P Ligands

Diorganophosphanylphosphinidenes as Complexed Ligands: Synthesis via an Anionic Terminal Phosphide of Niobium**

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Compounds with multiple bonding between adjacent phosphorus atoms are of interest both as free molecules and as complexed ligands.[1] As one proceeds formally from triply bonded P_2, via intermediate states of reduction, all the way to two equivalents of PH_3, several interesting P−P bonded systems (and isomers thereof) may be considered. Phosphanylphosphinidene, PPH_2, a neutral isomer of HP=PH (diphosphene) is an intriguing parent species in this regard and its geometric and electronic structure have been the subject of several theoretical investigations.[2–5]

Organic derivatives of phosphanylphosphinidene have generated interest as complex ligands capable of η^2-binding to transition-metal centers.[2] A prototypical example is the structurally characterized complex $[(\eta^2\text{-}t\text{Bu}_2\text{PP})\text{Pt}(\text{PPh}_3)_2]$.[6] That organic phosphanylphosphinidenes, exemplified by $t\text{Bu}_2\text{PP}$, are novel π-electron ligands in a manner reminiscent of alkenes or alkynes is recognized and was the subject of a recent review article.[7] Fritz and co-workers have pioneered the synthesis of such derivatives by utilization of the "phosphanylphosphinidene transfer" reagent, $t\text{Bu}_2\text{PP}{=}\text{PX}(t\text{Bu}_2)$ (X = Me or Br),[6,7] which represented, until now, the only synthetic entry to complexes of phosphanylphosphinidenes.

Herein we report an alternative synthetic entry to complexed organic derivatives of phosphanylphosphinidene. Our method takes advantage of our ability to synthesize an unprecedented anionic, niobium, terminal phosphide complex, $\text{Na}^+[\text{PNb}(\text{N}[\text{Np}]\text{Ar})_3]^-$ (Np = neopentyl, Ar = 3,5-$\text{Me}_2\text{C}_6\text{H}_3$) that permits assembly[8] of R_2PP ligands directly within the metal's protective coordination sphere. Furthermore, the complexes $[(\eta^2\text{-R}_2\text{PP})\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]$, are the first examples of η^2-phosphanylphosphinidene complexation by an early-transition-metal fragment.

Our recent discovery that the niobaziridine-hydride complex $[\text{Nb}(\text{H})(\eta^2\text{-}t\text{Bu}(\text{H})\text{C}{=}\text{NAr})(\text{N}[\text{Np}]\text{Ar})_2]$ reacts with white phosphorus (P_4) to afford the dinuclear, bridging diphosphide complex $[(\mu_2{:}\eta^2,\eta^2\text{-P}_2)\{\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3\}_2]$ (**1**)[9] presented us with a unique entry into low-coordinate

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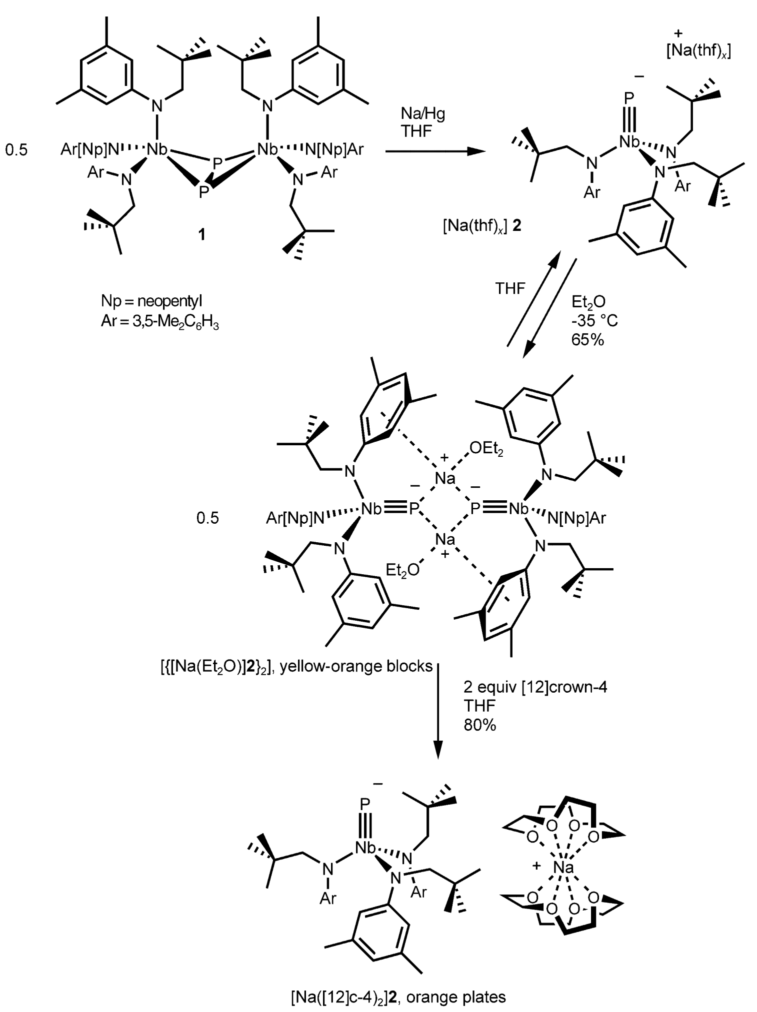
phosphorus chemistry. It was recognized that the P_2 unit in complex **1** could be further reduced by two electrons to afford a species featuring a terminal, uninegative phosphorus atom bound to a single niobium center. Accordingly, treatment of a green THF solution of **1** with an excess of 1.0% sodium amalgam gradually produced a dark orange mixture over 2.5 h. Analysis of the crude reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy indicated the presence of a new signal centered near $\delta = 1010$ ppm, characteristic of early-transition-metal phosphido species containing one-coordinate phosphorus.[10]. Solvent removal followed by diethyl ether extraction and crystallization produced the hydrocarbon-soluble, sodium etherate dimer $[\{[Na(Et_2O)]\mathbf{2}\}_2]$ (Scheme 1), as yellow orange blocks in 65% yield.[11]

The $^{31}P\{^1H\}$ NMR spectrum of pure $[\{[Na(Et_2O)]\mathbf{2}\}_2]$ in C_6D_6 solution gives rise to a single signal located at $\delta = 949.2$ ppm ($\nu_{1/2} = 495$ Hz), which shifts to 1019.8 ppm ($\nu_{1/2} = 166$ Hz) when the spectrum is obtained in THF solution. Whereas the broad nature of the signals is caused by relaxation effects owing to the quadrupolar niobium nucleus,[12] the chemical shift difference presumably arises from formation of a monomeric $[Na(thf)_x]\mathbf{2}$ species in THF solution. Such downfield movement in ^{31}P chemical shift in polar solvents may be attributed to diminished Na–P contact ion pairing, with concomitant strengthening of $P_{(p\pi)} \rightarrow Nb_{(d\pi)}$ bonding interactions as the electropositive niobium center compensates for the build-up of negative charge.[13] Complete sequestration of the sodium counterion from the phosphorus nuclei can be achieved by treatment of a THF solution of $[\{[Na(Et_2O)]\mathbf{2}\}_2]$ (i.e. $[Na(thf)_x]\mathbf{2}$) with 2.0 equivalents of the crown ether [12]crown-4 ([12]c-4). The resulting hydrocarbon insoluble salt, $[Na([12]c\text{-}4)_2]\mathbf{2}$, gives rise to a single ^{31}P NMR signal at 1110.2 ppm ($\nu_{1/2} = 170$ Hz, $[D_8]$THF), further emphasizing the downfield progression of chemical shift as the $[PNb(N[Np]Ar)_3]^-$ unit becomes discrete and separated from its counterion.

Crystallization from a THF/*n*-pentane mixture produced red-orange plates of $[Na([12]c\text{-}4)_2]\mathbf{2}$ in 80% yield. The single-crystal X-ray structure of $[Na([12]c\text{-}4)_2]\mathbf{2}$ (Figure 1) clearly shows the anion–cation separation imposed by 2.0 equivalents of [12]c-4 and confirms the terminal nature of the phosphido substituent. The Nb–P bond length of 2.186(2) Å in $[Na([12]c\text{-}4)_2]\mathbf{2}$ is short when compared to the related four-coordinate, tantalum phosphinidene complex, $[PhP{=}Ta(OSi\text{-}tBu_3)_3]$ (Ta–P 2.317(4) Å), which can be viewed as containing a short Ta–P double bond.[14] However, the Nb–P bond length in $[Na([12]c\text{-}4)_2]\mathbf{2}$ agrees well with the Mo–P triple bonds in $[P{\equiv}Mo(N[tBu]Ar)_3]$ (2.119(4) Å)[15] and $[P{\equiv}Mo(N[iPr]Ar)_3]$ (2.116(3) Å),[16] when the 0.07 Å difference in covalent radii between Nb and Mo is considered.[17] Thus, we suggest $[Na([12]c\text{-}4)_2]\mathbf{2}$ is accurately described as containing a Nb–P triple bond, the notion of which has also been substantiated by DFT calculations on the model complex $[PNb(NH_2)_3]^-$.[18]



Scheme 1.

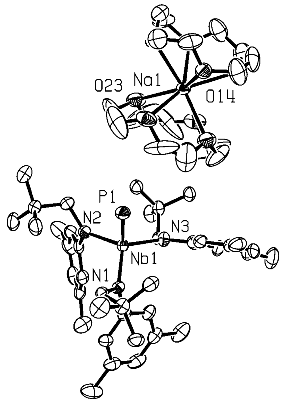


Figure 1. ORTEP diagram of $[Na([12]c\text{-}4)_2]\mathbf{2}$ (ellipsoids set at 35% probability). Selected bond lengths [Å] and angles [°]: Nb1-P1 2.186(2), Nb-N 2.073 av; P-Nb-N 103.43 av.

It is also noteworthy that $[Na([12]c\text{-}4)_2]\mathbf{2}$ is the first definitive example of a terminal phosphide complex of a transition metal outside of group 6.[19]

The terminal phosphorus atom in $[Na(thf)_x]\mathbf{2}$ has proven to be nucleophilic and readily provides terminal phosphinidenes upon treatment with electrophiles. For example, treatment of thawing THF solutions of $[Na(thf)_x]$**2** with 0.95 equivalents[20] of trimethylsilyl or trimethylstannyl chloride produced the trimethysilyl, $[Me_3SiP{=}Nb(N[Np]Ar)_3]$ (**3**), and trimethylstannyl, $[Me_3SnP{=}Nb(N[Np]Ar)_3]$ (**4**), phosphinidene complexes in 75 % and 85 % yield, respectively (see Scheme 2). The $^{31}P\{^1H\}$ NMR spectral resonances for **3** (δ = 528.6 ppm) and **4** (δ = 607.0 ppm) indicate bent[14,21] phosphinidene moieties typical for four-coordinate early-transition-metal phosphinidene complexes supported by hard, π-donating, ancillary ligands.[22] A solid-state structural determination of **4**[23] confirmed this spectroscopic assignment and revealed an elongated Nb–P bond (2.2731(8) Å) relative to that in $[Na([12]c\text{-}4)_2]$**2**, consistent with formulation of this product as a doubly bonded Nb=P phosphinidene. Furthermore, the P–Sn bond length of 2.4778(8) Å matches the sum of covalent radii for these atoms,[17] attesting to a single bond between tin and phosphorus in **4**.[24]

Our attention then turned to the construction of η^2-bound phosphanylphosphinidenes, species known to contain multiple bonding between adjacent phosphorus atoms.[7] Accordingly, treatment of a thawing THF solution of $[Na(thf)_x]$**2** with 0.95 equivalents[20] of di-*tert*-butylchlorophosphane ($t Bu_2PCl$) readily provided the orange phosphanylphosphinidene complex, $[(\eta^2\text{-}t Bu_2PP)Nb(N[Np]Ar)_3]$ (**5**) in 65 % yield (Scheme 2). Formation of phosphanylphosphinidene **5** from **2** and $t Bu_2PCl$ represents a synthetic method complementary to Fritz and co-workers' use of a transfer reagent[6,7] in which the P–P bond is already intact. However, our method is applicable to the synthesis of novel, Nb-complexed R_2PP derivatives. Thus, treatment of $[Na(thf)_x]$**2** with diphenylchlorophosphane (Ph_2PCl) afforded the red diphenylphosphanylphosphinidene complex, $[(\eta^2\text{-}Ph_2PP)Nb(N[Np]Ar)_3]$ (**6**) in 60 % isolated yield.

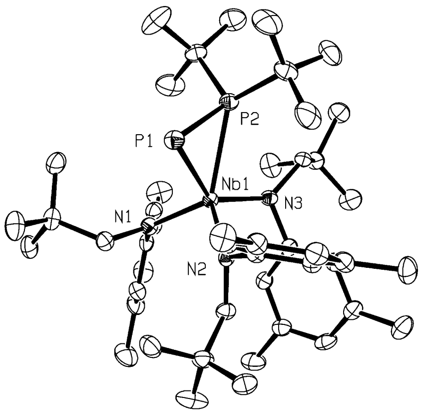


Figure 2. ORTEP diagram of **5** (ellipsoids set at 35 % probability). Selected bond lengths [Å] and angles [°]: Nb1-P1 2.4149(12), Nb1-P2 2.6126(11), P1-P2 2.0888(15), Nb1-N 2.027 av; Nb1-P1-P2 70.49(4), P1-P2-Nb1 60.61(4), P1-Nb1-P2 48.90(4).

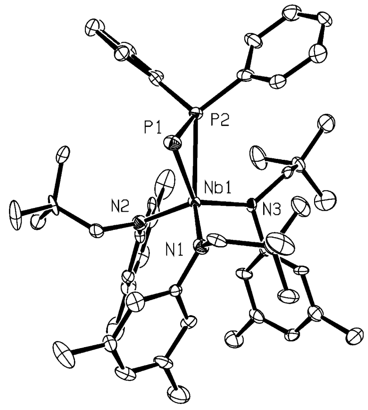
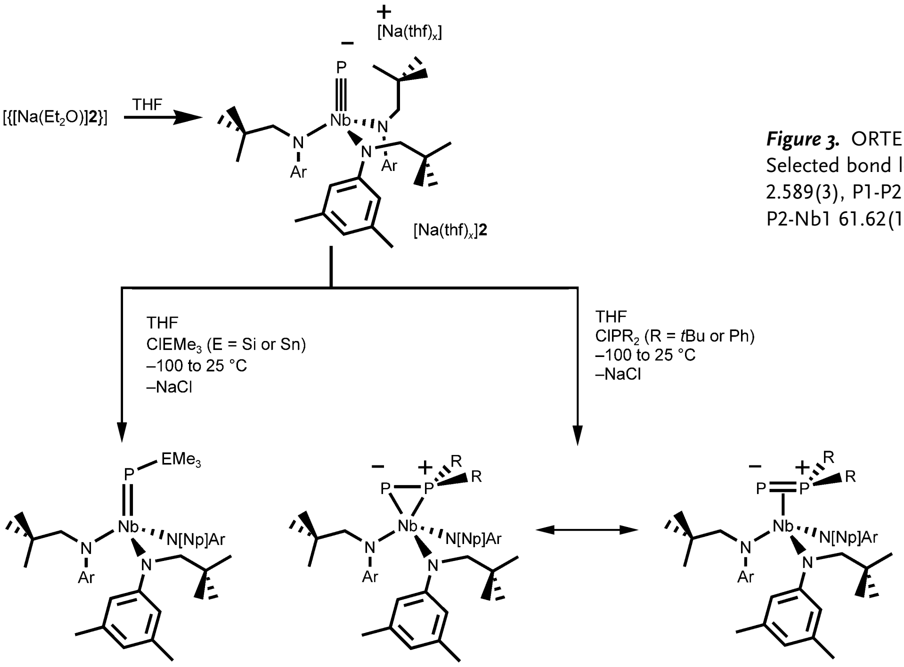


Figure 3. ORTEP diagram of **6** (ellipsoids set at 35 % probability). Selected bond lengths [Å] and angles [°]: Nb1-P1 2.429(3), Nb1-P2 2.589(3), P1-P2 2.073(4), Nb1-N 2.016 av; Nb1-P1-P2 69.71(11), P1-P2-Nb1 61.62(10), P1-Nb1-P2 48.66(9).



3, E = Si, orange blocks, 75%
4, E = Sn, red blocks, 85%

5, R = *t*Bu, orange blocks, 65%
6, R = Ph, red plates, 60%

Scheme 2.

The solid-state structures of **5** and **6** (Figure 2 and Figure 3, respectively) show the η^2-interaction of the R_2PP unit with the niobium center. The Nb1–P1 bond for both **5** and **6** (2.4149(12) and 2.429(3) Å, respectively) are much longer than typically found in early-transition-metal phosphinidene complexes[22] and more closely approximate an Nb–P single bond. Contrastingly, the P1–P2 separations of 2.0888(15) and 2.073(4) Å in **5** and **6**, respectively are approximately 0.13 Å shorter than expected for a P–P single bond,[25] lending credence to the notion of multiple-bond character in R_2PP unit, itself complexed according to the standard Dewar–Chatt–Duncanson model. Resonance structures including those shown in Scheme 2 may reasonably approximate the bonding attendant with R_2PP complexation in this system.[26]

The $^{31}P\{^1H\}$ NMR spectrum of **5** (C_6D_6) exhibits two sets of doublets located at $\delta = 405.5$ and 80.6 ppm for the phosphinidene (P_α) and phosphanyl (P_β) atoms, respectively, with a large $^1J_{P,P}$ coupling constant of 425 Hz also reflective of multiple-bonding interactions[27] ($P_\alpha = 401.3$ ppm, $P_\beta = 19.0$ ppm, $^1J_{P,P} = 439$ Hz for **6**). NMR calculations carried out on the hypothetical construct, $[(\eta^2\text{-}Me_2PP)Nb(NH_2)_3]$, support the assignment of a downfield shift for P_α relative to P_β in this system.[26] However, the highly downfield signals for P_α in **5** and **6** are in stark contrast to the mononuclear $[(\eta^2\text{-}t\text{Bu}_2PP)PtL_2]$ (L = phosphane) complexes of Fritz and coworkers,[6] in which P_α resonates upfield of P_β, which indicates a small contribution from P_α in the frontier-orbital region[28] for the latter and nicely highlighting a major spectroscopic differentiation between these early- and late-transition-metal systems.

In conclusion, nucleophilic, terminal, triply-bonded functional groups are of interest for building novel complexed moieties "from the ground up", as demonstrated previously for niobium nitride[8,29] and molybdenum carbide[13,30] anions. Now to this category we add the niobium phosphide anion, the versatility of which is demonstrated by the present synthesis of novel stannyl and phosphanyl phosphinidene complexes. Furthermore, incorporation of phosphorus atoms derived directly from the element into complexed ligands represents a potentially powerful method for the generation of synthetically useful phosphorus-containing molecules.

Experimental Section

General: Unless otherwise stated, all manipulations were preformed at room temperature in a glovebox (N_2) using dried and deoxygenated solvents and reagents. Full spectroscopic details for all new compounds can be found in the Electronic Supporting Information.

$[\{[Na(Et_2O)]\mathbf{2}\}_2]$: 1.0% sodium amalgam (Na: 0.115 g, 3.3 equiv/Nb) was added to a green THF solution of **1**[9] (1.00 g, 1.50 mmol, 10 mL). The mixture was stirred vigorously for 2.5 h, it gradually changed in color to dark orange. The supernatant solution was decanted from the amalgam, filtered through Celite, and evaporated to dryness. The resulting dark orange residue was then dissolved in Et_2O (5 mL), filtered through Celite again, and cooled at −35 °C for 3 days whereupon large yellow-orange crystals were obtained. Yield: 0.759 g, 65% in two crops.

$[Na([12]c\text{-}4)_2]\mathbf{2}$: A THF solution of [12]crown-4 (0.040 g, 0.231 mmol, 2 mL) was added to a solution of $[\{[Na(Et_2O)]\mathbf{2}\}_2]$ (0.100 g, 0.115 mmol) dissolved in THF (5 mL) over the course of 5 min. The reaction mixture was stirred for 30 min, after which it was concentrated to a volume of 2 mL and filtered through a small plug of Celite. *n*-Pentane (2 mL) was added and the resulting solution was stored at −35 °C overnight whereupon small red-orange crystals were obtained. Yield: 0.099 g, 80%.

3–6: Separately, a solution of $[\{[Na(Et_2O)]\mathbf{2}\}_2]$ (0.250 g, 0.316 mmol) dissolved THF (5 mL) and a THF solution (2 mL) containing 0.95 equiv of the corresponding electrophile ($ClSiMe_3$ for **3**, $ClSnMe_3$ for **4**, $ClPt\text{Bu}_2$ for **5**, and $ClPPh_2$ for **6**) were frozen in a glove box cold well (liquid N_2). Upon removal from the cold well, approximately 0.6 mL of the thawing solution containing the electrophile was added dropwise over 1 min to the thawing solution of $[\{[Na(Et_2O)]\mathbf{2}\}_2]$, eliciting a color change from dark yellow to red-orange. The reaction mixture stirred for an additional 3 min whereupon both solutions were placed back into the cold well. This procedure was repeated two more times until complete addition of the electrophile was achieved. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 30 min before being evaporated to dryness in vacuo. The residue was extracted with *n*-pentane (3 mL), filtered through Celite, and the filtrate evaporated to dryness again in vacuo. Crystallizations were effected by storing Et_2O (**3**, **4**, **6**) or *n*-pentane (**5**) solutions at −35 °C for 1–2 days. Color, yield: **3**: Orange, 75%; **4**: Red, 85%; **5**: Orange, 65%; **6**: Red, 60%.

Crystallographic Data: Crystal data can be found in the Supporting Information. CCDC-218230 ($[\{[Na(Et_2O)]\mathbf{2}\}_2]$), CCDC-218231 ($[Na([12]c\text{-}4)_2]\mathbf{2}\cdot(THF)$), CCDC-218229 (**4**), CCDC-218232 (**5**), CCDC-218228 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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