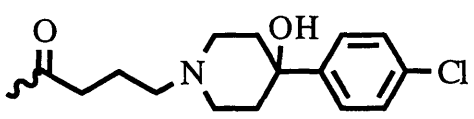


16a

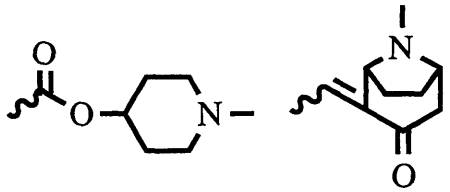


16b

One research group has found an interesting application for these technetium tricarbonyls of the form (**10**). By varying the functional group R, Wenzel has found that these complexes (**10**) can cross the blood-brain barrier and localize in the brains of rats and might possibly be used as brain imaging agents.[21] These complexes have only been synthesized on the tracer level using ^{99m}technetium, the metastable isotope ($t_{1/2}$ = 6.1 h vs. 2.12 x 10^5 y). The reaction uses a mixture of $^{99m}TcO_4^-$, $Mn(CO)_5Br$, and a ferrocene with the appropriate cyclopentadienyl ligand heated in THF in a glass vessel. The complexes (**10**) are separated by chromatography after the carbonyl and cyclopentadienyl ligands have transferred to the technetium. There have been many derivatives of (**10**) made with a variety of R groups. These include the haloperidol derivative (**10b**) which has an affinity for the lungs,[22] the N-methylpiperdine derivative (**10c**) which has a high affinity for the brain,[21,23] and the tropinone derivative (**10d**) which exhibits the best brain affinity of all the complexes.[22]

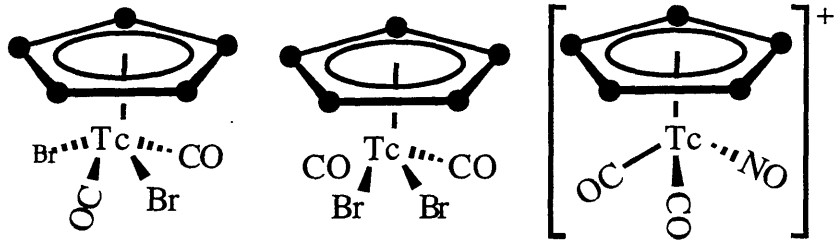


R of **10b**



R of **10c** R of **10d**

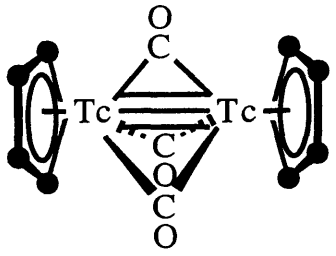
Several research groups have been working on making chemical derivatives of (**9**) and (**11**). The photochemical reaction of (**9**) or (**11**) with triphenylphosphine results in $CpTc(CO)_2PPh_3$ (**16a**) and $Cp^*Tc(CO)_2PPh_3$ (**16b**) respectively.[24] The X-ray crystal structures for both were determined; (**16b**) was found to be homologous to the rhenium analog, although the structure for (**16a**) showed that its triphenylphosphine ligand was much closer to the Cp ring because of the lower steric bulk on the ring without the five methyl groups. Treatment of (**16b**) with a bromine/trifluoroacetic acid mixture results in the formation of two isomers of the dicarbonyl, *trans*-$Cp^*Tc(CO)_2Br_2$ (**17a**) and *cis*-$Cp^*Tc(CO)_2Br_2$ (**17b**), analogous to the chemistry of the rhenium complexes.[19] They are isolated in a 3:1 ratio of *trans* (**17a**) to *cis* (**17b**) after separation by chromatography. With $NOPF_6$ in acetonitrile, (**16b**) can also be converted to the nitrosyl cation $[Cp^*Tc(CO)_2NO]^+$ (**18**) in good yield.[19]



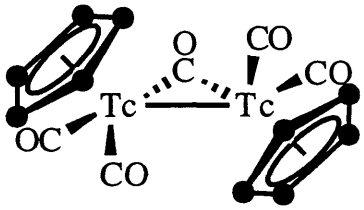
17a **17b** **18**

However, when (**11**) is irradiated in cyclohexane, two different carbonyl bridged dimers are formed. The first is the cylindrically symmetric $Cp^*_2Tc_2(CO)_3$ (**19**) with three bridging carbonyls and a Tc-Tc triple bond of 2.413(3) Å.[25] The second dimer $Cp^*_2Tc_2(CO)_5$ (**20**) is believed to have the same structure as the rhenium analog, with one bridging carbonyl and a Tc-Tc single bond. If (**20**) is photolyzed, both the

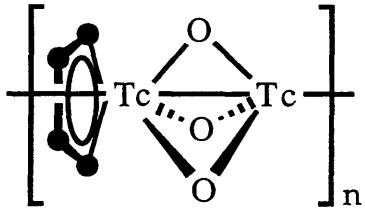
original complex (**11**) and the other dimer (**19**) are formed; a $Cp^*Tc(CO)_2$ fragment is predicted to be an intermediate.[25]



19



20

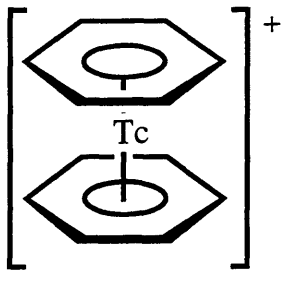


21

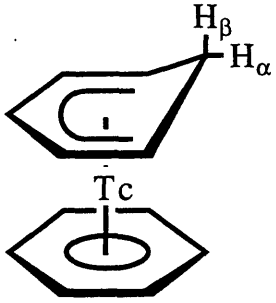
The final organometallic technetium dimer is the one surrounded by the most controversy. When (**11**) is treated with hydrogen peroxide, a yellow crystalline product with the empirical formula, $Cp^*Tc_2O_3$ (**21**), is obtained.[26] An X-ray crystallographic analysis of (**21**) shows that it is a linear polymer in the solid state, with three bridging oxos between the two technetiums supported by a bond with order 3.5. The Tc-Tc bond length is 1.867(4) Å, which is unusually short, but understandable with three bridging ligands and a high bond order. The terminal technetium is bound to the Cp* ring of the next unit, and all the rings are crystallographically planar. Elemental and mass spectral analyses as well as NMR and IR spectroscopies support the polymeric structure. However, Herrmann does not believe that the polymeric structure is correct; he feels that the Tc-Tc bond length is unreasonable, the IR bands represent terminal oxos, and that the unsatisfactorily solved structure of Cp^*ReO_3 is too similar to that of (**21**).[27] He postulates that the product is really the monomeric Cp^*TcO_3. Hoffmann has done calculations that support the geometric structure of the polymer. He feels that the electronic structure gives an approximate bond order of 2.5, but the short Tc-Tc bond length is perfectly reasonable.[28]

Arene and Alkene Complexes

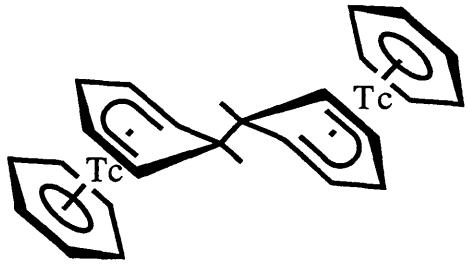
In 1961, the cationic technetium analog of bis(benzene)chromium, $(C_6H_6)_2Tc$ (**22**), was synthesized for the first time, but by a rather circuitous method. Using bis(benzene)molybdenum as a source, neutron bombardment afforded (**22**) initially in small amounts[29] and later in larger quantities;[30] both require allowing time for the ^{99m}technetium to decay to ^{99}technetium. The first practical synthesis of (**22**) came later using $TcCl_4$ with aluminum and $AlCl_3$ in benzene.[31] The synthesis could also be extended to make $(C_6Me_6)_2Tc$ (**22a**), the permethylated analog of (**22**), by using hexamethylbenzene as a solvent.[32] Treatment of (**22**) or (**22a**) with lithium aluminum hydride results in the complexes $(C_6H_6)(C_6H_7)Tc$ (**23**) and $(C_6Me_6)(C_6Me_6H)Tc$ (**23a**) which are neutral complexes with one arene ligand converted into a hexadienyl ligand. In the case of the permethylated (**23a**), the methyl group is located in the α position as evidenced by NMR spectroscopy.[32] If (**22**) and (**22a**) are reduced with lithium, dimers with the formulas $[Tc(C_6H_6)_2]_2$ (**24**) and $[Tc(C_6Me_6)_2]_2$ (**24a**) respectively are isolated, where there is a carbon-carbon bond between one benzene ring from each technetium, giving each metal a coordination environment like that of (**23**).[32]



22



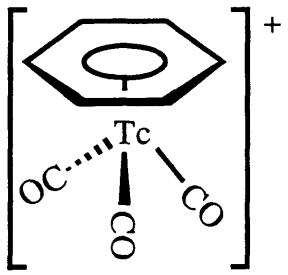
23



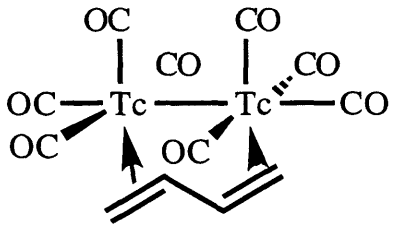
24

Recently, Wester has used complexes of bis(arene)technetium cations (**22**) for a study in ^{99m}technetium biological uptake. Using $^{99m}TcO_4^-$, $Al/AlCl_3$ or Zn/HCl, and the appropriate arene, complexes of the form (**22**) could be isolated after chromatography.[33] Over two dozen complexes of the form (**22**) were synthesized with a variety of arenes; however, only the complexes of 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene were made on a large enough scale to isolate. The study showed a substantial uptake of technetium in the heart tissue when the arene had between 4 and 6 carbon based substituents on the ring, *i.e.*, the uptake was directly correlated to the lipophilicity of the arene.[33]

There is only one arene complex of technetium that features non-arene or non-hexadienyl ligands. This complex is $[Tc(CO)_3(C_6H_6)]^+$ (**25**), which was synthesized by taking Herrmann's cluster complex, $NaTc_3(CO)_9(OCH_3)_4$, and reacting it with hydrochloric acid and benzene.[20] It was achieved in 52% yield, but no subsequent work has been done on (**25**). The last complex of technetium featuring an olefinic π system is $Tc_2(CO)_8(C_4H_6)$ (**26**). This η^4-butadiene complex was formed by taking the $Tc_2(CO)_{10}$ (**1**) dimer in pentane and photolysing it at low temperature with butadiene present. The X-ray structure of (**26**) was determined and it was found to be isomorphous to the rhenium and manganese analogs.[34]



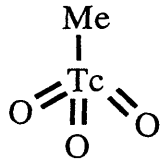
25



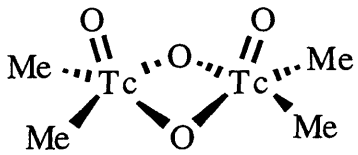
26

Complexes Featuring Anionic Sigma Donors

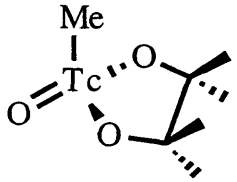
The first high oxidation state complex of technetium synthesized was $TcMeO_3$ (**27**). This complex can be made in appreciable yields from the reaction of Tc_2O_7 with either $SnMe_4$ or $MeTi(^iPr)$.[27] Unlike its more robust rhenium analog, it decomposes above 20 °C and is moisture sensitive. In light of the recent advances with Sharpless' epoxidations of olefins with the rhenium analog of (**27**),[35] the chemistry of (**27**) could be very fruitful and interesting, but it has been hindered by the instability, radioactivity, and extremely high vapor pressure (about 1 atm at room temperature) of (**27**).[9] In the synthesis of (**27**), there is always a large amount of $Tc_2O_4Me_4$ (**28**) present in the reaction mixture. This complex, (**28**), has two paramagnetic technetium(VI) centers; its crystal structure shows distorted square pyramidal structure for each technetium with a Tc-Tc distance that could be a single bond, but must have no bond to account for paramagnetism of the complex.[27] Herrmann has found that (**27**) is capable of catalytically forming *cis*-diols from alkenes with H_2O_2. He hypothesizes complex TcOMe(diolate)(**29**) as an intermediate in the process; the process is unfortunately extremely sensitive to water.[9] Though he could not isolate (**29**), he feels that the process is analogous to *cis*-diol formation with OsO_4 and matches the reactivity of $TcClO_3$(phenanthroline), which reacts with olefins to make a complex analogous to (**29**).[36] A density functional analysis on (**27**) and some of its base adducts has shown that (**27**) has a polarizabilty that matches that of a late transition metal and can account for its reactivity with soft Lewis bases such as olefins.[37]



27

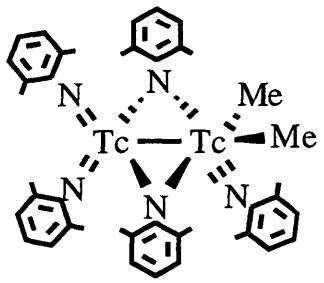


28

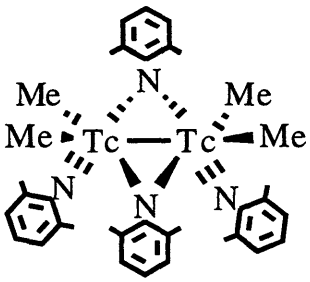


29

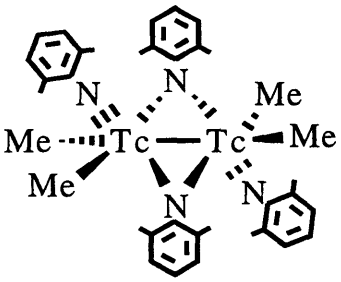
The reaction of $Tc_2(NAr)_4(\mu\text{-}NAr)_2$ (Ar = 2,6-dimethylphenyl) with two equivalents of methyl Grignard yields $Tc_2(NAr)_3(\mu\text{-}NAr)_2Me_2$ (**30**) in which an imido ligand has been replaced by two methyl groups. The X-ray structure of (**30**) shows an asymmetric dimer with a distorted square pyramid geometry for one technetium and a distorted tetrahedral geometry for the other.[38] If (**30**) is treated with two more equivalents of methyl Grignard, $Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4$ (**31**) is obtained; (**31**) is similar in structure to the oxo bridged (**28**). This complex can exist as two isomers, E (**31a**) and Z (**31b**); the X-ray structure for (**31**) shows that it has a Z structure in the solid state with two roughly square pyramidal metal centers where the methyl groups reside on opposite sides of the plane formed by the technetiums and the bridging imidos.[38] In contrast to the structure of (**31**), the oxo bridged analog (**28**) shows an E structure.[27]



30



31a

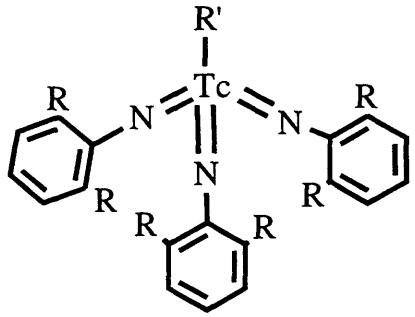


31b

The remaining organometallics in the higher oxidation states are all of the form $Tc(NAr)_3R$ (**32**) where a technetium(VII) center is bound to

three bulky imido groups and one alkyl group. Starting from $Tc(NAr)_3OSiMe_3$ (where Ar = 2,6-diisopropylphenyl), treatment with the appropriate Grignard reagents results in the formation of the methyl (**32a**), ethyl (**32b**) or allyl (**32d**) complexes where the alkyl group (R) substituted for the trimethylsilyl group.[39] The trimethylsilylmethyl derivative (**32c**) can be synthesized by using a lithium salt instead of the Grignard reagent. If the less sterically hindered 2,6-dimethylphenyl imido precursor is used as a synthon, treatment with methyl Grignard does afford (**32f**), the methyl derivative.[39] These complexes are resistant to reduction and are only moderately air-sensitive.

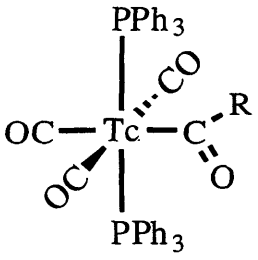
R = Pr^i : **32a** R' = Me
32b R' = Et
32c R' = CH_2SiMe_3
32d R' = η^1-C_3H_5
32e R' = η^1-C_5H_5
R = Me : **32f** R' = Me

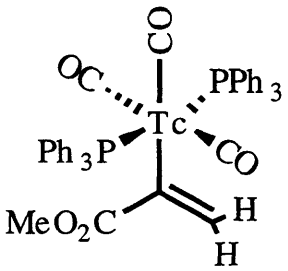


Similarly, $Tc(NAr)_3I$ (where Ar = 2,6-diisopropylphenyl) reacts with potassium cyclopentadienide to afford $Tc(NAr)_3(Cp)$ (**32e**) the monohapto-Cp complex.[40] This green complex is both air and water stable; an X-ray structural analysis shows a roughly tetrahedral technetium with an η^1-Cp ring that is nearly planar. The reaction does not work with pentamethylcyclopentadienyl sources. However, if (**32e**) is treated with an excess of KCp, a complex $K[Cp_2Tc(NAr)_3]$ (**33**) is isolated.[40] The proton NMR spectrum of (**33**) shows a very symmetrical arrangement of the two Cp rings, but no X-ray structural analysis has been performed. Under weak protic conditions, (**33**) can be converted back to (**32e**).

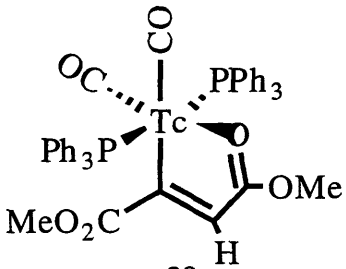
In 1963, Hieber reported that he could synthesize alkoxycarbonyl complexes starting from *trans*-$[Tc(CO)_4(PPh_3)_2]^+$ (**34**) (using the $AlCl_4^-$ salt). In a methanol or ethanol solution of strong base, (**34**) could be converted to *trans*-$Tc(CO)_3(PPh_3)_2C(=O)R$ (**35**), where R is methyl (**35c**) and ethyl (**35d**), respectively.[41] However, to make the benzyl analog (**35f**), a solution of $C_6H_5CH_2ONa$ in THF was employed.[41] In 1996, using a newly improved synthesis for the BF_4^- salt of (**34**), (**35c**), and (**35d**) were resynthesized, and it was noted that (**35c**) could be converted to (**35d**) by stirring it overnight in ethanol.[42] The aryloxy derivate (**35e**) [R = O(*p*-tolyl)] was also made by taking a THF solution of (**34**) and adding the potassium salt of 4-methylphenoxide. However, if (**34**) is treated with strong base in acetonitrile, the hydroxycarbonyl complex, $Tc(CO)_3(PPh_3)_2C(=O)OH$ (**35b**), is isolated. The formyl complex, $Tc(CO)_3(PPh_3)_2C(=O)H$ (**35a**), can be isolated in good yield from the reaction of (**34**) with $LiEt_3BH$.[42] The only η^1-acyl complex on technetium was synthesized by treating $Cp^*Tc(CO)_3$ (**11**) with phenyl lithium; the resulting anion was $[Cp^*Tc(CO)_2C(O)Ph]^-$ (**36**) and displayed one benzoyl group.[43]

35a R = H
35b R = OH
35c R = OMe
35d R = OEt
35e R = O(*p*-tolyl)
35f R = O(benzyl)





38



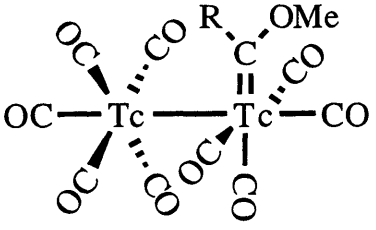
39

The complex *trans*-$HTc(CO)_3(PPh_3)_2$ (**37**) reacts with alkynes to make novel organometallic complexes on technetium. Using the electron deficient methyl propionate as the alkyne affords $Tc(CO)_3(PPh_3)_2(C_4H_5O_2)$

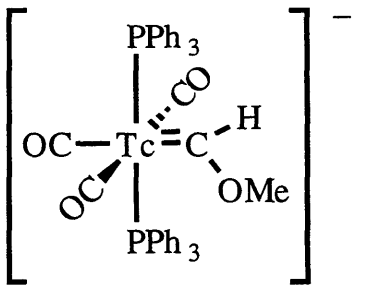
(**38**), where the alkyne inserts into the Tc-H bond to form a vinylic organometallic ligand.[44] However, when dimethylacetylenedicarboxylate is used, the hydride insertion affords complex $Tc(CO)_3(PPh_3)_2(C_6H_7O_4)$ (**39**) which displays a vinylic ligand that acts as a chelate through the carbonyl oxygen, forming a five-membered ring. The geometries and eventual location of the hydride for (**38**) and (**39**) are confirmed by NMR spectroscopy; alkynes with more steric bulk do not react with (**37**).[44]

Complexes Featuring Technetium-Carbon Multiple Bonding

There are only a handful of technetium organometallic complexes that have metal-carbon multiple bonds. In 1972, the first carbene complexes were made by treating $Tc_2(CO)_{10}$ (**1**) with either methyllithium or phenyllithium (with subsequent treatment with Me_3OBF_4) to yield $Tc_2(CO)_9[=C(OMe)R]$, (**40a**) and (**40b**) respectively;[45] these complexes are classical Fischer carbenes. Using IR and proton NMR spectroscopy, Fischer determined that the carbene ligand must occupy an equatorial position on the dimer. More recently, Cook found that the reaction of the formyl complex (**35a**) with methyl triflate in toluene affords the Fischer carbene anion, $[Tc(CO)_3(PPh_3)_2(=C(OMe)H)]^-$ (**41**), in good yield.[42]

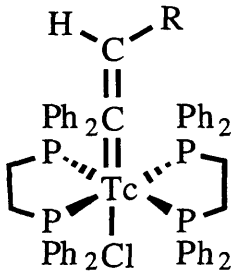


40a R = Me
40b R = Ph



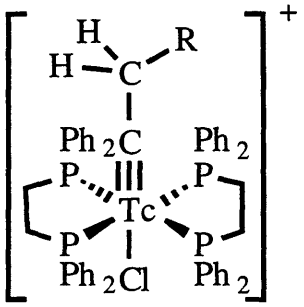
41

Burrell has found that the five-coordinated technetium(I) complex $Tc(dppe)_2Cl$ (where dppe = 1,2-bis(diphenylphosphino)ethane) reacts with terminal alkynes. The result of this reaction is the formation of a family of orange-colored vinylidene complexes $Tc(dppe)_2Cl(=C=C(H)R)$ (**42**); the methyl (**42a**) , *tert*-butyl (**42b**) and phenyl (**42c**) derivatives have been synthesized.[46] The X-ray structural analysis of (**42a**) shows a distorted octahedral geometry for technetium having a nearly linear vinylidene unit with bond lengths in agreement with standard double bonds. Treatment of either (**42a**) or (**42b**) with acid results in the formation of the associated colorless alkylidyne cation $[Tc(dppe)_2Cl(=C=C(H)R)]^+$ (**43**).[46] The X-ray structure for (**43b**), where R = ^{t}Bu, shows a distorted octahedral geometry for the technetium along with a short technetium-carbon bond length, appropriate for a triple bond. Burrell reported that Alberto has prepared but not published $Tc(=CNMeCH_2CH_2NMe)_2(CO)_4$ a complex with two carbenes.[46] Additionally, the complex $[Tc(CN^tBu)_4(bipyridine)]^+$ (**44**) can be made by the photolysis of $[Tc(CN^tBu)_6]^+$ (**3**) in the presence of bipyridine. One of the isocyanide ligands in the cation (**44**) shows a shortened technetium-carbon bond and a bent C-N-C 148° angle;[47] this data is consistent with a bent C-N-C 148° angle;[47] this data is consistent with a resonance structure of the form $Tc=C=N-^tBu$.



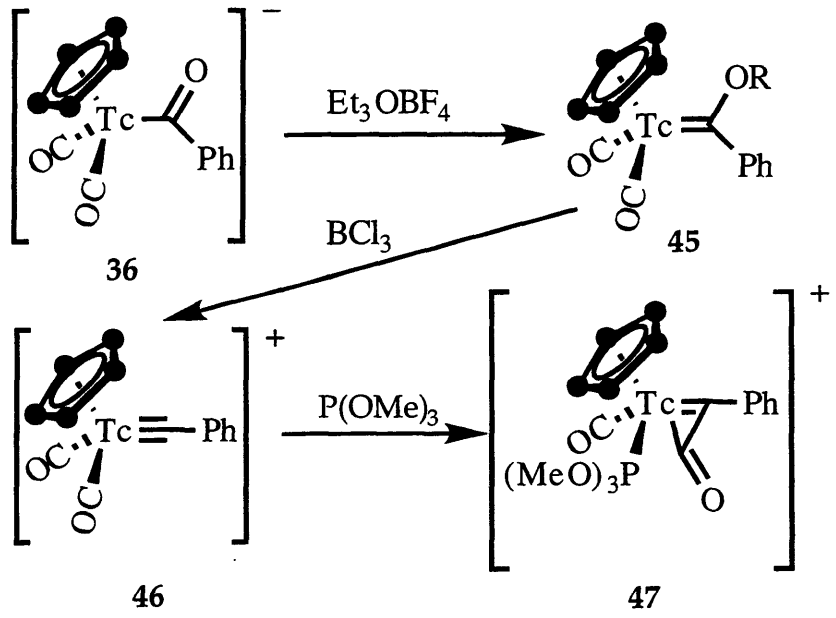
42

42a and **43a** R = Ph
42b and **43b** R = ^{t}Bu
42c R = Me



43

The most recent innovations in technetium organometallic chemistry are all derived from Fischer's acyl anion, $[Cp^*Tc(CO)_2C(O)Ph]^-$ (**36**). If (**36**) is treated with Et_3OBF_4, the neutral Fischer carbene, $Cp^*Tc(CO)_2(=C(Ph)OR)$ (**45a**) (where R = Et) is isolated in 73% yield.[43] The reaction of (**45a**) with BCl_3 affords the alkylidyne cation $[Cp^*Tc(CO)_2(\equiv C(Ph)]^+$ (**46**); (**46**) can also be formed by the direct reaction of oxalyl bromide on (**36**). The solid state structure of (**46**) shows the that complex is isostructural with the rhenium analog and has a nearly perpendicular orientation of the alkylidyne to the ring. Nucleophiles such as NaOCy (Cy = cyclohexyl) react with (**46**) to form complexes like (**45b**) (where R = Cy); this is analogous to the chemistry of the rhenium analog.[43] If (**46**) is treated with trimethylphosphite, rather than forming a ylide as the rhenium analog does, a metallacyclopropene, $[Cp^*Tc(CO)P(OMe)_3(C_2OPh)]^+$ (**47**), is formed by coupling of the carbyne and a carbonyl.[43] This is the first organometallic metallacycle of technetium.



Scheme 1: Recent Fischer organometallic chemistry

Technetium-Carbon Bonds in Organometallic Complexes

There are only twenty-one X-ray structures published for technetium organometallics with more than basic isonitriles and carbonyls for ligands. These are organized in Table 1 according to ligand type. Many of these structures feature an η^5-cyclopentdienyl ligand. There are thirteen unique Tc-Cp(centroid) distances among these structures. The average value for the distance of Tc-Cp(centroid) is 1.925 Å with a standard deviation of 0.0627 Å. There is one complex that has an η^4-butadiene bridging two technetiums; the average Tc-C distance in that complex is 2.390 Å.

A variety of organometallic η^1-ligands are present in these known structures. There are thirteen distinct technetium-carbon single bonds; twelve of them are similar and have an average distance of 2.136 Å with a standard deviation of 0.020 Å. The thirteenth value is for an η^1-cyclopentadienyl ligand; its length is 2.30 Å and would bring the Tc-C average up to 2.148 Å. There are three structures with techentium-carbon double bonds. Two of these are alkylidenes while the third is an isonitrile with a very strong π-backbonding interaction. The average Tc=C bond distance is 1.844 Å. Only one alkylidyne has been structurally characterized on technetium; thus, the only Tc≡C bond length is 1.724 Å. This series of complexes yields a perfect correlation between bond distance and bond strength where single < double < triple, and 2.148 Å > 1.844 Å > 1.724 Å.

Conclusion

Considering that technetium is a radioactive element that is researched by only a small number of laboratories across the world, the organometallic chemistry of technetium, while a still small field, has undergone a renaissance in the past fifteen years. While a number of cyclopentadienyl complexes on technetium have now been made, as well as a handful of multiply bonded organometallic ligands, many organometallic motifs are still missing from technetium chemistry. The following chapter will discuss some of the work that has gone into expanding the organometallic chemistry of technetium.

Table 1: Technetium-carbon bond lengths from crystal structures

Tc≡C	Tc=C	Tc-C	Tc-Cp(centroid)	Complex
			1.8725(5)	**6**[12]
			1.8810(5)	
			1.944(6)	**11**[17]
			1.962(5)	**12**[17]
			1.942(5)	**13**[17]
			1.9567(5)	**14**[18]
			1.94(4)	**15**[19]
			1.96(1)	**16a**[24]
			2.26(1)-2.33(1)*	**16b**[24]
			1.90(2)	**19**[25]
			2.040(4)	**21**[26]
			2.390(8)**	**26**[34]
		2.30(2)	1.8833(2)	**8**[13]
			1.7811(3)	
		2.133(2)		**28**[27]
		2.129(3)		
		2.128(3)		
		2.086(3)		

* The structural data for (**16b**) only include the M-C distances and not the distance from Tc to the ring centroid.[24]

** This value is for the average Tc-C distance to the η^4-butadiene ligand, not for a Cp ring centroid.

Tc≡C	Tc=C	Tc-C	Tc-Cp(centroid)	Complex
		2.144(17)		**30**[38]
		2.119(17)		
		2.134(2)		**31b**[38]
		2.149(2)		
		2.159(2)		
		2.153(2)		
		2.136(17)		**32a**[3]
		2.156(3)		**32e**[40]
	1.861(9)			**42a**[46]
	1.90(2)***			**44**[47]
	1.92(2)		1.966(1)	**45a**[43]
1.724(7)				**43b**[46]

*** This value is for the technetium isonitrile complex where the Tc-C bond is too short to be a M-C single bond.

References

(1) Holman, B. L. J., A.G.; Lister-James, J.; Davison, A.; Abrams, M.J.; Kirshenbaum, J.M.; Tumeh, S.S.; English, R.J. *J. Nucl. Med.* **1984**, *25*, 1350.

(2) Alberto, R. *Top. Curr. Chem.* **1996**, *176*, 149-187.

(3) Bryan, J. C.; Sattelberger, A. P. In *Comprehensive Organometallic Chemistry II*; C. P. Casey, Ed.; Permagon: 1995; Vol. 6; pp 167-230.

(4) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press Inc.: Tarrytown, NY, 1984, pp 1236.

(5) Elschenbroich, C.; Salzer, A. *Organomteallics: A Concise Introduction*; VCH: New York, 1992.

(6) Michels, G. D.; Svec, H. J. *Inorg. Chem.* **1981**, *20*, 3445.

(7) Alberto, R.; Schibli, R.; Egli, A.; Schubiger, P. A.; Herrmann, W. A.; Artus, G.; Abram, U.; Kaden, T. A. *J. Organomet. Chem.* **1995**, *493*, 119.

(8) Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E.; Pang, H. *Inorg. Chem.* **1983**, *22*, 2798.

(9) Alberto, R.; Herrmann, W. A.; Bryan, J. C.; Schubiger, P. A.; Baumgartner, F.; Mihalios, D. *Radiochim. Acta* **1993**, *63*, 153-161.

(10) Huggins, D. K.; Kaesz, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 4474-4475.

(11) Fischer, E. O.; Schmidt, M. W. *Angew. Chem.* **1967**, *79*, 99-100.

(12) Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1990**, *396*, 315-326.

(13) Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *411*, 171-179.

(14) Baumgartner, F.; Fischer, E. O.; Zahn, U. *Naturwissenschaften* **1962**, *49*, 156.

(15) Palm, C.; Fischer, E. O.; Baumgartner, F. *Naturwissenschaften* **1962**, *49*, 279.

(16) Fischer, E. O.; Fellmann, W. *J. Organomet. Chem.* **1963**, *1*, 191-199.

(17) Raptis, K.; Dornberger, E.; Kanellakopulos, B.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *408*, 61-75.

(18) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Meyer, D.; Raptis, K.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1994**, *476*, 77-84.

(19) Knight Castro, H. H.; Meetsma, A.; Teuben, J. H.; Vaalburg, W. *J. Organomet. Chem.* **1991**, *410*, 63-71.

(20) Herrmann, W. A.; Alberto, R.; Bryan, J. C.; Sattelberger, A. P. *Chem. Ber.* **1991**, *124*, 1107-1111.

(21) Kuntschke, D.; Wenzel, M.; Schulze, P. *J. Labelled Compd. Radiopharm.* **1995**, *36*, 193-203.

(22) Wenzel, M. *J. Labelled Compd. Radiopharm.* **1992**, *31*, 641-650.

(23) Wenzel, M.; Saidi, M. *J. Labelled Compd. Radiopharm.* **1993**, *33*, 77-80.

(24) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Meyer, D.; Nuber, B.; Raptis, K.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1995**, *492*, 199-210.

(25) Raptis, K.; Banellakopulos, B.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *405*, 323-331.

(26) Kanellakopulos, B.; Nuber, B.; Raptis, K.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1055.

(27) Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgartner, F. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 189-191.

(28) Chan, A. W. E.; Hoffmann, R.; Alvarez, S. *Inorg. Chem.* **1991**, *30*, 1086-1093.

(29) Baumgartner, F.; Fischer, E. O.; Zahn, U. *Naturwissenchaften* **1961**, *48*, 478.

(30) Baumgartner, F.; Fischer, E. O.; Zahn, U. *Chem. Ber.* **1961**, 2198-2203.

(31) Palm, C.; Fischer, E. O. *Tetrahedron Letters* **1962**, 253-254.

(32) Fischer, E. O.; Schmidt, M. W. *Chem. Ber.* **1969**, *102*, 1954-1960.

(33) Wester, D. W.; Coveney, J. R.; Nosco, D. L.; Robbins, M. S.; Dean, R. T. *J. Med. Chem.* **1991**, *34*, 3284-3290.

(34) Kanellakopulos, B.; Nuber, B.; Raptis, K.; Ziegler, M. L. *Z. Naturforsch.* **1991**, *46b*, 55-59.

(35) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189-6190.

(36) Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981.

(37) Kostlmeier, S.; Nasluzov, V. A.; Herrmann, W. A.; Rosch, N. *Organometallics* **1997**, *16*, 1786-1792.

(38) Burrell, A. K.; Bryan, J. C. *Organometallics* **1993**, *12*, 2426-2428.

(39) Bryan, J. C.; Burrell, A. K.; Miller, M. M.; Smith, W. H.; Burns, C. J.; Sattelberger, A. P. *Polyhedron* **1993**, *12*, 1769-1777.

(40) Burrell, A. K.; Bryan, J. C. *Organometallics* **1992**, *11*, 3501-3503.

(41) Hieber, W.; Luz, F.; Herget, C. *Z. Naturforsch.* **1965**, *20b*, 1159-1165.

(42) Cook, J.; Davison, A. *J. Organomet. Chem.* **1996**, *507*, 47-51.

(43) Fischer, E. O.; Apostolidis, C.; Dornberger, E.; Filippou, A. C.; Kanellakopulos, B.; Lungwitz, B.; Muller, J.; Powietzka, B.; Rebizant, J.; Roth, W. *Z. Naturforsch.* **1995**, 1383-1395.

(44) Cook, J.; Davison, A.; Davis, W. M.; Jones, A. G. *Organometallics* **1995**, *14*,

(45) Fischer, E. O.; Offhaus, E.; Muller, J.; Nothe, D. *Chem. Ber.* **1972**, *105*, 3027-3035.

(46) Burrell, A. K.; Bryan, J. C.; Kubas, G. J. *Organometallics* **1994**, *13*, 1067-1069.

(47) O'Connell, L. A.; Dewan, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1990**, *29*, 3539-3547.

Chapter 5

The Synthesis and Reactivity of Technetium Aryl Complexes

Introduction

The chemistry of technetium was largely unexplored until the 1980's. Since then, the rapidly increasing use of technetium in the biomedical industry for imaging agents has spurred a world-wide flurry of research.[1] While much of the early research had dealt with coordination chemistry, recent interest has focused on technetium organometallic chemistry. This change in the focus of technetium exploration was influenced both by the several important biomedical agents that employ organometallic ligands on technetium[2,3] and the recent inroads and achievements in the organometallic chemistry of its congener, rhenium.[4]

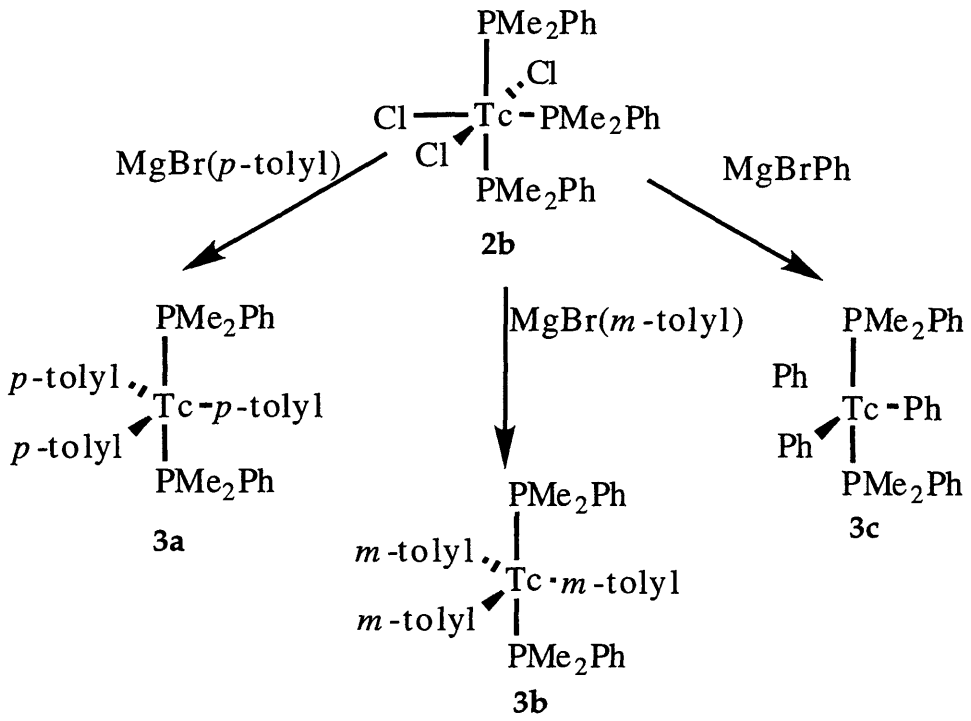
Despite a large number of recent advances, the chemistry of technetium is less explored than other transition metals due to the limited number of technetium laboratories. Several major constraints exist for technetium chemistry at MIT that do not exist for rhenium. The license to work with radioactive compounds at MIT sets forth guidelines to comply with rigorous governmental safety standards. These limitations include: at most 1.6 mCi of radiation (about 0.9 mmol) can be used in any one reaction, powders must be avoided to prevent the risk of contamination by static electricity, and volatility of radioactive material must be avoided to prevent widespread radioactive contamination. The source of all technetium for laboratory purposes is aqueous pertechnetate, TcO_4^-. Only complexes that can be derived from pertechnetate can be used as synthetic precursors. Carbonyl complexes such as $Tc_2(CO)_{10}$ and other volatile complexes such as $MeTcO_3$ are too dangerous to work with as precursors. Therefore, while the expanse of unexplored technetium chemistry is large, many practical constraints limit research opportunities.

Since many rhenium precursors employed in this field are volatile, synthetic routes to useful precursors had to preceede exploration of the organometallic chemistry. This chapter explores some new areas of technetium organometallic chemistry. As described in the previous chapter, relatively few technetium organometallic complexes exist especially compared to other transition metals. In some cases, the extant technetium complexes are directly analogous to those of rhenium, as for the bis(cyclopentadienyl) chemistry. The chemistry can also be quite different, such as in the high oxidation state chemistry of RMO_3 complexes and their reactivity toward alkenes.[5] In the chemistry that follows, both similarities and differences between technetium and rhenium will be presented.

Discussion

In Chapters 2 and 3, the field of rhenium(III) polyaryl chemistry was expanded to include a wider variety of complexes of the form $Re(Ar)_3L_2$ (where Ar = aryl, L = neutral donor). Originally, only Re(*p*-tolyl)$_3$(PEt$_2$Ph)$_2$ (**1a**) and RePh$_3$(PEt$_2$Ph)$_2$[6] (**1b**) were known. None of these complexes had analogs with technetium. Only one of the precursors to the analogous rhenium chemistry, *mer*-ReCl$_3$(PMe$_2$Ph)$_3$ (**2a**), had a technetium analog, *mer*-TcCl$_3$(PMe$_2$Ph)$_3$ (**2b**).[7] Thus, the search for and synthesis of starting materials for technetium chemistry was imperative.

The synthesis for the complexes of the form ReAr$_3$(PMe$_2$Ph)$_2$ requires treating *mer*-ReCl$_3$(PMe$_2$Ph)$_3$ with an excess of aryl Grignard and a subsequent aqueous extraction to remove unwanted byproducts. The method to synthesize the technetium analogs, TcAr$_3$(PMe$_2$Ph)$_2$ (**3**) is similar. The reaction between the aryl Grignard and (**2b**) occurs on the time of mixing, versus several minutes for the rhenium analog. This reaction cleanly forms the *p*-tolyl (**3a**), *m*-tolyl (**3b**), and phenyl (**3c**) derivatives of (**3**) in moderate yields (Scheme 1). The work-up of the reaction must be modified to compensate for the increased air sensitivity of the technetium complexes (**3**) as compared to their rhenium analogs. For (**3a**) and (**3b**) the reaction solution can be reduced to dryness *in vacuo* and washed with methanol to remove the excess Grignard and magnesium and technetium containing byproducts. These blue solids can be recrystallized from toluene/acetonitrile if necessary. Since (**3c**) is readily soluble in methanol, the blue residue of the reaction can be extracted with hexanes and then recrystallized from pentane at -40 °C.



Scheme 1: Synthesis of technetium tris(aryl) complexes

These complexes (**3**) show unshifted proton NMR spectra indicating that they are diamagnetic. The 2:3 ratio of phosphine ligands to equivalent aryl resonances, along with the diamagnetism, support a trigonal bipyramidal geometry. A deep blue color is also seen for all of the derivatives of (**3**) (*vide supra*). All these facts indicate a close analogy of these complexes of technetium to the corresponding rhenium complexes. They differ from their rhenium analogs in that if solutions of (**3**) are exposed to air, they instantly and visibly begin to decompose; these complexes are only stable in the solid state in air for a few hours. However, these technetium aryl complexes can be stored indefinitely in an inert atmosphere in solution or as a solid. Another unfortunate analogy to the rhenium chemistry is the end product of the decomposition of (**3**); after exposure to air, the blue technetium complex forms the corresponding biphenyl and a brown, oily non-homogenous residue. A

Geiger counter was used to confirm that the intractable brown material contains the technetium.

From the crystals of (**3a**) obtained from toluene/acetonitrile, an X-ray structural analysis was performed. Data collection parameters are given in Table 1 and the experimental section. A full set of bond lengths, angles, and positional parameters are given in Tables 2, 3, and 4 at the end of the chapter along with the ORTEP diagram (Figure 4).

The structure of Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3a**) is a nearly ideal trigonal bipyramid; the P-Tc-P angle is 180°, the P-Tc-C angles range from 89.4° to 90.6°, and C-Tc-C angles in the equatorial plane are all 120.7° or 118.6°. The molecule has a C_2 axis of symmetry through the middle of one of the *p*-tolyl rings; this was used to generate the other half of the molecule. The structure for RePh$_3$(PEt$_2$Ph)$_2$ (**1b**) showed this same symmetry motif (Figure 2, Chapter 2).[8]

Complex (**3a**) shows the same type of bonding that is seen in both RePh$_3$(PEt$_2$Ph)$_2$ (**1b**) and Re(*p*-tolyl)$_3$(THT)$_2$ (**4**) (THT = tetrahydrothiophene). The three aryl rings are canted into a propeller arrangement; the torsional angles for (**3a**) are 10°, 13°, and 13°, which are very similar to those of the rhenium analogs. This propeller arrangement allows for the steric requiements of the *ortho* hydrogens; planar rings would intolerable contacts. The average bond length for the Tc-C bond in (**3a**) is 2.037Å; this value falls in between the average values for the two rhenium tris(aryl) structures with 2.027 Å(**1b**) and 2.040 Å (**4**).[8] This similarity between rhenium and technetium complexes is not surprising because their atomic radii are nearly identical due to the lanthanide contraction. The average Tc-C bond in (**3a**) also shows shortening due to its coordination to a five-coordinate metal center (Shannon-Prewitt radii).

The family of complexes $Tc(aryl)_3(PMe_2Ph)_2$ (**3**) are the first examples of several types of technetium compounds. Before these complexes, only η^6-arene complexes existed; the compounds (**3**) are the first complexes on technetium with σ-aryl groups. These complexes are also the first organometallic technetium complexes with three anionic σ-donor ligands; previously, there were only dimers with two methyl groups on one technetium center. The tris(aryl) compounds (**3**) are the first organometallic complexes of technetium(III) that do not have cyclopentadienyl ligands. These complexes are the first technetium organometallic complexes that display trigonal bipyramidal geometry, and $Tc(p\text{-tolyl})_3(PMe_2Ph)_2$ (**3a**) is the first of this geometry to be structurally characterized. Some of the organometallic dimers might approach this geometry at one technetium center, but this geometry has not been seen on monomeric organometallic complexes.

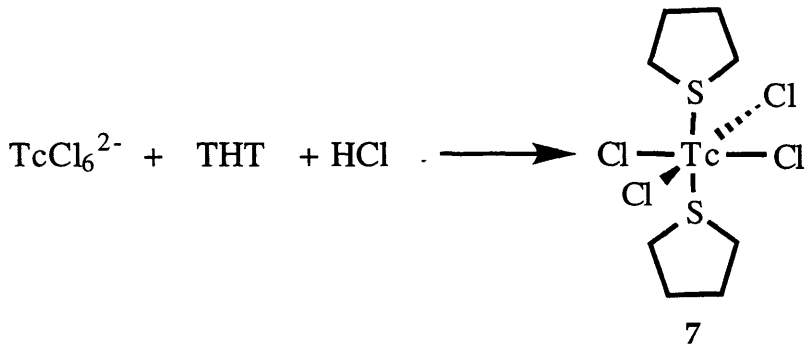
In an effort to change the electron donating ability or the steric bulk of the aryl ring, several variations of aryl groups were employed. The*p*-trifluoromethylphenyl Grignard reagent, with an electron-withdrawing aryl group, was found to be unreactive toward $TcCl_3(PMe_2Ph)_3$ (**2b**) even if the ethers were removed from the Grignard reagent *in vacuo*. The same was true for Grignard reagents with more sterically demanding aryl groups, including 2,4,6-mesityl, *o*-tolyl, and 3,5-xylyl. As in the case of the rhenium chemistry, the aryl Grignards with an *ortho* or two *meta* substitutions did not react with $TcCl_3(PMe_2Ph)_3$, which could subsequently be recovered intact.

Attempts were made using other synthons to achieve additional technetium aryl complexes. The complex $TcCl_3(pyridine)_3$ reacts with aryl Grignards but produced no isolable products; further treatment of the

reaction mixture with phosphines to stabilize a possible solution product did not allow for isolation of any technetium complexes. Another technetium complex, $TcCl_3(PPh_3)_2(MeCN)$, reacts with aryl Grignards quickly to form a brown solution which contains a mixture of several complexes by proton NMR spectroscopy. Several times, this reaction yielded a very small amount of a pale blue powder that was methanol-insoluble. Due to the scale limitations of reactions that can be done on technetium (< 50 mg), this product could not be isolated and characterized. Based on the starting material, the color of the product, and the established trends, the best candidate for the blue complex is $Tc(p\text{-tolyl})_3(PPh_3)_2$. The analogous reaction for rhenium shows no reaction at all between Grignard reagents and $ReCl_3(PPh_3)_2(MeCN)$.

In the chemistry of rhenium(III) aryls, the complex $ReBr_3(THT)_3$ (**5**) reacts with *p*-tolyl Grignard to form $Re(p\text{-tolyl})_3(THT)_2$ which in turn can substitute its thioether ligands for phosphines. The technetium analog of (**5**) was not previously known; the rhenium analog (**5**) was synthesized by reducing $ReBr_4(THT)_2$ (**6**) with zinc in neat THT.[9] The technetium analog of (**6**) was not previously known either. Starting from K_2ReBr_6, (**6**) can be made by refluxing THT and HBr together with the hexabromodianion; the analogous compounds with chlorides can be made by similar methods.[9] The complex $TcCl_4(THT)_2$ (**7**), a dark orange solid, can be synthesized from $(NH_4)_2TcCl_6$, a pale yellow solid, in refluxing THT overnight with hydrochloric acid (Scheme 2). The reaction does not work if the acid is not present or if a more weakly coordinating solvent like THF is used. Synthesis of the bromo analog of (**7**) from K_2TcBr_6 was problematic and did not yield the desired THT adduct. In neat THT, (**7**) does not reduce to form a technetium(III) THT complex even in the presence of zinc,

magnesium, or sodium borohydride, with or without heating. If $TcCl_3(THT)_3$ were formed, it would be expected to exhibit a contact-shifted proton NMR spectrum because of a d^4 octahedral electronic configuration. Resonances due to $TcCl_3(THT)_3$ would be easy to detect because (**7**) is a paramagnetic, d^3 complex and exhibits no proton NMR spectrum.



7

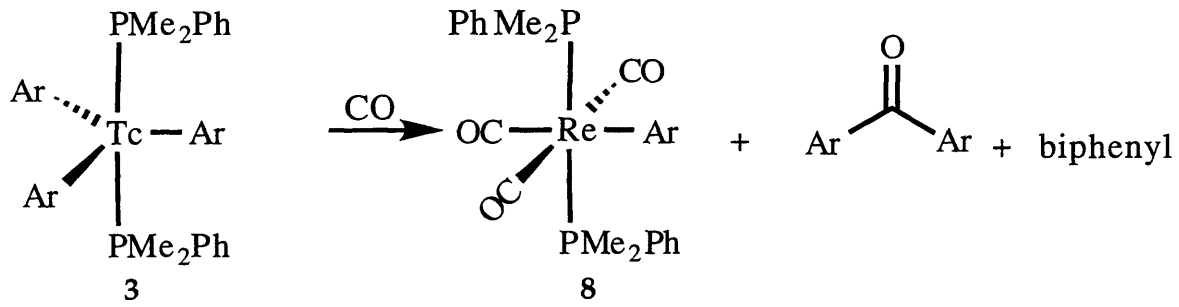
Scheme 2: The formation of $TcCl_4(THT)_2$ (**7**)

Crystals of (**7**) can be grown from concentrated solutions of methylene chloride at low temperature. From these crystals, an X-ray diffraction structural analysis was carried out. Data collection parameters are given in Table 5 and the experimental section. A full set of bond lengths, angles, and position parameters are given in Tables 6 and 7 at the end of the chapter along with the ORTEP diagram (Figure 5). The compound $TcCl_4(THT)_2$ (**7**) displays nearly perfect octahedral coordination geometry with the technetium lying on a crystallographic inversion center; therefore, all the *trans* technetium angles are 180°. Each of the octahedral angles fall between 85.24(2)° and 95.35(2)°. The Tc-S bonds are 2.4952(6) Å and the Tc-Cl bonds have a 2.321 Å average; these lengths fall within the expected ranges.[10]

The complex Tc(*p*-tolyl)$_3$(PMe_2Ph)$_2$ (**3a**) reacts with carbon monoxide, analogously to the rhenium chemistry (*vide infra*). With

technetium, the reaction proceeds more slowly, but the product is the analogous *mer-trans*-$Tc(CO)_3(PMe_2Ph)_2$(*p*-tolyl) (**8a**). This complex is a colorless crystalline solid that can be separated from its byproducts via crystallization. There is retention of the *trans* phosphine coordination as the complex (**3a**) reacts with carbon monoxide and reductively eliminates organic molecules to result in a technetium(I) complex.

In the corresponding rhenium chemistry, the byproduct of the reaction is 4,4'-dimethylbiphenyl. This biphenyl is also produced with the technetium reaction starting from (**3a**); however, the biphenyl is accompanied by 4,4'-dimethylbenzophenone, an almost equimolar amount as determined by proton NMR spectroscopy (Scheme 3). The presence of the benzophenone indicates insertion of a carbon monoxide molecule into a carbon-technetium bond at some point during the reaction. There is no evidence of the benzophenone in the chemistry of the rhenium analog, as determined by mass spectral analysis. For the technetium reaction of (**3a**), no evidence exists for the formation of the acyl complex $Tc(CO)_3(PMe_2Ph)_2(C(=O)$(*p*-tolyl)) as inspected by NMR and IR spectroscopies. The absence of an acyl complex indicates that if carbon monoxide insertion occurs, the reductive elimination of the acyl and an aryl is preferred over the elimination of two aryl groups. A crossover reaction between (**3a**) and (**3b**) was carried out using carbon monoxide. The organic products from the reaction showed only coupling between aryl groups on the same starting technetium center; this result matches those seen for rhenium and does not favor a bimolecular decomposition pathway.



Scheme 3: Reaction of tris(aryl) complexes with carbon monoxide

The reaction to form the technetium(I) carbonyl complex from a technetium(III) tris(aryl) complex also works for the synthesis of $Tc(CO)_3(PMe_2Ph)_2$(*m*-tolyl) (**8b**) from (**3b**) and carbon monoxide. Colorless crystals of (**8b**) can be grown from hot methanol; an X-ray diffraction structural analysis was performed on these crystals of (**8b**). Data collection parameters are given in Table 8 and the experimental section. A full set of bond lengths, angles, and positional parameters are given in Tables 9, 10, and 11 at the end of the chapter along with the ORTEP diagram (Figure 6). The structure for (**8b**) shows nearly ideal octahedral geometry; the X-Tc-Y angles range from 94.40° to 85.22°, and the *trans* angles range from 172.28° to 179.4°.

In the structure of (**8b**), the technetium-carbon distances for the carbonyls fall within the range of the known technetium complexes, 2.02 to 1.82 Å.[11] A technetium-carbon distance of 2.242 Å for the *ipso* carbon of the aryl ring is the longest recorded Tc-C bond for an anionic σ-donating ligand. This longer bond distance is not surprising because the currently published Tc-C bonds are all for methyl groups bound to lower-coordinate technetium. The length of 2.246 Å for the aryl group in (**8b**) is much longer than that of the 2.037 Å average for (**3a**); this difference is due to the larger apparent radius of a six-coordinate metal center (Shannon-

Prewitt radii) whereby the five-coordinate metal has more space near the nucleus. The difference between five and six-coordination can easily account for a difference of 0.2 Å between the two rhenium-carbon atoms.

The complex (**3b**) also reacts with isonitriles, which are electronically similar but can be sterically different than carbon monoxide. Rhenium complexes such as Re(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ react almost instantly with isonitriles to form mixtures of non-isolable products and biphenyl. The technetium complex (**3b**) reacts over the course of hours with ^{t}BuNC to form a pale yellow solution. From this reaction mixture, biphenyl and a technetium complex with a coordinated aryl group are detected by proton NMR spectroscopy. One byproduct of the reaction can be isolated; this white oily solid was shown to be [Tc(PMe$_2$Ph)$_2$(CN^{t}Bu)$_4$]$^+$ by mass spectrometry. The aryl complex is a yellow diamagnetic oil that could not be completely purified by crystallization or chromatography. The proton NMR spectrum of the oil showed a 1:3 ratio of coordinated aryl doublets to two types of isonitrile resonances, but the spectrum was obscured by impurities. The presence of a virtual triplet resonance in the proton NMR spectrum indicates a *trans* phosphine arrangement. The isonitrile complex decomposes during chromatography on alumina, reacts with the matrix for mass spectrometry, and it has evaded crystallization as well. The IR spectrum shows peaks at 1902.09(s), 1957.3(s), and 2036.5(w) cm^{-1} which are typical values for coordinated isonitriles. This leads to a formulation of the isonitrile complex as *mer-trans*-Tc(CN^{t}Bu)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl). When 2,6-dimethylphenylisonitrile is used the reaction yields a mixture, which shows no coordinated aryl groups remaining by proton NMR spectroscopy.

Conclusion

The technetium aryl complexes described in this chapter fill in more of the gaps in the chemistry of technetium. These complexes complement the existing technetium organometallic compounds. The existence of polyaryl complexes of technetium only two synthetic steps from the starting material pertechnetate demonstrates that many more compounds may be accessible with technetium. These complexes may have important uses ranging from studies of catalysis to biomedical applications.

In the aforementioned research, the chemistry of technetium and rhenium aryl complexes is quite similar. However, the reactivities of these two metals differ in three major respects. The technetium tris(aryl) complexes are more sensitive to dioxygen. The reactions of the technetium aryl complexes with strong σ-donating π-accepting ligands, such as carbon monoxide or isonitriles, proceed considerably more slowly than the analogous reactions with the rhenium complexes. Finally, the reaction of technetium tris(aryl) with carbon monoxide affords a benzophenone and biphenyl, while the rhenium analog only produces biphenyl. These results are very clear examples of the types of reactivity differences observed between second and third row congeners. While both metals are similar in size due to the lanthanide contraction, their reactivity often varies due to their difference in oxidation-reduction potentials and in the size and extent of their valence orbitals.

Experimental

Caution! Technetium-99 is a weak β^--emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12 x 10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[12]

All chemistry was performed either on a Schlenk line under an argon atmosphere or in a dry box under a dinitrogen atmosphere with dried, deoxygenated solvents unless otherwise specified. The solvents were either purchased dry or distilled from a sodium-benzophenone ketyl pot. The Grignard reagents were purchased from Aldrich with the exception of the phenyl Grignard, which was purchased from Strem. The *t*-butyl isocyanide was purchased from Fluka, while 2,6-xylyl isocyanide, 4-bromoanisole (99% purity), and tetrahydrothiophene were purchased from Aldrich. ^1H and ^{31}P NMR spectra were recorded on a Varian XL-300, a Varian Unity-300 or a Varian 500-VXR spectrometer. The chemical shifts were referenced to the residual proton impurity in the deuterated solvents obtained from Cambridge Isotopes Laboratory. ^{31}P chemical shifts are reported relative to an external standard of 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 series spectrophotometer as KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were carried out by Atlantic Microlab, Norcross, GA.

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. The complexes $TcCl_3(PMe_2Ph)_3$,[7] $TcCl_6(NH_4)_2$,[13] and $TcCl_3(PPh_3)_2(MeCN)$[14] were prepared by previously published methods.

Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (3a):

A solution of $TcCl_3(PMe_2Ph)_3$[7] (87.8 mg, 0.142 mmol) in toluene (20 mL) was placed in a Schlenk flask, and a slight excess (3.9 equivalents) of *p*-tolylmagnesium bromide (0.56 mL, 0.56 mmol) was added as a 1.0 M ether solution. The orange-yellow solution instantly became a deep blue and was stirred for 1 minute. The solvent was removed under reduced pressure leaving a purple-blue solid residue. In air, methanol (20 mL) was added to the residue affording a brown solution containing the magnesium halide salt and a brown byproduct with the blue solid remaing insoluble. The blue powder can be isolated by filtration of the methanol solution through a fritted glass funnel (E porosity). Residual magnesium salt can be removed under inert atmosphere by dissolving the blue solid in toluene and filtering it through a fritted glass funnel. The solid can be recrystallized from toluene/acetonitrile. The solid is stable for a few hours in air; it is best kept under inert atmosphere. Yield 69.6 g (0.107 mmol, 76% yield).

Anal. Calcd. for $C_{37}H_{43}P_2Tc$: C, 68.52%; H, 6.68%. Found: C, 67.02%; H, 6.55%.[a] ^{1}H NMR (C_6D_6, 500 MHz) δ: 1.00 (t, 12H), 2.33 (s, 9H), 6.56 (d, 6H), 6.72 (m, 4H), 6.94 (d, 6H), 6.98 (m, 6H). ^{31}P NMR (C_6D_6, 300 MHz) δ: 13.90(s).

X-Ray Crystallographic Data Collection Parameters for (3a)

The data for (**3a**) were collected using a Siemens platform goniometer with a CCD detector using a molybdenum Kα radiation (λ =

---

[a] It has been previously reported that, although samples analyze extremely well for other elements, carbon analyses can be up to one carbon low.[15] A possible explanation is that an incomplete combustion results from the formation of residual refractory technetium carbide. This would require 66.67% for the carbon.

0.71073 Å). The data for (**3a**) were collected using a dark blue crystal having dimensions 0.25 x 0.15 x 0.15 mm. The crystal system was orthorhombic ($\alpha = \beta = \gamma = 90°$) with a = 13.709(2) Å, b = 12.227(2) Å, and c = 19.354(3) Å; this leads to a cell volume V = 3244.1(8) Å^3 with Z = 4. The space group was found to be *Pbcn*. The absorption coefficient was 0.566 mm^{-1}, the calculated density ρ = 1.326 g/cm^3, and F(000) = 1352. The data were obtained at 293(2) K in the θ range 2.23 to 23.24° with limiting indices $-15 \leq h \leq 15$, $-11 \leq k \leq 9$, and $-19 \leq l \leq 21$. Of the 6813 reflections collected, 2108 were independent (R_{int} = 0.0552). The structure was solved by direct methods (SHELXTL v5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Least squares refinement based upon F^2 with 2108 data, no restraints and 184 parameters converged with final residuals: R_1 = 0.0458, wR_2 = 0.1121, and GOF = 0.855 based upon $I > 2\sigma(I)$; the extinction coefficient was 0.0012(3).

Tc(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ (3b):

A solution of $TcCl_3(PMe_2Ph)_3$[3]^7 (92.8 mg, 0.150 mmol) in toluene (10 mL) was placed in a Schlenk flask, and an excess (4 equivalents) of *m*-tolylmagnesium bromide (0.60 mL, 0.60 mmol) was added as a 1.0 M ether solution. The orange-yellow solution instantly became a deep blue and was stirred for one minute. The solvent was removed under reduced pressure leaving a purple-blue solid residue. In air, methanol (20 mL) was added to the residue affording a brown solution containing the magnesium halide salt and a brown byproduct with the blue solid remaing insoluble. A blue powder can be isolated by filtration of the methanol solution through a fritted glass funnel (E porosity). Removal of residual magnesium salt was identical to that for (**3a**). The solid can be recrystallized from

toluene/acetonitrile. The solid is stable for a few hours in air; it is best kept under inert atmosphere. Yield 62.0 g (0.0956 mmol, 64% yield).

Anal. Calcd. for $C_{37}H_{43}P_2Tc$: C, 68.52%; H, 6.68%. Found: C, 68.67%; H, 6.73%. ^1H NMR (C_6D_6, 500 MHz) δ: 1.00 (t, 12H), 2.33 (s, 9H), 6.56 (d, 6H), 6.72 (m, 4H), 6.94 (d, 6H), 6.98 (m, 6H). ^{31}P NMR (C_6D_6, 300 MHz) δ: 14.5 (s).

Tc(phenyl)$_3$(PMe$_2$Ph)$_2$ (3c):

A solution of $TcCl_3(PMe_2Ph)_3$[7] (71.4 mg, 0.115 mmol) in toluene (10 mL) was placed in a Schlenk flask, and an excess (7 equivalents) of phenylmagnesium bromide (0.275 mL, 0.825 mmol) was added as a 3.0 M ether solution. The orange-yellow solution instantly became a deep purple color and was stirred for 1 minute. The solvent was removed under reduced pressure leaving a purple-blue solid residue. Since (**3c**) is soluble in methanol, this residue was extracted with hexanes (2 x 10 mL) affording a blue-purple solution and a white-brown solid remained (MgX_2). In the glove box, the solvent was removed *in vacuo*; the solid failed to crystallize from acetonitrile/toluene; evaporation of this solution and subsequent extraction into pentane followed. Crystals can be grown from this concentrated pentane solution at -40 °C. The solid is stable for a few hours in air; it is best kept under inert atmosphere. Yield 22 mg (0.036 mmol, 32% yield).

Anal. Calcd. for $C_{34}H_{37}P_2Tc$: C, 67.33%; H, 6.15%. Found: C, 67.33%; H, 6.28%. ^1H NMR (C_6D_6, 300 MHz) δ: 0.97 (s, 12H), 6.57 (m, 4H), 6.62 (d, 6H), 6.72 (t, 3H), 6.96 (m, 6H), 7.04 (t, 6H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz) δ: 14.37 (s).

***trans*-$TcCl_4(THT)_2$ (7):**

Using concentrated hydrochloric acid (12 M), $TcCl_6(NH_4)_2$, (183 mg, 0.526 mmol) was rinsed into a round-bottomed flask. Tetrahydrothiophene (20 mL) was added to the flask; it formed an immiscible layer on top of the aqueous acid. The flask was connected to a condenser and the solution was refluxed, as well as vigorously stirred. After 1.5 h, the organic layer had become red and only part of the yellow starting material remained unreacted; by seven hours, no starting material remained. The organic layer was decanted from the aqueous layer and reduced to dryness *in vacuo*. Crystals can be grown from concentrated solutions of methylene chloride at -40 °C. Recrystallized yield 105 mg (0.252 mmol, 48% yield). The solutions were often used *in situ* and were not isolated nor recrystallized.

Anal. Calcd. for $C_8H_{16}Cl_4S_2Tc$: C, 23.04%; H, 3.87%. Found: C, 23.77%; H, 3.92%.

X-Ray Crystallographic Data Collection Parameters for (7)

The data for (**7**) were collected using a Siemens platform goniometer with a CCD detector using a molybdenum Kα radiation (λ = 0.71073 Å). The data for (**7**) were collected using a crystal having dimensions 0.15 x 0.15 x 0.10 mm. The crystal system was monoclinic (α = γ = 90°) with a = 7.8100(3) Å, b = 9.3053(3) Å, c = 9.9973(4) Å, and β = 95.765(2)°; this leads to a cell volume V = 722.87(7) $Å^3$ with Z = 2. The space group was found to be $P2_1/n$. The absorption coefficient was 1.991 mm^{-1}, the calculated density ρ = 1.912 g/cm^3, and F(000) = 414. The data were obtained at 293(2) K in the θ range 3.16 to 23.27° with limiting indices -4 ≤ h ≤ 8, -10 ≤ k ≤ 10, and -11 ≤ l ≤11. Of the 2826 reflections collected,

1038 were independent (R_{int} = 0.0445). The structure was solved by direct methods (SHELXTL v5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Least squares refinement based upon F^2 with 1038 data, no restraints and 71 parameters converged with final residuals: R_1 = 0.0193, wR_2 = 0.0444, and GOF = 1.132 based upon I > 2σ(I); the extinction coefficient was 0.0091(12).

***mer*-Tc(CO)$_3$(PMe$_2$Ph)$_2$(*p*-tolyl) (8a):**

To deoxygenated THF (40 mL) was added Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (72.3 mg, 0.111 mmol). A steady stream of carbon monoxide was bubbled through. The deep blue solution first became darker and then paled to brown after 30 minutes. The solvent was removed by bubbling the carbon monoxide through the solution until it reached dryness. The residue was dissolved in methanol and filtered through cotton. The solvent was removed *in vacuo*, and the pentane soluble portion of the the residue was loaded onto an alumina/pentane column; the column was eluted with pentane and then with methanol. The methanol fraction contains (**8a**) along with some 4,4'-dimethylbiphenyl; complex (**8a**) can be recrystalized by dissolving it in a minimum amount of boiling methanol and allowing it to cool. The colorless needles can be isolated by decanting away the methanol. Yield 56 mg (0.10 mmol, 90% yield).

Anal. Calcd. for $C_{26}H_{29}O_3P_2Tc$: C, 56.74%; H, 5.31%. Found: C, 56.99%; H, 5.42%. ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 1.55 (t, 12H), 2.19 (s, 3H), 6.73 (d, 2H), 7.36 (d, 2H), 7.42 (m, 10H). ^{31}P NMR (d_6-acetone, 300 MHz) δ: 13.958(s). IR (KBr) ν(C≡O) 1904.2(s), 1926.1(s), 2025.9(w) cm^{-1}.

***mer*-Tc(CO)$_3$(PMe$_2$Ph)$_2$(*m*-tolyl) (8b):**

To deoxygenated THF (30 mL) was added Tc(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ (62.0 mg, 0.0956 mmol). A steady stream of carbon monoxide was bubbled through. The deep blue solution first became darker and then paled to a brown after an hour. The solvent was removed by bubbling the carbon monoxide through the solution until it reached dryness for an additional hour. The residue was dissolved in a methanol/pentane mixture. The solution was loaded onto an alumina/pentane column; the column was eluted with pentane and then with methanol. The two fractions were combined and reduced to dryness *in vacuo* since both contained 3,3'-dimethylbiphenyl, an oily liquid and (**8b**); complex (**8b**) can be recrystallized by dissolving this residue in a minimum amount of boiling methanol and allowing it to cool. The colorless needles can be isolated by decanting away the methanol. Yield 41 mg (0.074 mmol, 78% yield).

Anal. Calcd. for $C_{26}H_{29}O_3P_2Tc$: C, 56.74%; H, 5.31%. Found: C, 57.73; H, 5.60%. ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 1.53 (t, 12H), 2.09 (s, 3H), 6.68 (d, 1H), 6.73 (t, 1H), 7.18 (s, 1H), 7.25 (d, 1H), 7.35 (m, 10H). ^{31}P NMR (C_6D_6, 300 MHz) δ: 11.2 (s). IR (KBr) ν(C≡O) 1932.3(s), 1896.0(s), 2016.2(w) cm^{-1}.

X-Ray Crystallographic Data Collection Parameters for (8b)

The data for (**8b**) were collected using a Siemens platform goniometer with a CCD detector using a molybdenum Kα radiation (λ = 0.71073 Å). The data for (**8b**) were collected using a colorless crystal having dimensions 0.22 x 0.18 x 0.12 mm. The crystal system was triclinic with *a* = 13.709(2) Å, *b* = 12.227(2) Å, and *c* = 19.354(3) Å, and α = 98.2710(10)°, β = 90.0350(10)°, and γ = 97.5660(10); this leads to a cell

volume V = 1314.13(7)(8) Å^3 with Z = 2. The space group was found to be $P\bar{1}$. The absorption coefficient was 0.695 mm^{-1}, the calculated density ρ = 1.424 g/cm^3, and F(000) = 580. The data were obtained at 183(2) K in the θ range 1.42 to 23.24° with limiting indices $-9 \leq h \leq 9$, $-11 \leq k \leq 9$, and $-12 \leq l \leq 16$. Of the 5265 reflections collected, 3677 were independent (R_{int} = 0.0437). The structure was solved by direct methods (SHELXTL v5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995); a semi-empirical absorption correction was performed from psi-scans. Least squares refinement based upon F^2 with 3676 data, six restraints, and 292 parameters converged with final residuals: R_1 = 0.0439, wR_2 = 0.1268, and GOF = 0.855 based upon $I > 2\sigma(I)$.

Crossover Reaction for (3a) and (3b) with Carbon Monoxide:

In a round-bottomed flask containing toluene (20 mL) carbon monoxide was slowly bubbled through the solvent to remove any oxygen. Recrystallized samples of both Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3a**) (14.5 mg, 0.0224 mmol) and Tc(*m*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3b**) (26.4 mg, 0.0407 mmol) were added. After 30 minutes, the solution had changed from deep blue to pale blue; by 50 minutes the solution was colorless. The solvent was removed by continuing to bubble carbon monoxide through the solution. A proton NMR spectrum showed no organic products with mixed *meta* and *para* substitution.

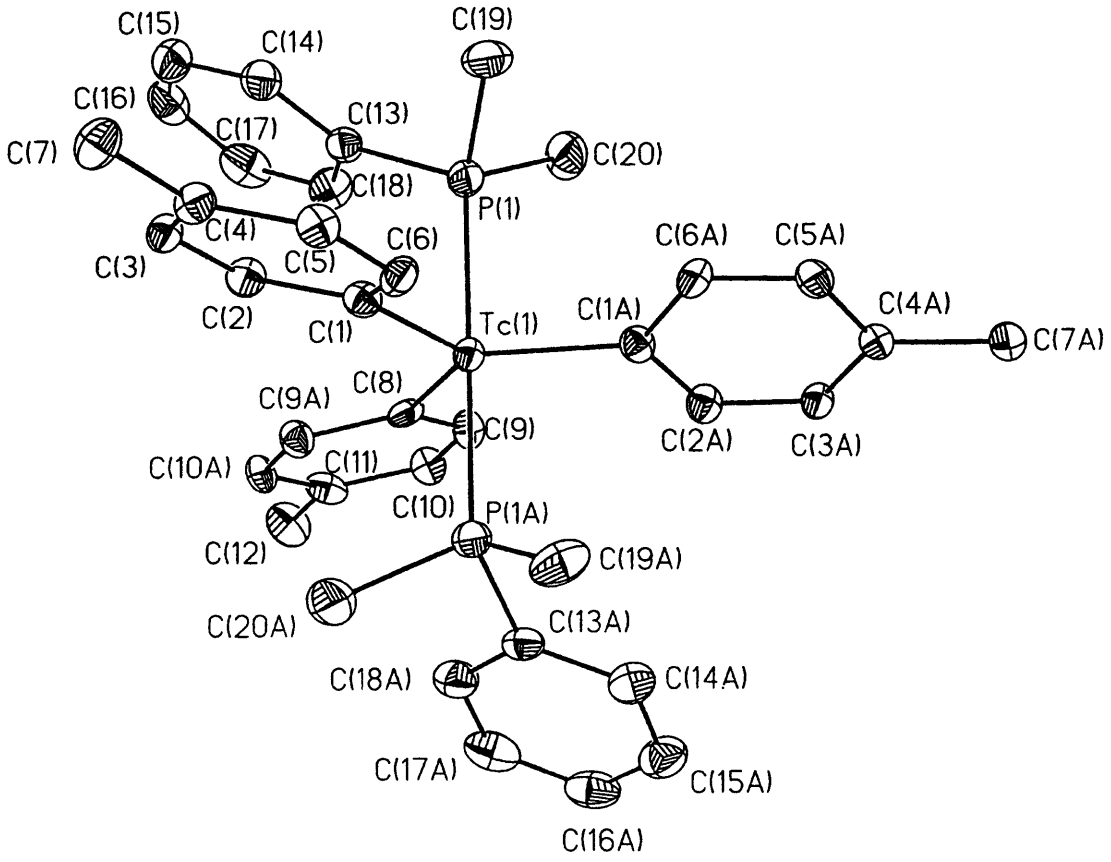


Figure 1: ORTEP of Tc(p-tolyl)$_3$(PMe_2Ph)$_2$ (**3a**) with 35% ellipsoids.

Table 1. Data collection parameters for Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3a**)

Empirical formula	$C_{37}H_{43}P_2Tc$
Formula weight	647.65 g/mol
Temperature	293(2) K
Radiation	Mo Kα
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	a = 13.709(2) Å α = β = γ = 90°
	b = 12.227(2) Å
	c = 19.354(3) Å
Volume	3244.1(8) Å^3
Z	4
Density (calculated)	1.326 g/cm^3
Absorption coefficient	0.566 mm^{-1}
F(000)	1352
Θ range for data collection	2.23 to 23.24 °
Limiting indices	$-15 \le h \le 15$, $-11 \le k \le 9$, $-19 \le l \le 21$
Reflections collected	6813
Independent reflections	2108 (R_{int} = 0.0552)
Diffractometer	Siemens SMART/CCD
Scan Type	ω scans
Refinement method	Full-matrix least-squares on F^2
Structure solution	Direct methods
Data / restraints / parameters	2108 / 0 / 184
Goodness-of-fit on F^2	0.855
Final R indices [I>2σ(I)]	R_1 = 0.0458, wR_2 = 0.1121
R indices (all data)	R_1 = 0.0647, wR_2 = 0.1322
Absolute structure parameter	0.0012(3)
Largest diff. peak and hole	0.445 and -0.289 eÅ^{-3}

Table 2: Bond lengths for Tc(p-tolyl)$_3$(PMe_2Ph)$_2$ (**3a**)

Atoms	Length (Å)	Atoms	Length (Å)
Tc(1)-C(8)	2.033(9)	Tc(1)-C(1A)	2.039(5)
Tc(1)-C(1)	2.039(5)	Tc(1)-P(1)	2.374(2)
Tc(1)-P(1A)	2.374(2)	P(1)-C(13)	1.819(6)
P(1)-C(19)	1.825(7)	P(1)-C(20)	1.828(6)
C(1)-C(6)	1.393(8)	C(1)-C(2)	1.402(8)
C(2)-C(3)	1.385(8)	C(3)-C(4)	1.382(8)
C(4)-C(5)	1.384(8)	C(4)-C(7)	1.516(8)
C(5)-C(6)	1.392(8)	C(8)-C(9)	1.411(7)
C(8)-C(9A)	1.412(7)	C(9)-C(10)	1.370(9)
C(10)-C(11)	1.400(7)	C(11)-C(10A)	1.400(7)
C(11)-C(12)	1.499(12)	C(13)-C(18)	1.390(9)
C(13)-C(14)	1.398(8)	C(14)-C(15)	1.405(9)
C(15)-C(16)	1.348(10)	C(16)-C(17)	1.372(10)
C(17)-C(18)	1.383(9)		

Table 3: Bond angles for Tc(*p*-tolyl)$_3$(PMe$_2$Ph)$_2$ (**3a**)

Atoms	Angle (°)	Atoms	Angle (°)
C(8)-Tc(1)-C(1A)	120.7(2)	C(8)-Tc(1)-C(1)	120.7(2)
C(1A)-Tc(1)-C(1)	118.6(3)	C(8)-Tc(1)-P(1)	90.06(4)
C(1A)-Tc(1)-P(1)	90.6(2)	C(1)-Tc(1)-P(1)	89.4(2)
C(8)-Tc(1)-P(1A)	90.06(5)	C(1A)-Tc(1)-P(1A)	89.4(2)
C(1)-Tc(1)-P(1A)	90.6(2)	P(1)-Tc(1)-P(1A)	179.88(9)
C(13)-P(1)-C(19)	103.7(3)	C(13)-P(1)-C(20)	102.0(3)
C(19)-P(1)-C(20)	101.4(3)	C(13)-P(1)-Tc(1)	116.3(2)
C(19)-P(1)-Tc(1)	115.2(2)	C(20)-P(1)-Tc(1)	116.1(2)
C(6)-C(1)-C(2)	116.7(5)	C(6)-C(1)-Tc(1)	123.2(4)
C(2)-C(1)-Tc(1)	120.1(4)	C(3)-C(2)-C(1)	121.2(6)
C(4)-C(3)-C(2)	122.0(5)	C(3)-C(4)-C(5)	117.1(5)
C(3) -C(4) -C(7)	122.1(5)	C(5)-C(4)-C(7)	120.9(6)
C(4)-C(5)-C(6)	121.8(6)	C(5)-C(6)-C(1)	121.2(5)
C(9)-C(8)-C(9A)	115.3(8)	C(9)-C(8)-Tc(1)	122.3(4)
C(9A)-C(8)-Tc(1)	122.3(4)	C(10)-C(9)-C(8)	122.2(6)
C(9)-C(10)-C(11)	122.2(6)	C(10)-C(11)-C(10A)	116.1(8)
C(10)-C(11)-C(12)	122.0(4)	C(10A)-C(11)-C(12)	122.0(4)
C(18)-C(13)-C(14)	117.9(6)	C(18)-C(13)-P(1)	119.8(5)
C(14)-C(13)-P(1)	122.2(5)	C(13)-C(14)-C(15)	119.7(7)
C(16)-C(15)-C(14)	120.9(7)	C(15)-C(16)-C(17)	120.1(7)
C(16)-C(17)-C(18)	120.3(7)	C(17)-C(18)-C(13)	120.9(7)

Table 4: Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for Tc(*p*-tolyl)$_3$(PMe_2Ph)$_2$ (**3a**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. Equivalent atoms (A) from (-x + 1, y, -z + 3/2).

atom	x	y	z	U(eq)
Tc(1)	5000	1155(1)	7500	24(1)
P(1)	3850(1)	1153(1)	6583(1)	31(1)
C(1)	5946(4)	304(5)	6890(3)	28(1)
C(2)	6417(4)	827(5)	6338(3)	31(1)
C(3)	7038(4)	259(5)	5903(3)	27(1)
C(4)	7206(4)	-849(5)	5979(3)	30(1)
C(5)	6743(4)	-1370(5)	6522(3)	29(1)
C(6)	6140(4)	-806(5)	6978(3)	31(2)
C(7)	7862(4)	-1480(5)	5489(3)	36(2)
C(8)	5000	2818(7)	7500	27(2)
C(9)	4253(4)	3435(5)	7816(3)	32(2)
C(10)	4261(4)	4556(5)	7821(3)	30(1)
C(11)	5000	5162(7)	7500	32(2)
C(12)	5000	6388(8)	7500	48(3)
C(13)	4088(4)	2096(5)	5876(3)	32(2)
C(14)	4531(4)	1761(6)	5261(3)	40(2)
C(15)	4708(5)	2528(7)	4735(3)	48(2)
C(16)	4462(5)	3588(7)	4817(4)	50(2)
C(17)	4053(5)	3936(6)	5426(4)	53(2)
C(18)	3874(4)	3201(6)	5954(3)	42(2)
C(19)	3683(5)	-161(6)	6152(3)	51(2)
C(20)	2595(4)	1497(7)	6817(4)	54(2)

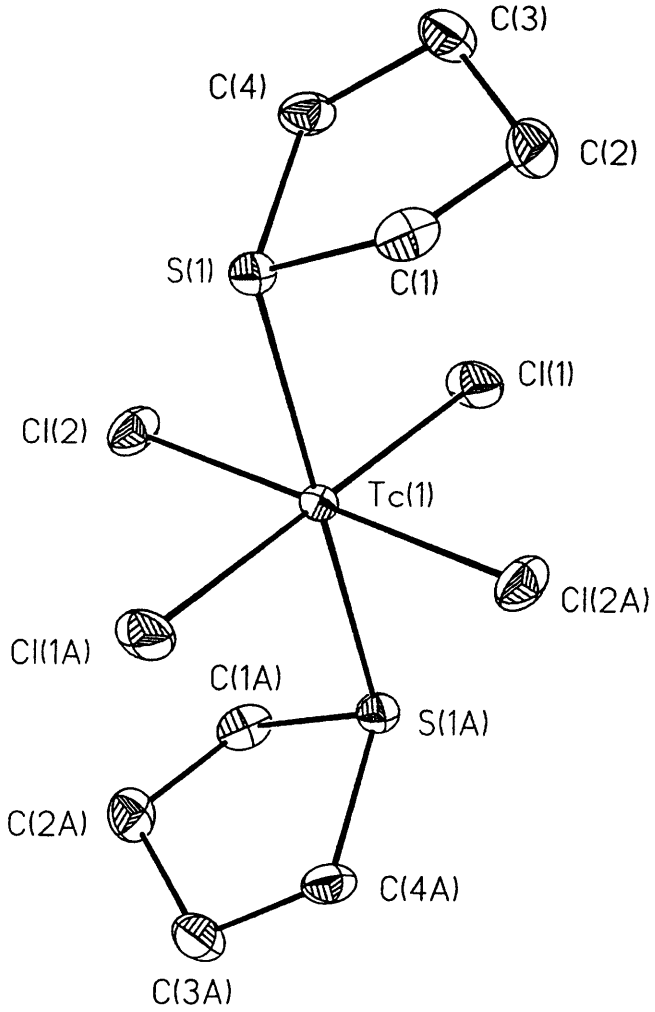


Figure 2: ORTEP of $TcCl_4(THT)_2$ (**7**) with 35% ellipsoids.

Table 5. Crystal and data collection parameters for $TcCl_4(THT)_2$ (**7**)

Empirical formula	$C_8H_{16}Cl_4S_4Tc$
Formula weight	416.13 g/mol
Temperature	293(2) K
Radiation	Mo Kα
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 7.8100(4) Å α = γ = 90°
	b = 9.3053(5) Å β = 95.756(2)°
	c = 9.9973(6) Å
Volume	722.87(7) $Å^3$
Z	2
Density (calculated)	1.912 g/cm^3
Absorption coefficient	1.991 mm^{-1}
F(000)	414
θ range for data collection	3.16 to 23.27 °
Limiting indices	$-4 \le h \le 8$, $-10 \le k \le 10$, $-11 \le l \le 11$
Reflections collected	2826
Independent reflections	1038 (R_{int} = 0.0445)
Diffractometer	Siemens SMART/CCD
Scan Type	ω scans
Refinement method	Full-matrix least-squares on F^2
Structure solution	Direct methods
Data / restraints / parameters	1038 / 0 / 71
Goodness-of-fit on F^2	1.132
Final R indices [I>2σ(I)]	R_1 = 0.0193, wR_2 = 0.0444
R indices (all data)	R_1 = 0.0205, wR_2 = 0.0449
Absolute structure parameter	0.0091(12)
Largest diff. peak and hole	0.260 and -0.259 $eÅ^{-3}$

Table 6: Bond lengths and angles for $TcCl_4(THT)_2$ (**7**)

Atoms	Length (Å)	Atoms	Length (Å)
Tc(1)-Cl(1)	2.3206(6)	Tc(1)-Cl(1A)	2.3206(6)
Tc(1)-Cl(2A)	2.3227(6)	Tc(1)-Cl(2)	2.3227(6)
Tc(1)-S(1A)	2.4952(6)	Tc(1)-S(1)	2.4952(6)
S(1)-C(1)	1.826(3)	S(1)-C(4)	1.834(3)
C(1)-C(2)	1.505(4)	C(2)-C(3)	1.508(4)
C(3)-C(4)	1.533(4)		

Atoms	Angle (°)	Atoms	Angle (°)
Cl(1)-Tc(1)-Cl(1A)	180.0	Cl(1)-Tc(1)-Cl(2A)	90.31(3)
Cl(1A)-Tc(1)-Cl(2A)	89.69(3)	Cl(1)-Tc(1)-Cl(2)	89.70(3)
Cl(1A)-Tc(1)-Cl(2)	90.30(3)	Cl(2A)-Tc(1)-Cl(2)	180.0
Cl(1)-Tc(1)-S(1A)	85.25(2)	Cl(1A)-Tc(1)-S(1A)	94.75(2)
Cl(2A)-Tc(1)-S(1A)	84.66(2)	Cl(2)-Tc(1)-S(1A)	95.35(2)
Cl(1)-Tc(1)-S(1)	94.76(2)	Cl(1A)-Tc(1)-S(1)	85.24(2)
Cl(2A)-Tc(1)-S(1)	95.34(2)	Cl(2)-Tc(1)-S(1)	84.65(2)
S(1A)-Tc(1)-S(1)	180.0	C(1)-S(1)-C(4)	93.99(12)
C(1)-S(1)-Tc(1)	108.56(9)	C(4)-S(1)-Tc(1)	108.79(9)
C(2)-C(1)-S(1)	104.9(2)	C(1)-C(2)-C(3)	107.2(2)
C(2)-C(3)-C(4)	109.3(2)	C(3)-C(4)-S(1)	106.6(2)

Table 7: Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for $TcCl_4(THT)_2$ (**7**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. Equivalent atoms (A) from (-x, -y, -z).

atom	x	y	z	U(eq)
Tc(1)	0	0	0	19(1)
Cl(1)	1931(1)	485(1)	1864(1)	39(1)
Cl(2)	1767(1)	-1854(1)	-593(1)	35(1)
S(1)	1555(1)	1471(1)	-1579(1)	25(1)
C(1)	941(4)	3351(3)	-1411(3)	31(1)
C(2)	2133(4)	3913(3)	-252(3)	37(1)
C(3)	3906(4)	3342(3)	-418(3)	37(1)
C(4)	3772(4)	1757(3)	-834(3)	31(1)

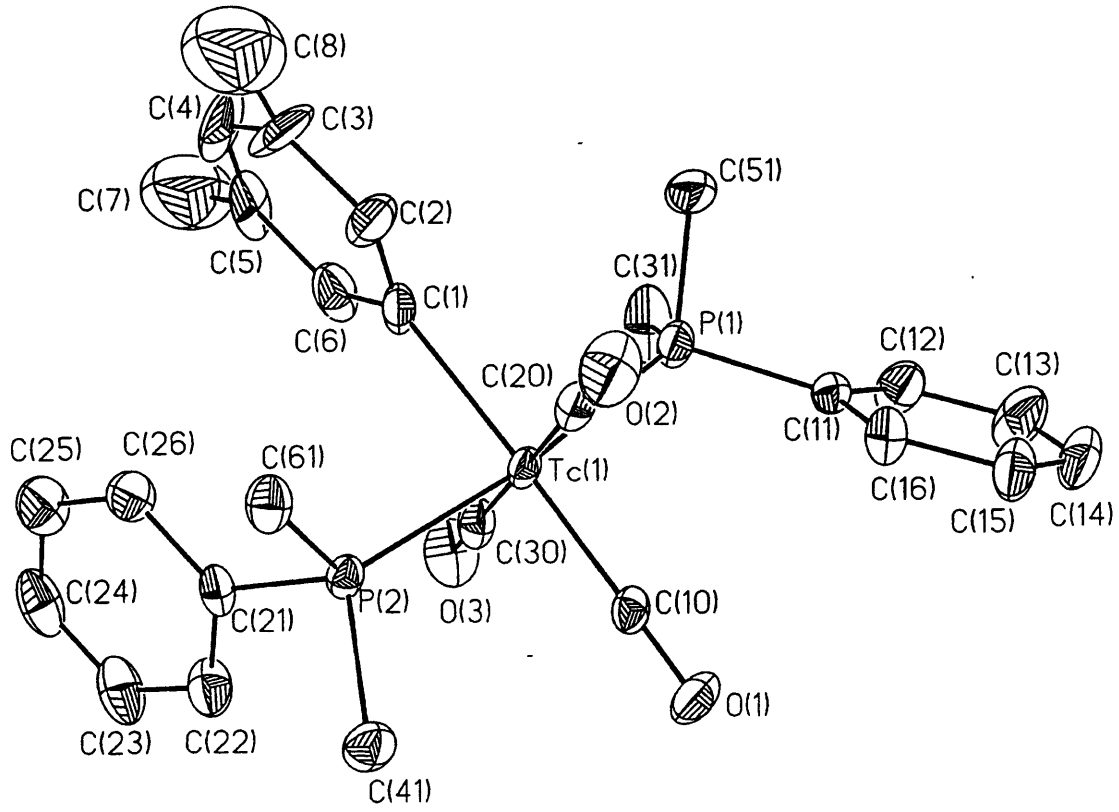


Figure 3: ORTEP of $Tc(CO)_3(PMe_2Ph)_2$(*m*-tolyl) (**8b**) with 35% ellipsoids

Table 8. Data collection parameters for $Tc(CO)_3(PMe_2Ph)_2$(*m*-tolyl) (**8b**)

Empirical formula	$C_{27}H_{31}O_3P_2Tc$
Formula weight	563.46 g/mol
Temperature	182(2) K
Radiation	Mo Kα
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.8717(3) Å α = 98.2710(10)°
	b = 10.3979(3) Å β = 90.0350(10)°
	c = 14.5248(5) Å γ = 97.5660(10)°
Volume	1314.13(7) $Å^3$
Z	2
Density (calculated)	1.424 g/cm^3
Absorption coefficient	0.695 mm^{-1}
F(000)	580
θ range for data collection	1.42 to 23.24 °
Limiting indices	$-9 \le h \le 9$, $-11 \le k \le 9$, $-12 \le l \le 16$
Reflections collected	5365
Independent reflections	3677 (R_{int} = 0.0437)
Max. and min. transmission	0.5733 and 0.4248
Diffractometer	Siemens SMART/CCD
Scan Type	ω scans
Refinement method	Full-matrix least-squares on F^2
Structure solution	Direct methods
Data / restraints / parameters	3677 / 6 / 292
Goodness-of-fit on F^2	0.935
Final R indices [I>2σ(I)]	R_1 = 0.0439, wR_2 = 0.1268
R indices (all data)	R_1 = 0.0453, wR_2 = 0.1323
Largest diff. peak and hole	0.668 and -0.943 $eÅ^{-3}$

Table 9: Bond lengths for $Tc(CO)_3(PMe_2Ph)_2$(*m*-tolyl) (**8b**)

Atoms	Length (Å)	Atoms	Length (Å)
Tc(1)-C(10)	1.928(4)	Tc(1)-C(20)	1.958(5)
Tc(1)-C(30)	1.994(5)	Tc(1)-C(1)	2.242(5)
Tc(1)-P(1)	2.4088(12)	Tc(1)-P(2)	2.4104(11)
P(1)-C(51)	1.826(6)	P(1)-C(11)	1.837(4)
P(1)-C(31)	1.842(6)	P(2)-C(21)	1.830(4)
P(2)-C(61)	1.828(4)	P(2)-C(41)	1.830(4)
O(1)-C(10)	1.166(5)	O(2)-C(20)	1.156(6)
O(3)-C(30)	1.140(6)	C(1)-C(2)	1.409(8)
C(1)-C(6)	1.434(8)	C(5)-C(4)	1.326(13)
C(5)-C(7)	1.348(13)	C(5)-C(6)	1.410(9)
C(2)-C(3)	1.388(8)	C(3)-C(8)	1.232(13)
C(3)-C(4)	1.356(13)	C(11)-C(12)	1.384(7)
C(11)-C(16)	1.392(7)	C(12)-C(13)	1.392(8)
C(13)-C(14)	1.389(9)	C(14)-C(15)	1.376(8)
C(15)-C(16)	1.387(7)	C(21)-C(22)	1.364(7)
C(21)-C(26)	1.390(7)	C(22)-C(23)	1.392(7)
C(23)-C(24)	1.368(9)	C(24)-C(25)	1.380(8)
C(25)-C(26)	1.385(7)		

Table 10: Bond angles for $Tc(CO)_3(PMe_2Ph)_2$(*m*-tolyl) (**8b**)

Atoms	Angle (°)	Atoms	Angle (°)
C(10)-Tc(1)-C(20)	90.6(2)	C(10)-Tc(1)-C(30)	90.0(2)
C(20)-Tc(1)-C(30)	179.4(2)	C(10)-Tc(1)-C(1)	178.5(2)
C(20)-Tc(1)-C(1)	89.2(2)	C(30)-Tc(1)-C(1)	90.3(2)
C(10)-Tc(1)-P(1)	94.40(13)	C(20)-Tc(1)-P(1)	90.11(14)
C(30)-Tc(1)-P(1)	90.16(13)	C(1)-Tc(1)-P(1)	87.07(11)
C(10)-Tc(1)-P(2)	93.32(13)	C(20)-Tc(1)-P(2)	89.92(14)
C(30)-Tc(1)-P(2)	89.73(13)	C(1)-Tc(1)-P(2)	85.22(11)
P(1)-Tc(1)-P(2)	172.28(4)	C(51)-P(1)-C(11)	100.7(2)
C(51)-P(1)-C(31)	103.3(4)	C(11)-P(1)-C(31)	103.8(2)
C(51)-P(1)-Tc(1)	114.7(2)	C(11)-P(1)-Tc(1)	117.61(14)
C(31)-P(1)-Tc(1)	114.8(2)	C(21)-P(2)-C(61)	103.1(2)
C(21)-P(2)-C(41)	102.9(2)	C(61)-P(2)-C(41)	101.6(2)
C(21)-P(2)-Tc(1)	116.39(13)	C(61)-P(2)-Tc(1)	114.8(2)
C(41)-P(2)-Tc(1)	116.0(2)	C(2)-C(1)-C(6)	113.3(5)
C(2)-C(1)-Tc(1)	123.2(4)	C(6)-C(1)-Tc(1)	123.3(5)
C(4)-C(5)-C(7)	111.9(9)	C(4)-C(S)-C(6)	123.1(8)
C(7)-C(5)-C(6)	125.1(12)	C(5)-C(6)-C(1)	121.4(8)
C(3)-C(2)-C(1)	121.3(7)	C(8)-C(3)-C(4)	109.1(9)
C(8)-C(3)-C(2)	126.4(12)	C(4)-C(3)-C(2)	124.1(8)
C(5)-C(4)-C(3)	116.6(7)	O(1)-C(10)-Tc(1)	178.4(4)
C(12)-C(11)-C(16)	118.8(4)	C(12)-C(11)-P(1)	122.9(4)
C(16)-C(11)-P(1)	118.3(3)	C(11)-C(12)-C(13)	119.9(5)
C(14)-C(13)-C(12)	120.6(5)	C(15)-C(14)-C(13)	119.8(5)
C(14)-C(15)-C(16)	119.4(5)	C(11)-C(16)-C(15)	121.4(5)
O(2)-C(20)-Tc(1)	178.3(4)	C(22)-C(21)-C(26)	118.9(4)
C(22)-C(21)-P(2)	121.1(4)	C(26)-C(21)-P(2)	119.9(3)
C(21)-C(22)-C(23)	120.3(5)	C(24)-C(23)-C(22)	120.4(5)
C(23)-C(24)-C(25)	119.9(5)	C(24)-C(25)-C(26)	120.2(5)
C(25)-C(26)-C(21)	120.4(5)	O(3)-C(30)-Tc(1)	179.5(4)

Table 11: Atomic coordinates [x 10^{-4}] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for $Tc(CO)_3(PMe_2Ph)_2$(*m*-tolyl) (**8b**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Tc(1)	1617(1)	236(1)	2951(1)	28(1)
P(1)	-59(2)	-1081(1)	1772(1)	42(1)
P(2)	3416(1)	1724(1)	3967(1)	29(1)
O(1)	483(4)	-1343(3)	4523(2)	51(1)
O(2)	4086(5)	-1614(4)	2481(3)	67(1)
O(3)	-850(4)	2110(4)	3442(3)	64(1)
C(1)	2514(6)	1406(5)	1839(3)	47(1)
C(5)	2564(13)	3319(6)	993(5)	101(3)
C(6)	1858(9)	2512(5)	1613(4)	74(2)
C(7)	2072(16)	4418(12)	788(8)	166(4)
C(2)	3843(7)	1187(6)	1344(4)	65(2)
C(3)	4454(9)	2025(10)	738(4)	102(3)
C(4)	3833(12)	3088(9)	555(5)	126(5)
C(8)	5695(16)	2016(12)	359(8)	166(4)
C(10)	888(5)	-745(4)	3928(3)	32(1)
C(11)	-1003(5)	-2666(4)	2032(3)	37(1)
C(12)	-2510(6)	-3124(5)	1799(4)	55(1)
C(13)	-3127(7)	-4371(6)	1959(4)	72(2)
C(14)	-2246(7)	-5161(6)	2360(4)	68(2)
C(15)	-757(6)	-4700(5)	2614(4)	56(1)
C(16)	-142(5)	-3460(4)	2448(4)	46(1)
C(20)	3173(5)	-920(4)	2642(3)	39(1)
C(21)	3156(5)	3458(4)	4106(3)	35(1)
C(22)	2261(5)	3988(5)	4803(4)	51(1)
C(23)	2029(6)	5297(5)	4876(4)	61(2)
C(24)	2680(6)	6071(5)	4258(4)	58(2)
C(25)	3566(7)	5550(5)	3556(4)	61(2)
C(26)	3797(6)	4248(5)	3475(3)	48(1)
C(30)	48(5)	1430(5)	3260(3)	41(1)
C(31)	-1633(8)	-270(6)	1400(5)	84(2)
C(41)	3515(5)	1403(5)	5171(3)	45(1)
C(51)	858(8)	-1599(7)	681(4)	83(2)
C(61)	5400(5)	1743(4)	3625(3)	40(1)

References

(1) Deutsch, E.; Libson, K. In *Technetium in Chemistry and Nuclear Medicine*; E. Deutsch, M. Nicolini and H. N. Wagner, Eds.; Raven Press: New York, 1983; Vol. 1; pp 29-36.

(2) Holman, B. L. J., A.G.; Lister-James, J.; Davison, A.; Abrams, M.J.; Kirshenbaum, J.M.; Tumeh, S.S.; English, R.J. *J. Nucl. Med.* **1984**, *25*, 1350.

(3) Wester, D. W.; Coveney, J. R.; Nosco, D. L.; Robbins, M. S.; Dean, R. T. *J. Med. Chem.* **1991**, *34*, 3284-3290.

(4) Casey, C. P. *Science* **1993**, *259*, 1552-1558.

(5) Simpson, R. D.; Thomas, J. A.; Davison, A.; Jones, A. G.; Davis, W. M. In *Technetium and Rhenium in Chemistry and Nuclear Medicine*; M. Nicolini, G. Bandoli and U. Mazzi, Eds.; SG Editoriali: Padue, 1994; Vol. 4; pp 39-44.

(6) Chatt, J.; Garforth, J. D.; Rowe, G. A. *J. Chem. Soc. A* **1966**, 1834-1836.

(7) Mazzi, U.; DePaoli, G.; Di Bernardo, P.; Magon, L. *J. Inorg. Nucl. Chem.* **1976**, *38*, 721-725.

(8) Carroll, W. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 825-826.

(9) Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3688-3695.

(10) Melnik, M.; Van Lier, J. *Coord. Chem. Rev.* **1987**, *77*, 275.

(11) Bryan, J. C.; Sattelberger, A. P. In *Comprehensive Organometallic Chemistry II*; C. P. Casey, Ed.; Permagon: 1995; Vol. 6; pp 167-230.

(12) Davison, A.; Orvig, C.; Trop, H. S.; DePamphilis, B.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988.

(13) Dalziel, J.; Gill, N. S.; Nyholm, R. S.; Peacock, R. D. *J. Chem. Soc.* **1958**, 4012-4016.

(14) Pearlstein, R. M.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3332.

(15) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728.

Acknowledgments

A tremendous amount of pressure is put on this section. I know full-well that this is the section that will be read most by the people who see my thesis. It is also an important section of the thesis because so many other people are responsible for its production. To thank all the people, I am opting for a Faulkneresque stream of consciousness approach.

Well, anyone who knows me, knows the relationship I have with my family. It would not have been possible for me to complete this thesis if it weren't for my frequent calls home. Dad tried to become involved in my chemistry by checking up on the colors of my reactions (*i.e.*, brown = bad, blue = good). Mom was a constant source of support and for that "I love her more no backs." My sister, a frequent visitor to our homestead, was very proud of me even if I had become a big nerd.

During my chemical career, I have been given the opportunity to work for three different Welshmen. Russ Hughes introduced me to synthetic organometallic chemistry and somehow managed to keep me from becoming a theoretical physical chemist. Alun Jones provided our research group with a supportive "other side." Where do I begin with Alan Davison? He gave me opportunities that no other advisor would have. He let me teach eight different courses during my tenure here. Without his support and pride in my teaching and chemical abilities, I would not have survived MIT, nor would I have a future career.

While the Davison group has been small, it has had some big people in it. Bob and Jess were there in the early years to get the four of us all started. Afterward, Melissa took the reins; I can remember her wedding well (at least parts of it) and the occasional Ernie-sitting. Sean and I were the group movie watchers; we'd each see 50 movies a year and still manage to have no overlap. Then Evan came along; he fit into our odd little group, and he lets me harass him about the Mets. Then there's Terry; he is the senior member of the group and holds us all together. Thankfully, Terry has really good taste in food, so he often goads us into off-campus meals. There's also Ann and Jed, but I'll get to them later.

After leaving Ashdown, I moved to 2 Brastow Ave. After four years and four roommates, I don't have a single complaint (but I think they all have a few, *i.e.*, the snooze alarm). Deb left us years ago, and the house has

never been as clean since then. Deb has been a willing recipient of my flowers and chocolate over the years. Carlos has provided me with many hours of unintelligible Spanish and sangria-induced stupors. Stoph, the other Chris and the token non-chemist, has made me realize that Californians aren't all bad, vegetables can be food too, and Henry Miller was very strange. And then there's Jed. He deserves his own paragraph since he's logged the most hours with me over the past five years.

So here's Jed's paragraph. Jed did the lion's share of editing on my thesis; I have almost mentally recovered from some of his comments. I met Jed on a cruise, and he attacked me for being from Dartmouth. Thus, began our first of several thousand bickering sessions. In spite of this, we joined the same research group and moved in together. Somehow when we were spending all our waking hours together, we didn't manage to kill each other. Even though Jed isn't "my type," people still accuse us of being "an old married couple."

Well, since Jed got his own paragraph, Ann should get her own paragraph. Without Ann, I would a) be in an insane asylum; b) still be writing Chapter 1; c) not have a job; d) have a huge number of speling mistekes everywhere; e) all of the above. With Ann often comes a Ray (who by the way only has known Ann for as long as I have lived with Jed). The two of them have become a big part of my life (and the lives of my friends and roommates).

I should thank all the other chemistry people. On the "other side" there's Ash, Eva, Jim, and for a while John. Ash is our most frequent visitor, especially when we head to Bertucci's. Bill Davis had done a tremendous job helping me with all my structures (that Evan and Melissa didn't solve). Li Li worked on my mass spec samples, and Jeanne and Debbie helped me with my (and Ash's) NMR's.

While I was here at MIT, I kept up with College Bowl and met wonderful people here (Jon and Jason) and afar as part of my travels. I even got to suck up to the Harvard team thanks to Felicia. I also did a little good by joining Contact Line. I even managed to drag all these people from different walks of life to join in on the Mystery Hunt and see how crazy I really am.

My social life at MIT has been very good from hanging out with my old Dartmouth friends (locally: Dan, Erik, Ted, Larry, and Gregg) to meeting

my new "dancing friends." There is the "original" Ann who let me serenade her with ABBA songs, passed notes with me in Dietmar's class, and also willingly accepted my flowers and baked goods. Diego let me beat him at chess and hung out at Tosci's almost as much as I did. Then there's the two token Davison group members. Marc spent lots of time serenading us with his painful puns and Canadian sensibility. John kept my chemistry in line and allowed me to use my Dartmouth-speak. I owe a huge debt to the Anns and the Anna for allowing me to figure out who I really am. Nina helped me figure out MIT and my advisees, and Seth supported my ego and came to my 4th year talk.

Continuing with the social part of the chemistry department, Chem Outreach allowed me to meet my future Think Twice nemesis Dave, as well as, the studio audience (Evan, Ben, *etc.*). Even though Matt couldn't tear himself away from lab for the filming, I will ever remember hanging out with him at his uncle's (and of course all the sweater vests). Thankfully, my hockey team, Total Reflux, is allowing me to return next year (because Tufts doesn't have a rink). There are two women in the Schrock group I would like to mention. Gretchen has been a wonderful helpful friend who has listened to my chatter about coins and stuff. Myra, who I promise to visit in Switzerland, was a wonderful neighbor who helped me a lot through the past two years.

Since teaching was such an important part of my time here, I have to thank the Chemistry Department, Interphase, and ESG. I don't know what I would have done without Holly (who listened to all my problems), Melinda (who finally let me teach 5.11), Launa (who liked all my sweaters), Peter (who let me "borrow" things from the office), Miriam (who nominated me for my medal), and Bob Field (who gave me the freedom to influence 5.11 as a TA and become what I am today). They all helped me so much in achieving what I did with education. All my students have meant a lot to me, and I'll never forget them.

I would also like to thank anyone I might have missed and anyone I zephyred.

Biographical Note

The author was born on a rainy Monday, September 13, 1971 at St. Vincent's Hospital in Connecticut. After elementary schooling in Stratford, Connecticut, he moved to Amherst, New Hampshire at the age of eleven. Here he attended Milford AREA Senior High School where he graduated in 1989 as class salutatorian. Afterward, he attended Dartmouth College where he worked in the labs of Russell Hughes and Charles Braun. In 1993, he graduated from Dartmouth College *magna cum laude* with high honors, as a member of Phi Beta Kappa. Later that year, he entered MIT and began working towards a doctorate in the laboratory of Alan Davison. While working on his Ph.D., he earned the Goodwin Medal for "conspicuously effective teaching by a graduate student" and appeared on the TV gameshow Jeopardy! After obtaining his Ph.D., the author is moving to Tufts University to start an appointment with a focus in chemical education.