Shuttling P(3) [P \textsubscript{3}] from Niobium to Rhodium: The Synthesis and Use of Ph(3)SnP(3)(C(6)H(8)) [Ph \textsubscript{3} Sn P \textsubscript{3} (C \textsubscript{6} H \textsubscript{8})]

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Shuttling P$_3$ from Nb to Rh: The Synthesis and Use of Ph$_3$SnP$_3$(C$_6$H$_8$) as a P$_3^{1–}$ Synthon

Brandi M. Cossairt, and Christopher C. Cummins

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139

Received December 22, 2009; E-mail: ccummins@mit.edu

Seeking new methods for phosphorus incorporation directly from its molecular elemental form, P$_4$, we have begun to focus on cyclo-P$_3$ complexes as a versatile class of intermediates. 1–4 While it is well documented that a common result of P$_4$ activation by transition-metal complexes is replacement of a single vertex of the P$_4$ tetrahedron by an ML$_n$ fragment, such cyclo-P$_3$ complexes were not recognized until recently for their potential as phosphorus transfer agents. 2–6 Accordingly, anionic cyclo-P$_3$ complexes of niobium have been shown to serve as sources of P$_3^{1–}$ upon stoichiometric treatment with suitable tripositive electrophiles, including acid chlorides leading to triphosphabutadiene intermediates, 3,5 or AsCl$_3$ leading to AsP$_3$. 4,7 With the present work we illustrate a new approach to phosphorus transfer chemistry by way of a P$_3^{1–}$ synthon, the Ph$_3$SnP$_3$(C$_6$H$_8$) molecule, that is both nucleophilic at phosphorus and capable of losing neutral 1,3-cyclohexadiene upon treatment with an appropriate P$_3^{1–}$ acceptor. The Ph$_3$SnP$_3$(C$_6$H$_8$) molecule is itself obtained in an efficient three-step sequence involving P$_4$ activation, functionalization with triphenyltin chloride, and pyridine-N-oxide-elicited triphosphirene elimination in the presence of 1,3-cyclohexadiene (Scheme 1).

Facile access to [Na][O(η$^3$-P$_3$)Nb(ODipp)$_3$] (Dipp = 2,6-Pr$_2$C$_6$H$_3$), a convenient source of P$_3^{3–}$, is gained through reduction of the complex Cl$_5$Nb(ODipp)$_3$ in the presence of white phosphorus, 4,8,9 The anionic nature of this cyclo-P$_3$ niobium complex imparts demonstrable nucleophilic character at the P$_3$ ring, allowing for reaction with a range of mild electrophiles. 1,4 Treatment of [Na][O(η$^3$-P$_3$)Nb(ODipp)$_3$] with Ph$_3$SnCl results in loss of NaCl and formation of (η$^2$-Ph$_3$SnP$_3$)Nb(ODipp)$_3$ (1, Scheme 1). The phosphorus NMR spectrum of 1 consists of a single sharp singlet at $–235$ ppm with $^{117/119}$Sn satellites $^{1}J_{117/119}$Sn–P $= 336$ Hz, $^{1}J_{117/119}$Sn–P $= 321$ Hz (Figure 1a). This sharp singlet is indicative of whizzing of the Ph$_3$Sn moiety about the cyclo-P$_3$ ring. 1,10–12 Variable temperature NMR spectra obtained as low as $–90$ °C reveal no locking out of this movement on the NMR time scale.

The niobium-phosphorus interaction in 1 may be regarded as side-on coordination of a diphosphine (RP=PR) to a strongly π-donating d$_2$ Nb(ODipp)$_3$ fragment. 13 To liberate the triphosphirene molecule P$_3$SnPh$_3$ from niobium, complex 1 was treated with a stoichiometric amount of pyridine-N-oxide in the presence of excess 1,3-cyclohexadiene, 14,15 the latter to serve as a trapping agent; this protocol results in formation of the desired Diels-Alder adduct Ph$_3$SnP$_3$(C$_6$H$_8$), 2, together with 0.5 equiv of the known niobium oxo dimer [ONb(ODipp)$_3$)$_2$ (Scheme 1). 16 Compound 2 was isolated in 65% yield by filtration as it selectively precipitated upon concentration of the etheral reaction mixture. Conveniently, compound 2 could also be prepared directly in a single pot, without isolation of complex 1, in an overall yield of 64% over the two steps.

The phosphorus NMR spectrum of 2 features a sharp doublet and a sharp triplet flanked by $^{117/119}$Sn satellites centered at $–234$ ppm ($^{3}J_{117/119}$Sn–P $= 105$ Hz) and $–321$ ppm ($^{1}J_{117/119}$Sn–P $= 736$ Hz),
respectively (Figure 1b).\(^1\) X-ray quality crystals of 2 were grown from a saturated THF solution at \(-35\) °C (Figure 2). The Sn–P interatomic distance is 2.528(1) Å, which is typical for a Sn–P single bond, and the olefin double bond is found between C44 and C45 with a distance of 1.330(6) Å as compared with the C41 to C42 interatomic distance which is found to be 1.549(6) Å. As can be seen in both the phosphorus NMR spectrum and the crystal structure for compound 2, only a single isomer is observed due to the endo effect stemming from secondary orbital interactions with P3 during the cycloaddition reaction. This appears to be a general feature of this class of cycloaddition products.\(^{1,15}\)

The reaction between complex 1 and ONC\(_2\)H\(_5\) in the presence of 20 equiv 1,3-cyclohexadiene was monitored by \(^{31}\)P and \(^1\)H NMR spectroscopy in toluene. At room temperature, the reaction was found to proceed rapidly with no observable intermediates; the disappearance of \(^{31}\)P NMR resonances for 1 was concomitant with appearance of those assigned to 2. However, when the reaction was monitored at \(-10\) °C, complex 1 was consumed giving rise to a single new species with a phosphorus NMR resonance at \(-170\) ppm. This species appears stable at \(-10\) °C for several hours and was identified by \(^1\)H and \(^{31}\)P NMR spectroscopy as the ONC\(_2\)H\(_5\) adduct of (\(\eta^1\)-Ph\(_3\)SnP\(_3\))Nb(ODipp)\(_2\)), 1-ONC\(_2\)H\(_5\). Complex 1-ONC\(_2\)H\(_5\) precipitated from toluene solution as a pink powder when held at \(-10\) °C for several minutes and it was necessary to gently warm the reaction mixture to resolubilize the complex and monitor its conversion to 2. Accordingly, upon warming to \(30\) °C, conversion of 1-ONC\(_2\)H\(_5\) to compound 2 was observed with no other major species growing in.\(^9\) These observations suggest that ONC\(_2\)H\(_5\) binding is the rate-determining step in the formation of compound 2 at \(20\) °C.

The outcome of the reaction of 1 with ONC\(_2\)H\(_5\) in the presence of 1,3-cyclohexadiene is rationalized by loss of a free triphosphine, that is, a species with a cyclo-P\(_3\) unit bound in an \(\eta^1\) fashion to the Ph\(_3\)Sn fragment.\(^{17-19}\) In order to study the feasibility of such a hypothesis we turned to calculations to investigate the pos-

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Figure 2. Solid-state structure of 2 with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.\(^{25}\)

The phosphorus NMR spectrum of 3 displays a doublet of quartets for the phosphorus P atoms (31 ppm, \(^{1}J_{PH-P} = 150\) Hz, \(^2J_{P-P} = 16\) Hz) and an overlappin gpair of quartets for the cyclo-P\(_3\) moiety (\(-191\) ppm, \(^{1}J_{PH-P} = 32\) Hz, \(^2J_{P-P} = 16\) Hz) (Figure 1c), which is quite similar to the spectral properties reported for (\(\eta^1\)-P\(_3\))Rh(triphos) (triphos = CH\(_2\)C(CH\(_2\))P\(_3\))\(_2\)), which was obtained via P4 activation as described by DiVaira and Sacconi.\(^{26,27}\) X-ray quality crystals of 3 were grown by vapor diffusion of Et\(_2\)O into a concentrated solution of CH\(_2\)Cl\(_2\) at \(-35\) °C (Figure 3). Complex 3 displays a symmetric cyclo-P\(_3\) unit where the Rh-P4,P5,P6 interatomic distances average to 2.374 Å and the Rh-P1,P2,P3 interatomic distances average to 2.420 Å.

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Figure 3. Solid-state structure of 3 with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.\(^{25}\)

It was found additionally in the course of this study that [Na][\((\eta^1\)-P\(_3\))Nb(ODipp)\(_2\)] on its own can transfer a triphosphorus unit to Wilkinson’s catalyst via the bimetallic complex (Ph\(_3\))P\(_2\)Rh(\(\mu_2\))(\(\eta^1\)-P\(_3\))Nb(ODipp)\(_2\)) with loss of NaCl, however the subsequent elimination of 3 and formation of niobium oxo complex \(_2\)Cl\(_2\) is neither as efficient nor as clean as is the P\(_3\) transfer with compound 2.\(^9\) The use of compound 2 as a source of P\(_3\) represents a new methodology for accessing phosphorus-containing molecules. This method for the synthesis of 3 bears close relation to the installation of a nitrido functional group using deprotonated...
2,3:5,6-dibeno-7-azabicyclo[2.2.1]hepta-2,5-diene (dbabh) as an N1+ source with loss of anthracene.28,29 A defining feature of the P3+-transfer reaction yielding 3 is the conversion of rhodium from the +1 to the +3 oxidation state.30,31 It is of note that compound 2 should also be a viable source of an unusual phosphido ligand by loss of Ph3SnX with retention of 1,3-cyclohexadiene, or potentially as a bulky phosphane ligand with coordination to Lewis acidic centers at the Sn-bound phosphorus atom with retention of both diene and triphenyl. One of the most attractive properties of compound 2 is its modular synthesis from [Na][(η2−P3)Sn(ODipp)]3. The Ph3Sn3+ moieties can be replaced by other electrophiles including Ph3C+, Ph3Si+, and Me2Si+ via the salt elimination procedure.3 The diene reaction partner is similarly variable in the second step of the synthesis.9 This modularity will allow for the assembly of a library of P3+-transfer reagents having variable reactivity properties.

**Experimental Section.** General experimental details as well as the syntheses of (η2−Ph3SnP3)Nb(ODipp)3, (η2−Ph3P2Sn(ODipp)3), and (η2−Me2SiP3)Nb(ODipp)3, details of the direct reaction of [Na][(η3−P3)Sn(ODipp)]3 with CIRh[Ph3p3] and an updated synthesis of [Na][(η2−P3)Sn(ODipp)]3 may be found in the supporting information document accompanying this manuscript.32

**Ph3SnP3(C6H5).** 2. One pot procedure. [Na][(η3−P3)Sn(ODipp)]3 (1.5 g, 1.57 mmol) was dissolved in 50 mL of Et2O. To this solution was added Ph3SnCl (604 mg, 1.57 mmol) with stirring. The reaction mixture was allowed to stir for 1 h after which the time reaction mixture was filtered through a plug of Celite into a fresh reaction flask. To the filtrate was added 1,3-cyclohexadiene (2.5 g, 31.3 mmol). With vigorous stirring, solid OCNH2 (149 mg, 1.57 mmol) was added. The reaction mixture was stirred for 1.5 h during which the time reaction mixture took on a golden yellow color. Following the reaction time the reaction mixture was concentrated to half the original volume under reduced pressure resulting in precipitation of an off-white powder. This powder was isolated atop a glass frit and was washed three times with 10 mL of Et2O and dried to constant mass resulting in pure Ph3SnP3(C6H5) in 64% yield (529 mg, 1.01 mmol). X-ray quality crystals of this material were afforded by recrystallization using 1:1 toluene/THF at ~35 °C. Elemental Analysis calculated for C28H18P3Sn: C 55.11, H 4.47, P 17.76. 1H NMR (CD2Cl2): 1.25 (m, 2H), 2.43 (m, 2H), 5.27 (m, 2H), 7.18 (m, 2H), 1.77 (m, 6H) ppm. 13C NMR (CD2Cl2): 22.8 (s), 29.2 (m), 118.4 (m), 128.1 (s), 129.0 (s), 129.4 (s), 137.7 (s) ppm. 31P NMR (CD2Cl2): −235 (d, 2P, 1Jp−p = 163 Hz, 2J111/119Sn−p = 105 Hz), −321 (t, 1P, 1Jp−p = 163 Hz, 1J111/119Sn−p = 736 Hz) ppm. 119Sn NMR (CD2Cl2): −88 ppm (d, 1J119Sn−p = 739 Hz, 2J119Sn−p = 107 Hz).

(η2−P3)Rh[Ph3P3]3. 3. Ph3SnP2(C6H5) (120 mg, 0.229 mmol) was dissolved in 7 mL of THF and the solution was frozen. Wilkinson’s catalyst (212 mg, 0.23 mmol) was likewise dissolved in 7 mL of THF and the solution was frozen solid. Upon thawing, the solution of Ph3SnP2(C6H5) was added to the solution of Wilkinson’s catalyst with stirring. The reaction mixture was allowed to stir at 20 °C for 2 h, after which the time reaction mixture was taken to dryness under reduced pressure. The resulting brown residue was stirred in hexane (10 mL) for 20 minutes and then was dried again under reduced pressure. The resulting brown powder was stirred vigorously in Et2O for 30 minutes after which time it was collected by filtration as a sand-colored solid and a colorless filtrate. The colorless filtrate was taken to dryness resulting in a white powder which was a mixture of Ph3SnCl and a small quantity of Ph3P3.

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**Supporting Information.** Additional experimental procedures and characterization data for all new compounds. This information is available online free of charge at http://www.angewandte.org or from the authors.

**References**

9. Please see the supporting information document accompanying this text for additional details.
30. The assignment of rhodium(II) in complex 3 is in recognition of this as a d6, quasi-octahedral species (see supporting information for a calculated MO diagram) that is isolobal with other rhodium(III) derivatives such as Rh(N)(Cp)[P2(d2)]-2. See reference 31.
32. Crystallographic details can be found in the Supporting Information document accompanying this manuscript and from the CIDD under deposition numbers CCDC-745202 and 745203. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.
**Shuttling P₃’s.** A Ph₃SnP₃(C₆H₈) molecule has been synthesized by P₃⁻⁻⁻ transfer from a niobium cyclo-P₃ anion complex. This new molecule is shown to be a viable source of P₃⁻⁻⁻ in a proof of principle reaction. Loss of Ph₃SnCl and 1,3-cyclohexadiene from Ph₃SnP₃(C₆H₈) upon treatment with Wilkinson’s catalyst, ClRh(PPh₃)₃, gives rise to the new cyclo-P₃ complex (η³-P₃)Rh(PPh₃)₃.