Monoaryloxide Pyrrolide (MAP) Imido Alkylidene Complexes of Molybdenum and Tungsten That Contain 2,6-Bis(2,5-R[subscript 2]-pyrrolyl)phenoxide (R = i-Pr, Ph) Ligands and an Unsubstituted Metallacyclobutane on Its Way to Losing Ethylene

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Monoaryloxide Pyrrolide (MAP) Imido Alkylidene Complexes of Molybdenum and Tungsten That Contain 2,6-Bis(2,5-R_2-pyrrolyl)phenoxide (R = i-Pr, Ph) Ligands and an Unsubstituted Metallacyclobutane on Its Way to Losing Ethylene

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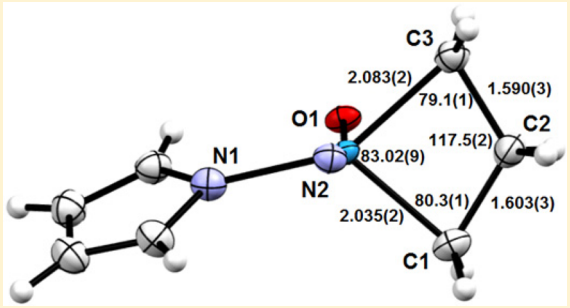
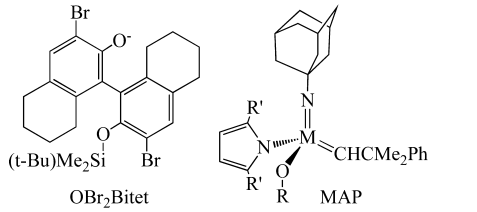
Supporting Information

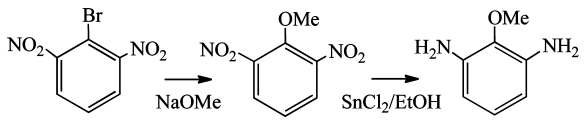
ABSTRACT: We report the synthesis of Mo and W MAP complexes that contain O-2,6-(2,5-R_2-pyrrolyl)$_2C_6H_3$ (2,6-dipyrrolylphenoxide or $ODPP^R$) ligands in which R = i-Pr, Ph. W(NAr)(CH-t-Bu)(Pyr)-($ODPP^{Ph}$) (**4a**; Ar = 2,6-disopropylphenyl, Pyr = pyrrolide) reacts readily with ethylene to yield a metallacyclobutane complex, W(NAr)(C_3H_6)(Pyr)($ODPP^{Ph}$) (**5**). The structure of **5** in the solid state shows that it is approximately a square pyramid with the WC_4 ring spanning apical and basal positions. This SP′ structure, which has never been observed as an actual intermediate, must now be regarded as an integral feature of the metathesis reaction.

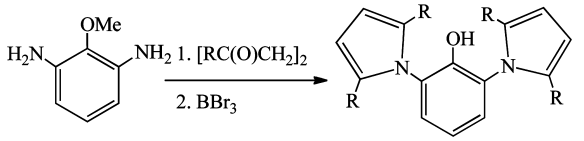


In the last several years sterically demanding phenoxide ligands have been employed to make Mo- and W-based MAP (monoaryloxide pyrrolide) catalysts for stereoselective olefin metathesis reactions. One of the first was OBr_2Bitet, an enantiomerically pure monophenoxide ligand that yielded diastereomeric mixtures of MAP catalysts (R′ = H, Me) for enantioselective ring-opening/cross-metathesis reactions.[1] In the process, it was found that the reaction was not only enantioselective but also *Z*-selective. The search for other suitable sterically demanding phenoxides led to terphenoxides such as O-2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3$ ($OHIPT$)[2] and O-2,6-(mesityl)$_2C_6H_3$ ($OHMT$),[3] which were employed to produce *Z*-selective catalysts for ROMP[4] and homometathesis of terminal olefins.[5] Decafluoroterphenoxide (O-2,6-($C_6F_5)_2C_6H_3$ = ODFT) has now been added to the list of 2,6-terphenoxides.[6] Recently it also has been possible to make bisaryloxide complexes that are especially efficient in certain stereoselective reactions, one example being Mo(NC_6F_5)-($CHCMe_2Ph$)(OF_2Bitet)$_2$, where OF_2Bitet is a fluorinated relative of OBr_2Bitet.[7] For all of the above reasons we felt it desirable to prepare and use other sterically demanding aryloxides in monoaryloxide or bisaryloxide olefin metathesis catalysts. Here we describe the synthesis of complexes that contain O-2,6-(2,5-R_2-pyrrolyl)$_2C_6H_3$ (2,6-dipyrrolylphenoxide or $ODPP^R$) ligands in which R = i-Pr, Ph.

2-Methoxy-1,3-diaminobenzene was prepared from 2-bromo-1,3-dinitrobenzene, as shown in eq 1. The pyrrolyl groups were then constructed by employing the desired γ-diketone in a Paal−Knorr condensation followed by deprotection with BBr_3. Both $DPP^{Ph}OH$ and $DPP^{iPr}OH$ were purified by employing column chromatography and recrystallized from hexane







R = Ph ($HODPP^{Ph}$) or i-Pr ($HODPP^{iPr}$)

($DPP^{iPr}OH$) or isopropyl alcohol. (See the Supporting Information for full details.)

Addition of 1 equiv of $DPP^{Ph}OH$ or $DPP^{iPr}OH$ to Mo(NAd)($CHCMe_2Ph$)(Pyr)$_2$, Mo(NAd)($CHCMe_2Ph$)-(Me_2Pyr)$_2$, Mo(NAr)($CHCMe_2Ph$)(Pyr)$_2$, and Mo(NAr)-($CHCMe_2Ph$)(Me_2Pyr)$_2$ (Ad = 1-adamantyl, Ar = 2,6-i-

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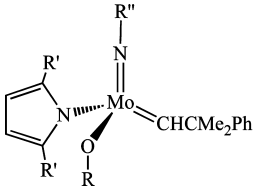
$Pr_2C_6H_3$, Pyr = pyrrolide; Me_2Pyr = 2,5-dimethylpyrrolide) produced MAP complexes[8] **1a**,**b**, **2a**,**b**, and **3a**,**b**.



1a; R" = Ad, R' = H, OR = $ODPP^{Ph}$
1b; R" = Ad, R' = H, OR = $ODPP^{iPr}$
2a; R" = Ad, R' = Me, OR = $ODPP^{Ph}$
2b; R" = Ar, R' = Me, OR = $ODPP^{Ph}$
3a; R" = Ar, R' = H, OR = $ODPP^{Ph}$
3b; R" = Ar, R' = H, OR = $ODPP^{iPr}$

The reaction to give **1a** required heating the mixture for 1 h at 80 °C, whereas the reaction to give **1b** was complete at 22 °C (~20 mM) within 4 h. For steric reasons, the reactions to give **2a**,**b** are slower than those that yield **1a**,**b**. It should be noted, for comparison, that both Mo(NAd)($CHCMe_2Ph$)(Pyr)(OHIPT)[5a] and Mo(NAr)($CHCMe_2Ph$)(Pyr)(OHIPT)[9] have been prepared (the latter in situ) from Mo(NR)($CHCMe_2Ph$)$(Pyr)_2$ (R = Ad, Ar) and 1 equiv of HIPTOH. Therefore, $ODPP^{Ph}$ and $ODPP^{iPr}$ behave approximately like the OHIPT ligand in terms of the synthesis of MAP species through protonation of bispyrrolides, although apparently small steric differences between ligands can have profound consequences.

The X-ray structure of Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)($ODPP^{Ph}$) (**2b**) is shown in Figure 1. The dihedral angles

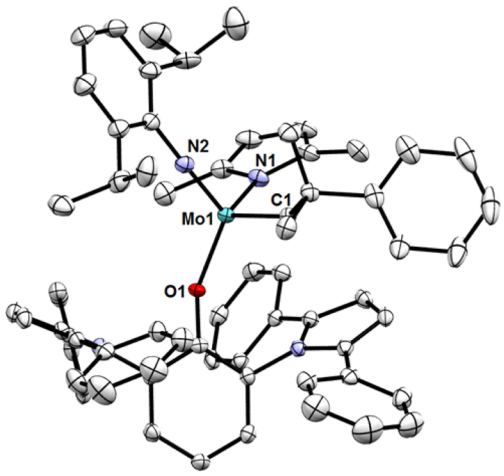


Figure 1. Thermal ellipsoid representation of the structure of **2b** at the 50% probability level. The solvent molecule and hydrogen atoms are omitted for clarity.

between the phenyl ring in $ODPP^{Ph}$ and the pyrrolyl rings are 83.7(3)° (C41−C42−N3−C47) and 68.7(3)° (C41−C46−N4−C67). In the structure of Mo(NAr)($CHCMe_2Ph$)(Pyr)($ODPP^{iPr}$) (**3b**) (Figure 2) the dihedral angles between the phenyl ring in $ODPP^{iPr}$ and the pyrrolyl rings are 70.3(2)° (C21−C22−N1−C30) and 80.8(2)° (C21−C26−N2−C37). The Mo−O−C angle is larger in **3b** (167.42(9)°) than in **2b** (153.7(1)°), consistent with the steric demand of the $ODPP^{iPr}$ ligand system being greater than that of the $ODPP^{Ph}$ ligand system. Other bond distances and angles in the two structures can be found in the Supporting Information.

Tungsten analogues of **3a**,**b** were also prepared, since tungsten complexes are emerging as more desirable for *Z*-selective reactions.[5] The reaction between W(NAr)(CH-t-Bu)$(Pyr)_2$(dme) and 1 equiv of $DPP^{Ph}OH$ led to W(NAr)(CH-t-Bu)(Pyr)($ODPP^{Ph}$) (**4a**). The reaction was performed in a sonicator bath due to the limited solubility of $DPP^{Ph}OH$ in

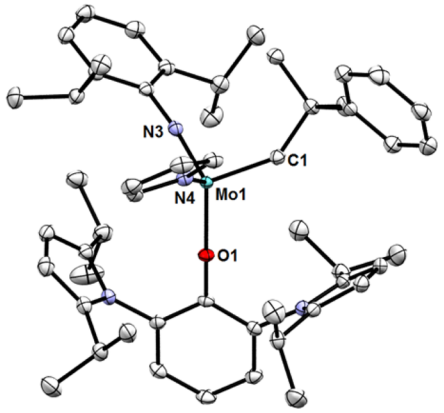
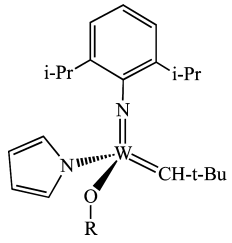


Figure 2. Thermal ellipsoid representation of the structure of **3b** at the 50% probability level. The solvent molecule and hydrogen atoms are omitted for clarity.

C_6H_6. Sonication was not required for the synthesis of W(NAr)(CH-t-Bu)(Pyr)($ODPP^{iPr}$) (**4b**).



4a; OR = $ODPP^{Ph}$
4b; OR = $ODPP^{iPr}$

Reactions of MAP complexes with ethylene are becoming routine means of assessing the stability of metallacyclobutane and methylidene complexes. For example, compound **4a** reacts readily with ethylene to yield a metallacyclobutane complex, W(NAr)(C_3H_6)(Pyr)($ODPP^{Ph}$) (**5**). According to proton and carbon NMR data, **5** has a TBP geometry. Surprisingly, the structure of **5** in the solid state (Figure 3) is closer to a square pyramid than a TBP, according to the τ value (0.26), which for an SP is 0 and for a perfect TBP is 1.[10] The metallacyclobutane carbon atom in approximately the apical position (W−C1 = 2.035(2) Å) is closer to the metal than is the carbon atom in the basal position (W−C2 = 2.083(2) Å) by a statistically significant amount (Figure 4). The $C_\alpha-C_\beta$ bond lengths (1.590(3) and 1.603(3) Å) are statistically essentially the same but vary in the direction which implies that an ethylene that contains C2 and C3 is approaching or leaving the CNO face of W(NAr)(CH_2)(Pyr)($ODPP^{Ph}$) approximately *trans* to the pyrrolide (Figure 4). The W−C(2) distance is 2.370(2) Å, which is 0.1−0.2 Å longer than a typical W−C single bond. Since the structure of **5** is different from that of a typical square-pyramidal complex (SP in Figure 5), in which the imido group is in the apical position and the metallacyclic ring in basal positions, another type that has been observed in the solid state and in solution,[11] we will call the structure of **5** an SP′ metallacyclobutane.

Selected distances and angles (averages) in the structures of five MAP unsubstituted tungstacyclobutane complexes with TBP structures, which have τ values from 0.47 to 0.68, are shown in Figure 5,[4a,5b,12] including both complexes in the asymmetric unit of the structure of W(NAr)(C_3H_6)(MePyr)(OBr_2Bitet).[12] In the *one β-substituted* SP structure (W(NAr)[$CH_2CH(Ph)CH_2$](Pyr)(OHIPTNMe$_2$),[11] τ = 0.06. It should be pointed out that τ values for the TBP metallacyclobutane

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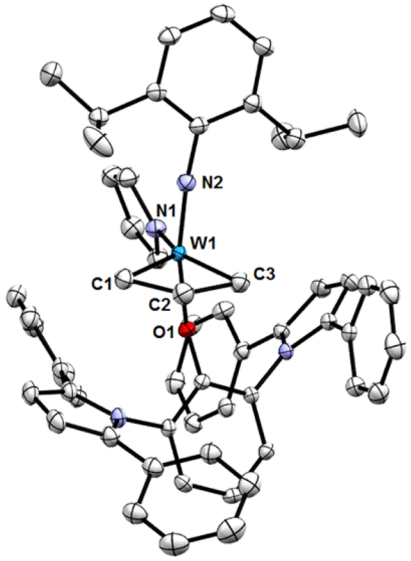

Figure 3. Thermal ellipsoid representation of the structure of **5** at the 50% probability level. The minor component of the tungsten disorder and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−O(1) = 1.986(2), W(1)−N(1) = 2.031(1), W(1)−N(2) = 1.752(2), W(1)−C(1) = 2.035(2), W(1)−C(3) = 2.083(2), W···C2 = 2.370(2), C(1)−C(2) = 1.603(3), C(2)−C(3) = 1.590(3); O(1)−W(1)−N(1) = 84.03(7), N(2)−W(1)−O(1) = 166.13(7), N(2)−W(1)−C(3) = 93.16(9), N(2)−W(1)−C(1) = 97.96(9), N(1)−W(1)−C(2) = 165.65(8), W(1)−C(3)−C(2) = 79.1(1), C(3)−C(2)−C(1) = 117.5(2), C(2)−C(1)−W(1) = 80.3(1), C(1)−W(1)−C(3) = 83.02(9), N(1)−W(1)−N(2) = 91.27(8), N(1)−W(1)−C(3) = 150.64(8).

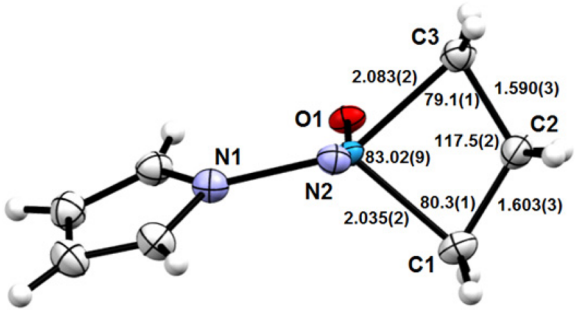

Figure 4. Thermal ellipsoid drawing (50%) of the metallacyclobutane moiety in **5** with bond lengths (Å) and angles (deg).

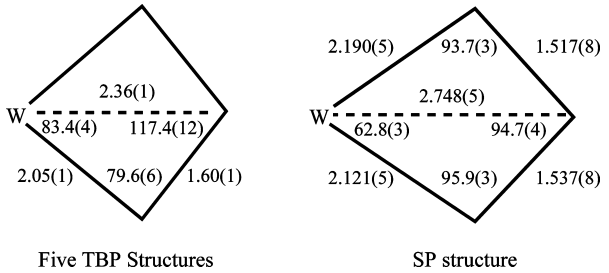

Figure 5. Selected distances and angles in five TBP structures (average) and one SP structure.

complexes would never approach 1, as a consequence of the constraints inherent in a complex that contains a metallacylobutane ring in the equatorial position; the maximum τ value is ~0.68. It should be noted that the W−C(2) distance of 2.370(2) Å in **5** is essentially what is found in the TBP structures.

Calculations concerning metallacyclobutanes made from MAP alkylidenes[13] suggest that the SP structure is further from the transition state for olefin loss than a TBP structure, and an SP′ structure is the closest. All three can be interconverted readily through five-coordinate rearrangements.[14] According to calculations the olefin approaches the more "open" CNO (imido/alkylidene/OR) face "*trans*" to the pyrrolide and forms an SP′ metallacyclobutane structure, *without* olefin binding to the metal, to give an intermediate alkylidene/olefin complex. The SP′ structure becomes a TBP when the O−M−N_{imido} angle opens to ~180° and the pyrrolide moves into an equatorial position where the N1−M−C3 and N1−M−C1 angles are equal. A continuation of the movement of N2, N1, and O leads to a second SP′ structure in which the metallacyclobutane again spans apical (now C3) and basal (now C1) sites and the ethylene that is leaving the coordination sphere contains C1 and C2. Both from experiments and in terms of calculations the barrier for interconversion of TBP and SP forms is relatively low.[14] TBP and SP′ metallacyclobutane structures would seem to be even more easily interconverted, since minimal movement of the imido and aryloxide ligands is required. The SP′/TBP/SP′ sequence is proposed to be the intimate mechanism of metathesis by a MAP catalyst, and the SP structure is a relatively low energy sink.

It is somewhat surprising that the SP′ structure, of which **5** is the first example to our knowledge, can be observed, but it is not clear why in this particular case. At this stage we can only offer that the energy difference between the SP′ and TBP structures is so low that intramolecular steric forces and/or packing forces in the crystal tip the balance in favor of SP′. So far there is no evidence for the SP′ structure in solution NMR spectra of **5**. Evidence would consist of a loss of mirror symmetry in the metallacylobutane ring at low temperatures.

It should be noted that in NMR studies of Mo and W metallacyclobutane species[9,12] it was found necessary to invoke a "methylidene/ethylene" intermediate in order that the kinetic scheme be self-consistent. However, no ethylene/methylidene has been found to be an intermediate through calculations.[13]

Therefore, an important question is whether the intermediate observed in the NMR studies is an SP′ metallacycle instead of an "ethylene/methylidene" complex.

The ROMP polymerization of 50 equiv of 5,6-dicarbomethoxynorbornadiene was chosen as an initial measure of the stereoselectivity of the six MAP catalysts described earlier. All polymers were found to have a >99% *cis,syndiotactic* structure, the same structure observed when the initiator is Mo(NAd)-$(CHCMe_2Ph)(Pyr)(OHIPT)$.[4a]

In contrast, compounds **4a,b** show markedly different behavior in the homometathesis of 1-octene (Table 1). For comparison, $W(NAr)(C_3H_6)(pyr)(OHIPT)$[4a] (**6**) was employed under identical conditions. Catalyst **4a** initially provides the product at a faster rate than **4b** or **6**, but selectivity for the *Z* product erodes over time, with 62% *Z* product being observed after 400 min. Catalyst **4b** is much slower, providing 83% conversion over 400 min, but the *Z* configuration of the product is maintained, as it is with **6**. The difference in performance between $ODPP^{iPr}$ and $ODPP^{Ph}$ highlights the extreme sensitivity of activity and *Z*-selectivity of MAP complexes to steric factors associated with the aryloxide.

Now that an SP′ metallacycle has been structurally characterized, a persistent question that remains is the degree

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Table 1. Homocoupling of 1-Octene with 4a,b[a]

catalyst	t (min)	conversn (%)	Z (%)
4a	10	62	>95
4a	40	72	90
4a	110	88	84
4a	400	>95	62
4b	10	24	-
4b	40	36	-
4b	110	59	>95
4b	400	83	94
6	10	5	-
6	40	16	-
6	110	46	>95
6	400	93	>95

[a]Conditions: 25 °C, 4 mol % catalyst loading, 0.3 M in C_6H_6. See the Supporting Information for details.

to which the structures and dynamics of *unsubstituted* metallacyclobutanes differ from the structures and dynamics of *substituted* metallacyclobutanes. Since substituted metallacyclobutanes are inherently more labile toward loss of olefin than unsubstituted metallacyclobutanes, obtaining answers to this question through experimental studies is likely to remain challenging.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, and CIF files giving experimental details for the synthesis of all compounds and details of X-ray structural studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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