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A Terminal Nitride-to-Phosphide Conversion Sequence Followed by Tungsten Phosphide Functionalization Using a Diphenylphosphenium Synthon**

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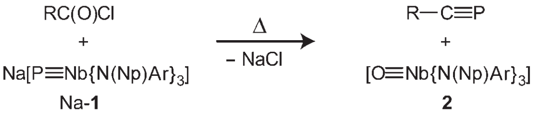
Dedicated to Professor Philip P. Power

The terminal, anionic niobium phosphide (P^{3-}) complex $Na[P{\equiv}Nb(N[Np]Ar)_3]$ (Na-**1**; Np = neopentyl, Ar = 3,5-$Me_2C_6H_3$) has served as a platform for the construction of multiply bonded, phosphorus-containing moieties as both complexed ligands and free entities.[1–5] Exemplifying the latter is the synthesis of phosphaalkynes ($RC{\equiv}P$) and $[O{\equiv}Nb\{N(Np)Ar\}_3]$ (**2**) by treatment of Na-**1** with acid chlorides (RC(O)Cl), a reaction [Eq. (1)] that proceeds with NaCl elimination and formation of a thermally unstable yet isolable metallacyclic acylphosphinidene intermediate of the form $[\{RC(O)P\}Nb\{N(Np)Ar\}_3]$.[5] We envisioned that a similar method could be employed to synthesize new transition-metal phosphide complexes, given the availability of a suitable reaction partner for Na-**1**. We recently reported an attractive candidate for this application: the tungsten oxide/chloride complex, $[O(Cl)W\{N(i\text{Pr})Ar\}_3]$ (**3**).[6] In a reaction similar to Equation (1), complex **3** is prepared by treating the corresponding nitride complex $[N{\equiv}W\{N(i\text{Pr})Ar\}_3]$ (**4**) with pivaloyl chloride (*t*BuC(O)Cl), and is quantitatively obtained as a blood-red, highly lipophilic solid of sufficient purity for further synthetic studies. We hypothesized that in the presence of Na-**1**, **3** would behave as an "inorganic acid chloride", engaging Na-**1** by elimination of NaCl. With subsequent intermetal exchange of P and O ligands, the known oxidoniobium complex **2** would be generated as well as a new terminal phosphide complex $[P{\equiv}W\{N(i\text{Pr})Ar\}_3]$ (**5**). Several examples of installing multiply bonded ligands (oxide, imide, and alkylidene) by intermetal ligand exchange have been reported;[7–16] herein, we extend this concept to the terminal phosphide functional group.



$$\begin{array}{c} RC(O)Cl \\ + \\ Na[P{\equiv}Nb\{N(Np)Ar\}_3] \\ Na\text{-}\mathbf{1} \end{array} \xrightarrow[-\,NaCl]{\Delta} \begin{array}{c} R{-}C{\equiv}P \\ + \\ [O{\equiv}Nb\{N(Np)Ar\}_3] \\ \mathbf{2} \end{array} \qquad (1)$$

Our hypothesis was tested by treating a yellow-orange, ethereal solution of Na-**1** with a red, ethereal solution of **3** at −35 °C, following in situ preparation of **3** from **4** and removal of *t*BuCN. Upon stirring for two hours at 22 °C, an orange-brown, homogeneous solution was obtained. Following solvent removal under reduced pressure the product mixture was dissolved in C_6D_6. The ^{1}H NMR spectrum of the product mixture revealed clean formation of **2** and a single, new isopropylanilide ligand environment. The $^{31}P\{^1H\}$ NMR spectrum contained only one feature, a singlet at very low field strength ($\delta = 1021$ ppm), flanked by a pair of satellites ($^1J_{PW} = 193$ Hz), consistent with a terminal phosphide ligand coupled to a ^{183}W nucleus ($I = {}^1\!/_2$, 14.3 % natural abundance).[17] Separation of **5** from NaCl was trivial; however, separation of **5** from coproduct **2** at first proved difficult, owing to their similar solubility properties. This was initially overcome by applying the Pasteur method,[18] whereby mixtures of crystalline **2** and **5** were manually separated.

A more efficient method of separating **5** from coproduct **2** was achieved by in situ conversion of **2** to the bistriflate complex $[(TfO)_2Nb\{N(Np)Ar\}_3]$ (**6**, Tf = CF_3SO_2),[5] a complex that is only sparingly soluble in common hydrocarbon solvents. Accordingly, treatment of a 1:1 mixture of **2** and **5** in Et_2O with neat triflic anhydride (Tf_2O, 1 equiv) at room temperature resulted in a color change from orange-brown to yellow-brown over several minutes as a yellow precipitate formed. Following solvent removal under reduced pressure, the product mixture was dissolved in C_6D_6. The ^{1}H NMR spectrum of the product mixture revealed clean and selective production of **6**, with **5** remaining unperturbed. The $^{31}P\{^1H\}$ NMR spectrum displayed only the downfield signal associated with **5**, thus confirming its role as a spectator in this reaction. Thus, a one-pot procedure for the synthesis and isolation of **5** was achieved wherein precipitate **6** is separated simply by filtration (Scheme 1). By this method, spectroscopically pure **6** was isolated in 92 % yield as a golden precipitate, and spectroscopically pure **5** was isolated as orange blocks in 66 % yield following overnight crystallization from Et_2O at −35 °C.[19]

X-ray structural analysis of **5** confirmed its monomeric formulation and the terminal coordination of the phosphide ligand (Figure 1). In the solid state, **5** is found to be isostructural to its molybdenum congener $[P{\equiv}Mo\{N(i\text{Pr})Ar\}_3]$,[20] crystallizing in the orthorhombic space group

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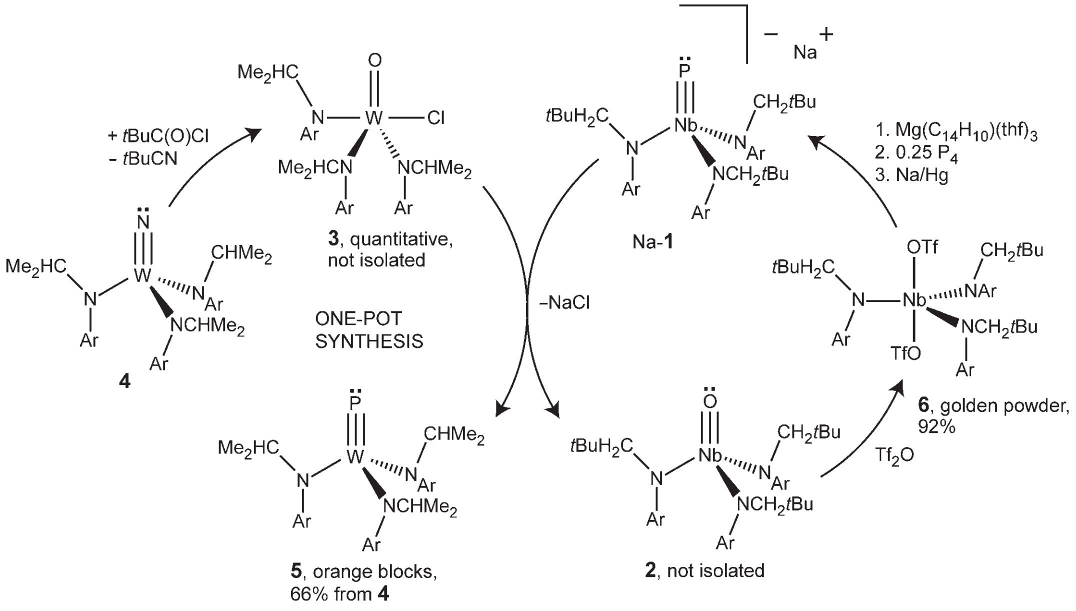


Scheme 1.

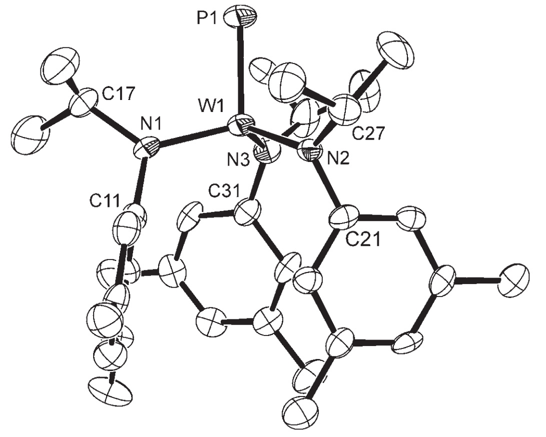


Figure 1. ORTEP rendering of **5** (one of two independent molecules shown, ellipsoids set at 50%). Selected bond lengths [Å] and angles [°]: W1-P1 2.119(3), W1-N 1.939 av; P1-W1-N 104.4 av.

$P2_12_12_1$ with two independent molecules per asymmetric unit. The W−P bond lengths of the two independent molecules (2.119(3), 2.122(3) Å) agree well with metal–phosphide bond lengths observed in previously reported terminal phosphide complexes.[20–24]

Previously reported routes to terminal phosphide complexes include metathesis of phosphaalkynes with $[W_2(OtBu)_6]$,[25–27] ancillary-ligand exchange at an existing terminal phosphide moiety,[14] activation of P_4 to yield complexed phosphide as a terminal ligand either directly or via intermediate bimetallic complexes containing μ-P_1 or μ:η^2,η^2-P_2 ligands,[2,5,20,21,28,29] and by treating $[(N_3N)WCl]$ ($N_3N = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) with either LiP(H)Ph (2 equiv) or $LiP(SiMe_3)_2$ (2 equiv).[22,30] Complete intermetal exchange of a phosphide ligand represents a new addition to this list. Increasing the attractiveness of the method described herein is the fact that **6** can be easily converted to the niobaziridine–hydride complex $[Nb(H)\{\eta^2\text{-}tBu(H)C{=}NAr\}\{N(Np)Ar\}_2]$,[31] from which the niobium phosphide reagent Na-**1** is ultimately derived (Scheme 1, right).[5]

DFT calculations were performed on a heterobimetallic model intermediate in order to further our understanding of the process by which **1** and **3** combine to exchange phosphide and oxide ligands.[19] The optimized structure of the model intermediate $[\{Ph(Me)N\}_3Nb(\mu\text{-}O)(\mu\text{-}P)W\{N(iPr)Ar\}_3]$ contains an unsymmetrical $\{Nb(\mu\text{-}O)(\mu\text{-}P)W\}$ core (Figure 2). The short W−P bond length (2.22 Å) and long W−O bond length (2.05 Å) are suggestive of an already significant W−P multiple-bond interaction and near complete transfer of the oxide ligand to the niobium center. Moreover, collapse of this model intermediate to the corresponding oxidoniobium complex $[O{\equiv}Nb\{N(Me)Ph\}_3]$ and **5** is calculated to be exothermic by 22 kcal mol^{-1}. Attempts to observe such an

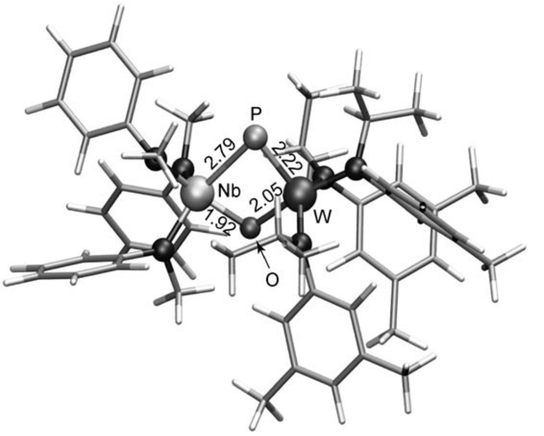
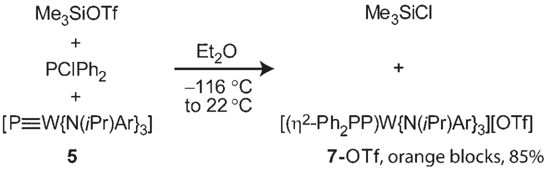


Figure 2. Optimized structure of model intermediate $[\{Ph(Me)N\}_3Nb(\mu\text{-}O)(\mu\text{-}P)W\{N(iPr)Ar\}_3]$. Selected bond lengths shown in Å.

intermediate by low-temperature $^{31}P\{^1H\}$ NMR spectroscopy were unsuccessful.[32]

Initial reactivity studies of **5** revealed its low nucleophilic character, exemplified by a lack of reaction with Me_3SiOTf (1 equiv) in Et_2O, CH_2Cl_2, or C_6D_6 for extended periods and at elevated temperatures. We were, however, able to productively exploit this observation with the construction of an η^2-bound phosphanylphosphinidene complex.[33–37] Accordingly, thawing solutions of **5** and Me_3SiOTf (1 equiv) in Et_2O and $PClPh_2$ in Et_2O were combined and allowed to stir for 3 h [Eq. (2)]. Over this time, the solution warmed to 22 °C and an orange solid slowly precipitated. Recrystallization of the precipitate from THF/*n*-pentane at −35 °C provided the cationic, orange diphenylphosphanylphosphinidene complex $[(\eta^2\text{-}Ph_2PP)W\{N(iPr)Ar\}_3][OTf]$ (**7**-OTf), in 85% yield.[19] Formation of **7**-OTf likely proceeds by the reaction of weakly nucleophilic **5** with an electrophilic phosphenium species generated by the reaction of Me_3SiOTf and $PClPh_2$.[38] The synthesis of **7**-OTf through Me_3SiCl elimination closely relates to the synthesis of the Group 5 η^2-phosphanylphosphinidene complexes $[(\eta^2\text{-}R_2PP)Nb\{N(Np)Ar\}_3]$ (**8**, R = *t*Bu; **9**, R = Ph),[2,39] and complements the work of Fritz and coworkers with their synthesis of Group 10 η^2-phosphanylphosphinidene complexes by tBu_2PP group transfer.[40,41]



$$\begin{array}{c} Me_3SiOTf \\ + \\ PClPh_2 \\ + \\ [P{\equiv}W\{N(iPr)Ar\}_3] \\ \mathbf{5} \end{array} \xrightarrow[\text{−116 °C to 22 °C}]{Et_2O} \begin{array}{c} Me_3SiCl \\ + \\ [(\eta^2\text{-}Ph_2PP)W\{N(iPr)Ar\}_3][OTf] \\ \mathbf{7}\text{-OTf, orange blocks, 85\%} \end{array} \qquad (2)$$

The $^{31}P\{^1H\}$ NMR spectrum of **7**-OTf in $CDCl_3$ contains two sets of doublets located at $\delta = 331.8$ (P_α, phosphinidene) and 6.7 ppm (P_β, phosphanyl) with a large $^1J_{PP}$ coupling constant (428 Hz) that is suggestive of multiple bonding between the phosphorus centers.[42] Additionally, satellites due to coupling between ^{183}W and ^{31}P are observed for P_β ($^1J_{WP} = 72$ Hz). Though such satellites are not resolved for P_α, the W–P_α coupling constant cannot exceed the magnitude of the base width of the $^{31}P_\alpha$ NMR peak (44 Hz). Such remarkably low values for J_{PW} may reflect low participation of the phosphorus-based s orbitals in the W–P interactions.[22]

Salt **7**-OTf crystallizes in the triclinic space group $P\bar{1}$, with three THF molecules of crystallization. The solid-state structure of **7**-OTf shows the η^2 interaction of the Ph_2PP fragment with the tungsten center (Figure 3). No close contacts are observed between the complex cation and triflate anion in **7**-OTf. The W1–P1 bond length (2.3312(9) Å) and W1–P2 bond length (2.4981(9) Å) in **7**-OTf are both approximately 0.09 Å shorter than analogous bond lengths observed in the related neutral complex **9**. The P1–P2 bond length (2.0873(12) Å) in **7**-OTf is approximately 0.014 Å longer than the analogous length observed in **9**, and is approximately 0.12 Å shorter that expected for a P–P single bond.[43] This further supports the view that the Ph_2PP ligand in **7**-OTf possesses multiple-bond character. Taken together, the spectral and structural features of **7**-OTf point to a view of the bonding situation as that of a doubly bonded phosphanylphosphinidene ligand complexed to a formally d^2 tungsten(IV) center according to the standard Dewar–Chatt–Duncanson model of π complexation.

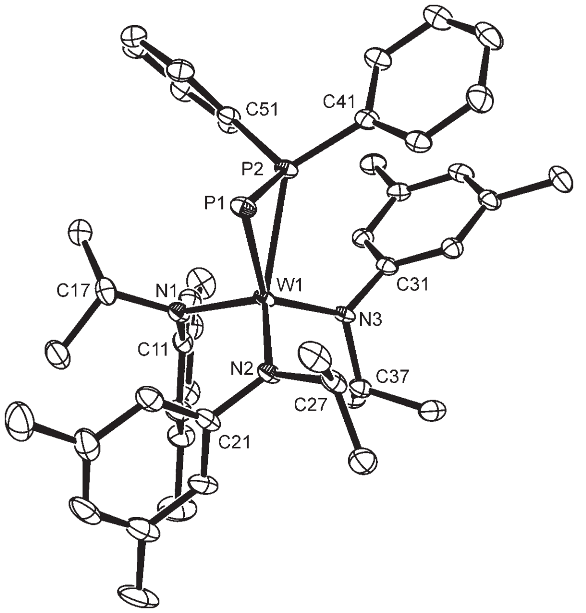


Figure 3. ORTEP rendering of complex cation **7** (ellipsoids set at 50%). Selected bond lengths [Å] and angles [°]: W1-P1 2.3312(9), W1-P2 2.4981(9), P1-P2 2.0973(12); W1-P1-P2 60.60(3), P1-P2-W1 60.32(3).

In conclusion, we now provide an example of a method for installing a terminal phosphide ligand through intermetal atom exchange. It is hoped that this methodology may make available terminal phosphide complexes of metals for which they are not known; isolable terminal phosphide systems currently are limited to Nb, Mo, and W. Additionally, an otherwise weakly nucleophilic terminal phosphide complex has been functionalized by generating a reactive electrophile in its presence, thus furthering the role of terminal phosphide complexes as platforms for the synthesis of complexed, phosphorus-containing moieties.

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