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Phosphorus Chemistry

Shuttling P_3 from Niobium to Rhodium: The Synthesis and Use of $Ph_3SnP_3(C_6H_8)$ as a P_3^- Synthon**

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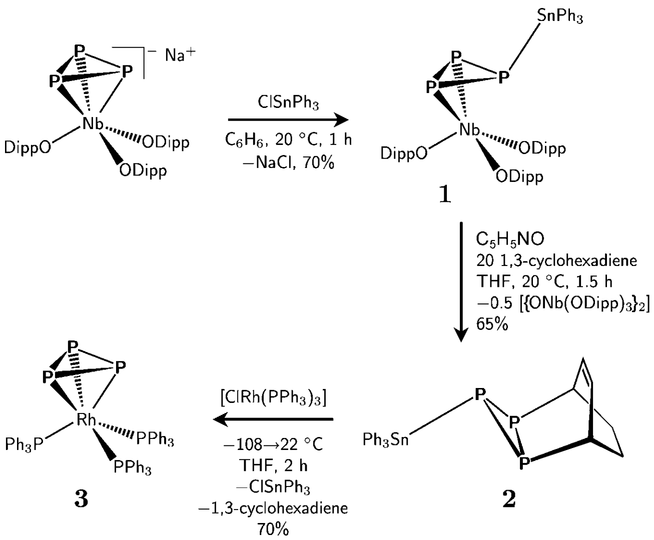
Seeking new methods for phosphorus incorporation directly from its molecular elemental form, P_4, we have begun to focus on cyclo-P_3 complexes as a versatile class of intermediates.[1–3] Although it is well-documented that a common result of P_4 activation by transition metal complexes is replacement of a single vertex of the P_4 tetrahedron by an ML_n fragment, such cyclo-P_3 complexes were not recognized for their potential as phosphorus transfer agents until recently.[2–4] Accordingly, anionic cyclo-P_3 complexes of niobium have been shown to serve as sources of P_3^{3-} upon stoichiometric treatment with suitable tripositive electrophiles, including acid chlorides, leading to triphosphabutadiene intermediates,[2] or $AsCl_3$, leading to AsP_3.[3,5] Herein, we illustrate a new approach to phosphorus transfer chemistry with a P_3^- synthon, the $Ph_3SnP_3(C_6H_8)$ molecule, that is both nucleophilic at phosphorus and capable of losing neutral 1,3-cyclohexadiene upon treatment with an appropriate P_3^- acceptor. The $Ph_3SnP_3(C_6H_8)$ 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 $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ (Dipp = 2,6-$i$$Pr_2C_6H_3$), a convenient source of P_3^{3-}, is gained through reduction of the complex $[Cl_2Nb(ODipp)_3]$ in the presence of white phosphorus.[3,6,7] 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.[1,3] Treatment of $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ with Ph_3SnCl results in loss of NaCl and formation of $[(\eta^2\text{-}Ph_3SnP_3)Nb(ODipp)_3]$ (**1**; Scheme 1). The ^{31}P NMR spectrum of **1** consists of a single sharp singlet at −235 ppm with $^{117/119}Sn$ satellites $^1J_{^{119}Sn,P} = 336$ Hz, $^1J_{^{117}Sn,P} = 321$ Hz (Figure 1a). This sharp singlet is indicative of circumambulation of the Ph_3Sn moiety about the cyclo-P_3 ring.[1,8–10] Variable-temperature NMR spectra obtained as low as −90 °C reveal no locking out of this movement on the NMR timescale.



Scheme 1. Transfer of the P_3^{3-} fragment from niobium complex **1** to rhodium complex **3** via **2**. Dipp = 2,6-diisopropylphenyl.

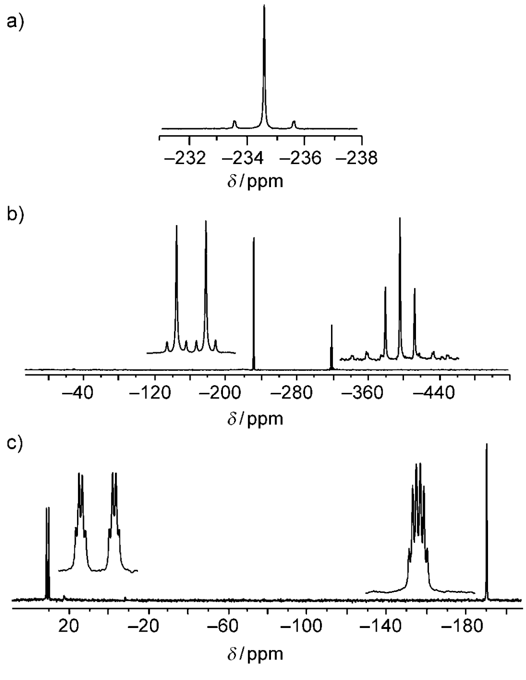


Figure 1. ^{31}P NMR spectra of a) **1** (C_6D_6), b) **2** (C_6D_6), and c) **3** ($[D_8]THF$) collected at 20 °C.

The niobium–phosphorus interaction in **1** may be regarded as side-on coordination of a diphosphene (RP=PR) to a strongly π-donating d^2 {Nb(ODipp)$_3$} fragment.[11] To liberate the triphosphirene molecule P_3SnPh_3 from niobium, complex **1** was treated with a stoichiometric amount of pyridine-*N*-oxide in the presence of excess 1,3-cyclohexa-

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diene;[12] the latter serves as a trapping agent. This procedure results in formation of the desired Diels–Alder adduct $Ph_3SnP_3(C_6H_8)$ (**2**) together with 0.5 equiv of the known niobium oxo dimer $[\{ONb(ODipp)_3\}_2]$ (Scheme 1).[13] Compound **2** was isolated in 65 % yield by filtration as it selectively precipitated upon concentration of the ethereal 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 ^{31}P NMR spectrum of **2** features a sharp doublet and a sharp triplet flanked by $^{117/119}$Sn satellites centered at −234 ppm ($^2J_{^{117/119}\mathrm{Sn,P}} = 105$ Hz) and −321 ppm ($^1J_{^{117/119}\mathrm{Sn,P}} = 736$ Hz), respectively (Figure 1 b).[1] X-ray quality crystals of **2** were grown from a saturated THF solution at −35 °C (Figure 2).[25] The Sn1−P3 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 (1.549(6) Å). As can be seen in both the ^{31}P NMR spectrum and the crystal structure for compound **2**, only a single isomer is observed owing to the endo effect arising from secondary orbital interactions with P3 during the cycloaddition reaction. This appears to be a general feature of this class of cycloaddition products.[12]

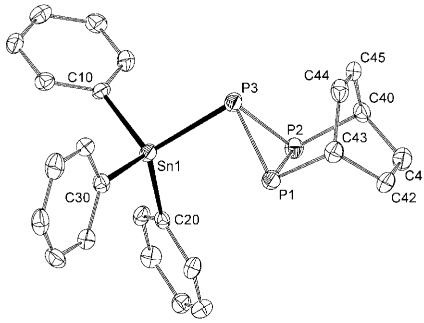

Figure 2. Solid-state structure of **2** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.[20]

The reaction between complex **1** and C_5H_5NO in the presence of 1,3-cyclohexadiene (20 equiv) 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 ^{31}P NMR resonance at $\delta = -170$ ppm. This species appears stable at −10 °C for several hours and was identified by ^{1}H and ^{31}P NMR spectroscopy as the C_5H_5NO adduct of $[(\eta^2\text{-}Ph_3SnP_3)Nb(ODipp)_3]$, **1**-$ONC_5H_5$. This adduct 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_5H_5 into compound **2** was observed with no other major species growing in.[7] These observations suggest that C_5H_5NO binding is the rate-determining step in the formation of compound **2** at 20 °C.

The outcome of the reaction of **1** with C_5H_5NO in the presence of 1,3-cyclohexadiene is rationalized by loss of a free triphosphirene, that is, a species with a cyclo-P_3 unit bound in an η^1 fashion to the Ph_3Sn fragment.[14,15] To study the feasibility of such a hypothesis, we turned to calculations to investigate the possible conformations of the proposed Ph_3SnP_3 intermediate; both $(\eta^1\text{-}P_3)SnPh_3$ and $(\eta^3\text{-}P_3)SnPh_3$ structures were considered. Despite the fact that six-coordinate tin is relatively common,[16] all attempts to optimize the $(\eta^3\text{-}P_3)SnPh_3$ structure resulted in convergence to the $(\eta^1\text{-}P_3)SnPh_3$ form, which is structurally very similar to **2** but without diene. The P=P distance in this intermediate was calculated to be 2.019 Å whilst the P−P distances average to 2.250 Å. The one short Sn−P interaction falls at 2.622 Å whereas the distances from the tin center to the phosphorus atoms of the diphosphene average 3.884 Å. This outcome suggests that the reactive $(\eta^1\text{-}P_3)SnPh_3$ intermediate does indeed harbor a free diphosphene unit, and this P=P moiety does not interact appreciably with the tin center.[7] To gain a further sense of the chemical nature of the transient $(\eta^1\text{-}P_3)SnPh_3$ intermediate, we investigated its fate in the absence of an added chemical trap. ^{31}P NMR spectroscopic analysis and elemental analysis suggest that $(\eta^1\text{-}P_3)SnPh_3$ cleanly oligomerizes to $(Ph_3SnP_3)_x$; however, both the value of x and the connectivity of this oligomer is unknown, and work is in progress to better characterize this interesting species.[7]

Compound **2** harbors many desirable properties as a potential P_3^- transfer agent. First, there is a reactive P−Sn bond, which can be cleaved with elimination of Ph_3SnCl.[17,18] Furthermore, the cyclic olefin that was installed by trapping the P=P unit with 1,3-cyclohexadiene acts as a protecting group for that reactive moiety, as it has been shown that retrocycloaddition reactions are accessible for such protected diphosphenes.[19]

As a proof of principle that **2** would be able to serve as a source of P_3^- in reaction chemistry, **2** was treated with 1 equiv of $[ClRh(PPh_3)_3]$ (Wilkinson's catalyst; Scheme 1). GCMS and ^{1}H, ^{31}P, and ^{119}Sn NMR spectroscopy gave evidence for loss of Ph_3SnCl and 1,3-cyclohexadiene in a 1:1 ratio. Following diethyl ether extraction of the crude reaction mixture, the sand-colored complex $(\eta^3\text{-}P_3)Rh(PPh_3)_3$ (**3**) was isolated in pure form.

The ^{31}P NMR spectrum of **3** has a doublet of quartets for the phosphane P atoms ($\delta = 31$ ppm, $^1J_{^{103}\mathrm{Rh,P}} = 150$ Hz, $^2J_{\mathrm{P,P}} = 16$ Hz) and an overlapping pair of quartets for the cyclo-P_3 moiety ($\delta = -191$ ppm, $^1J_{^{103}\mathrm{Rh,P}} = 32$ Hz, $^2J_{\mathrm{P,P}} = 16$ Hz; Figure 1 c), which is quite similar to values reported for $[(\eta^3\text{-}P_3)Rh(triphos)]$ (triphos = $CH_3C(CH_2PPh_2)_3$), which was obtained via P_4 activation as described by DiVaira and Sacconi.[21] X-ray quality crystals of **3** were grown by vapor diffusion of Et_2O into a concentrated solution of CH_2Cl_2 at −35 °C (Figure 3).[25] Complex **3** displays a symmetric cyclo-P_3 unit in which 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.

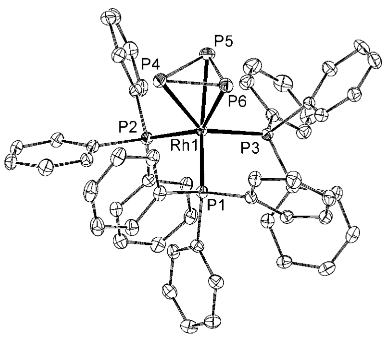

Figure 3. Solid-state structure of **3** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.[20]

In the course of this study, it was found that $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ can transfer a triphosphorus unit to Wilkinson's catalyst on its own via the bimetallic complex $[(Ph_3P)_3Rh(\mu_2{:}\eta^1,\eta^2\text{-}P_3)Nb(ODipp)_3]$ with loss of NaCl; however, the subsequent elimination of **3** and formation of the niobium oxo complex using C_5H_5NO is neither as efficient nor as clean as is the P_3^- transfer with compound **2**.[7] The use of compound **2** as a source of P_3^- is a new method for accessing phosphorus-containing molecules. The method used for the synthesis of **3** bears close relation to the installation of a nitrido functional group using deprotonated 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (DBABH) as an N^- source with loss of anthracene.[22] A defining feature of the P_3^- transfer reaction yielding **3** is the conversion of rhodium from the +1 into the +3 formal oxidation state.[23,24]

It is of note that compound **2** should also be a viable source of an unusual phosphanido ligand by loss of Ph_3SnX with retention of 1,3-cyclohexadiene, or potentially as a bulky phosphane ligand with coordination to Lewis acidic centers at the tin-bound phosphorus atom with retention of both diene and triphenyltin. One of the most attractive properties of compound **2** is its modular synthesis from $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$. The Ph_3Sn^+ moiety can be replaced by other electrophiles, including Ph_3C^+, Ph_3Si^+, and Me_3Si^+, by the salt-elimination procedure.[7] The diene reaction partner is similarly variable in the second step of the synthesis.[7] This modularity will allow the assembly of a library of P_3^- transfer reagents that have widely varied reactivity properties.

Experimental Section

General experimental details and the syntheses of $[(\eta^2\text{-}Ph_3SnP_3)Nb(ODipp)_3]$, $[(\eta^2\text{-}Ph_3CP_3)Nb(ODipp)_3]$, $[(\eta^2\text{-}Ph_3SiP_3)Nb(ODipp)_3]$, and $[(\eta^2\text{-}Me_3SiP_3)Nb(ODipp)_3]$, details of the direct reaction of $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ with $[ClRh(PPh_3)_3]$, and an updated synthesis of $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ are given in the Supporting Information.

2: $[Na(THF)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ (1.5 g, 1.57 mmol) was dissolved in Et_2O (50 mL). Ph_3SnCl (604 mg, 1.57 mmol) was then added to this solution with stirring. The reaction mixture was allowed to stir for a further 1 h, after which time the reaction mixture was filtered through a plug of Celite into a fresh reaction flask. 1,3-cyclohexadiene (2.5 g, 31.3 mmol) was added to the filtrate, and then solid C_5H_5NO (149 mg, 1.57 mmol) was added with vigorous stirring. The reaction mixture was stirred for a further 1.5 h, during which time it took on a golden yellow color. The reaction mixture was then concentrated to half the original volume under reduced pressure, resulting in precipitation of an off-white powder. This powder was isolated on a glass frit and was washed three times with Et_2O (10 mL) and dried to constant mass, resulting in pure $Ph_3SnP_3(C_6H_8)$ 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 (%) calcd for $C_{24}H_{23}P_3Sn$: C 55.11, H 4.47, P 17.36; found C 54.91, H 4.47, P 17.76. ^1H NMR (C_6D_6, 500 MHz): $\delta = 1.25$ (m, 4H), 2.43 (m, 2H), 5.27 (m, 2H), 7.18 (m, 9H), 7.77 ppm (m, 6H). ^{13}C NMR (C_6D_6, 126 MHz): $\delta = 22.8$ (s), 29.2 (m), 118.4 (m), 128.1 (s), 129.0 (s), 129.4 (s), 137.7 ppm (s). ^{31}P NMR (C_6D_6, 202 MHz): $\delta = -235$ (d, 2P, $^1J_{P,P} = 163$ Hz, $^2J_{^{117/119}Sn,P} = 105$ Hz), −321 ppm (t, 1P, $^1J_{P,P} = 163$ Hz, $^1J_{^{117/119}Sn,P} = 736$ Hz). ^{119}Sn NMR (C_6D_6, 186 MHz): −88 ppm (dt, $^1J_{^{119}Sn,P} = 739$ Hz, $^2J_{^{119}Sn,P} = 107$ Hz).

3: $Ph_3SnP_3(C_6H_8)$ (**2**; 120 mg, 0.229 mmol) was dissolved in THF (7 mL) and the solution was frozen. Wilkinson's catalyst (212 mg, 0.23 mmol) was also dissolved in THF (7 mL) and the solution frozen. Upon thawing, the solution of $Ph_3SnP_3(C_6H_8)$ 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 time the reaction mixture was taken to dryness under reduced pressure. The resulting brown residue was stirred in hexane (10 mL) for 20 min and then was dried again under reduced pressure. The resulting brown powder was stirred vigorously in Et_2O for 30 min, and thereafter collected by filtration as a sand-colored solid and a colorless filtrate. The filtrate was taken to dryness, resulting in a white powder, which was a mixture of Ph_3SnCl and a small quantity of PPh_3. The sand-colored solid was dried to a constant mass of 157 mg (70% crude yield). The solids were dissolved in CH_2Cl_2 (2 mL) into which Et_2O was slowly diffused at −35 °C, to furnish X-ray quality crystals of **3** (60% yield; 135 mg, 0.137 mmol). Elemental analysis (%) calcd for $C_{54}H_{45}P_6Rh$: C 66.00, H 4.61, P 18.91; found C 65.63, H 4.41, P 18.38. ^1H NMR ($[D_8]$THF, 500 MHz): $\delta = 5.14$ (t, 6H, $^1J_{H,H} = 7$ Hz), 5.23 (br m, 6H), 5.36 ppm (t, 3H, $^1J_{H,H} = 7$ Hz). ^{13}C NMR ($[D_8]$THF, 126 MHz): $\delta = 129.3$ (s), 129.4 (s), 133.1 (s), 135.3 ppm (m). ^{31}P NMR ($[D_8]$THF, 202 MHz): $\delta = 34$ (dq, $^1J_{^{103}Rh,P} = 150$ Hz, $^2J_{P,P} = 16$ Hz), −187 ppm (dq, $^1J_{^{103}Rh,P} = 32$ Hz, $^2J_{P,P} = 16$ Hz). MALDI-TOF MS: *m*/*z* 982.1004.

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Keywords: coordination modes · phosphorus · rhodium · structure elucidation · transfer reagents

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