An Unusual P-P Double Bond Formed via Phospha-Wittig Transformation of a Terminal PO Complex

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First reported in 1997, $(OP)Mo(N[^tBu]Ar)_3$ (**1**, Ar = 3,5-$Me_2C_6H_3$) is the only example of an isolable terminal phosphorus monoxide complex.[1] As a result, the chemistry of this unique functional group has remained largely unexplored. Initial reactivity studies indicated that **1** is electrophilic at phosphorus and nucelophilic at oxygen, as illustrated by its reaction with Cp_2ZrMe_2 to afford $Cp_2MeZrOP(Me)Mo(N[^tBu]Ar)_3$.[1] Extending this concept, we speculated that reaction of **1** with a suitable phospha-Wittig reagent might generate a diphosphenido ligand complexed atop the molybdenum trisanilide platform. High oxidation state, early metal phosphinidene complexes have been shown to serve as effective phospha-Wittig reagents in combination with a variety of reagents including aldehydes and ketones.[2-8] We have recently exploited a versatile niobium terminal phosphide anion as a precursor to a variety of phosphinidene complexes,[9-11] and the high degree of oxophilicty possessed by the niobium trisanilide fragment $Nb(N[CH_2^tBu]Ar)_3$ represents a formidable driving force for phosphorus transfer from niobium to main-group acceptors.[11,12]

The silylphosphinidene complex, $^iPr_3SiPNb(N[CH_2^tBu]Ar)_3$ (**2**) is formed by the reaction of $^iPr_3SiOTf$ (OTf = trifluoromethanesulfonate) and the sodium salt of $[PNb(N[CH_2^tBu]Ar)_3]^-$. Complex **2** is isolated as an orange solid in 61% yield by crystallization from Et_2O and displays a broad ^{31}P NMR resonance at 433 ppm. A single crystal X-ray diffraction study revealed a short Nb-P distance of 2.2454(6)Å and a Nb-P-Si angle of 158.34(4)° (Figure 1B).[13] At 22 °C, complex **2** reacts with the purple phosphorus monoxide complex **1** over the course of several minutes to afford the oxoniobium complex, $ONb(N[CH_2^tBu]Ar)_3$ (**3**) and one new species (**4**), identified by ^{31}P, ^1H, and ^{13}C NMR spectroscopies (Figure 1A). The ^{31}P NMR data for **4** are a very broad doublet at 543 ppm and a less broad doublet at 158 ppm with a large P-P coupling constant ($^1J_{PP}$ = 655 Hz). These data are consistent with the desired silyldiphosphenido product, $^iPr_3SiP=PMo(N[^tBu]Ar)_3$, where the downfield resonance is attributed to the phosphorus atom bound directly to the Mo center.[14,15] A red-orange single crystal grown from an Et_2O solution of the product mixture was subjected to an X-ray diffraction study.[13] The molecular structure of the diphosphenido complex (Figure 1C) can be described as "singly bent" (angles at P of 158.27(3)° and 104.46°(3)) in analogy to descriptions of diazenido complexes where the diazenido ligand serves as a $3e^-$ donor.[16] The Mo-P (2.1439(5) Å) and P-P (2.0398(7) Å) distances are *both* very short, an indication of multiple bonding across the Mo-P-P π system. These metrical parameters are in contrast to the few known diphosphenido complexes,[17-19] which are best described as "doubly bent", with their metal-phosphorus *single* bonds reflected in substantially longer M-P distances. In such complexes the α phosphorus maintains its lone pair, which has been shown to engage in chemistry with various electrophilic reagents.[19-21]
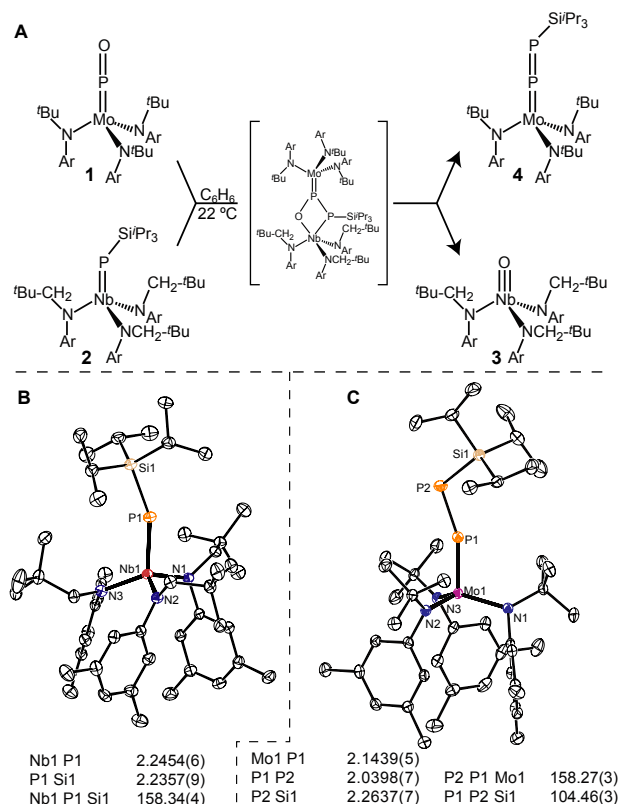

Figure 1. (**A**) The silyldiphosphenido complex **4** and oxoniobium **3** are generated via an O-for-$PSiR_3$ metathesis reaction between **1** and **2**. (**B** and **C**) ORTEP representations of complexes **2** and **4**, respectively, with 50% probability ellipsoids and selected interatomic distances (Å) and angles (°).

Nb1 P1	2.2454(6)		Mo1 P1	2.1439(5)	
P1 Si1	2.2357(9)		P1 P2	2.0398(7)	P2 P1 Mo1 158.27(3)
Nb1 P1 Si1	158.34(4)		P2 Si1	2.2637(7)	P1 P2 Si1 104.46(3)

Unlike nitrogen analogs of **4**, such as the silyldiazenido complex $Me_3SiNNMo(N[^tBu]Ar)_3$ and the azaphosphenido complex $MesNPMo(N[^tBu]Ar)_3$, the diphosphenido complex **4** is *not* stable in solution for extended periods of time.[22,23] Over the course of hours to days, or upon heating, complex **4** reacts to form $PMo(N[^tBu]Ar)_3$ (**5**), the cyclic phosphinidene trimer $(^iPr_3SiP)_3$ (**6**), and the phosphinidene tetramer $(^iPr_3Si)_2P_3P(Si^iPr_3)_2$ (**7**); the latter two were identified by their ^{31}P NMR spectra which were successfully simulated (see Supporting Information).[23-25] Attempts to make analogs of **4** bearing smaller silyl groups (Me_3Si, Ph_3Si) led to much more rapid formation of the corresponding phosphinidene trimers, such that the diphosphenido complexes were not observed. Also, the generation of terminal phosphide complex **5** was observed to proceed more rapidly in concentrated solutions of **4** than in dilute solutions.[26] Together, these observations lead us to postulate the following mechanism: a bimolecular reaction between 2 equiv of **4** generates 2 equiv of the terminal phosphide complex **5** and 1 equiv of $^iPr_3SiP=PSi^iPr_3$
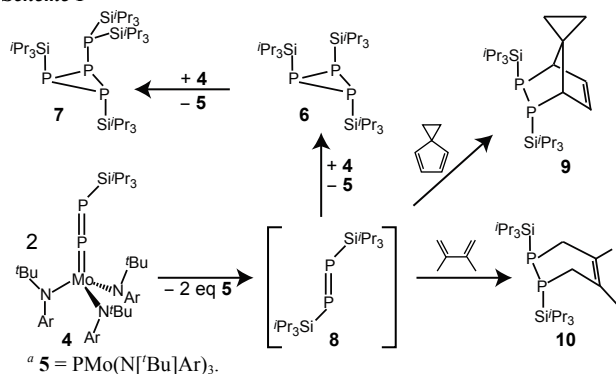
(**8**); this reactive diphosphene then consumes a third equivalent of **4** to yield the cyclic trimer **6**; the tetrameric product **7** arises from an insertion of the phosphinidene unit of a fourth equiv **4** into a P-Si bond of trimer **6** (Scheme 1).

Having invoked intermediate diphosphene **8**, we sought to engage it in trapping reactions.[27] Accordingly, complex **4** was warmed to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene and the product mixture was analyzed by ^{31}P NMR spectroscopy. The [2+4] cycloaddition product of *E*-diphosphene capture by the organic diene, **9**, was observed as a pair of doublets in the ^{31}P NMR spectrum (J_{PP} = 240 Hz) at –112.5 and –117.5 ppm.[28] When 2,3-dimethylbutadiene was used instead, the then C_2-symmetric product, **10**, displayed a single ^{31}P resonance at –138 ppm. The observed formation of **9** and **10** is consistent with the mechanism illustrated in Scheme 1.

To analyze the bonding in **4**, we carried out a DFT study on the slightly truncated complex Me$_3$SiPPMo(N[^{t}Bu]Ar)$_3$ (**4m**) using the ADF package.[29,30] The geometry optimization converged on a structure similar to that obtained from the X-ray study, with a nearly linear Mo-P-P angle (163º), a bent P-P-Si angle (106º), and short Mo-P (2.145 Å) and P-P (2.059 Å) distances. An examination of the frontier orbitals (Figure S12, Supporting Information) reveals that the HOMO and HOMO-1 of **4m** contain substantial contributions from the out-of-plane and in-plane *p* orbitals on the β-phosphorus, respectively. The HOMO can be considered as a back-bond from a reducing, formally d^2 metal center to the strongly π-accepting diphosphenido ligand. Conversely, the HOMO-1 is interpreted as ligand-to-metal π-donation. The LUMO is d_{z^2}-like at the metal, but also contains lobes on both the α and β phosphorus atoms, and is partially P-P σ-antibonding in character. The contributions from the β phosphorus to both the HOMO and LUMO are indicative of ambiphilic character, as might be expected in view of the proposed bimolecular reaction yielding **8**.

The diphosphenido complex **4** was found to engage in *reversible* phosphinidene transfer reactions with PPh$_3$ to form an equilibrium mixture of **4**, **5**, ^{i}Pr$_3$SiP=PPh$_3$, and PPh$_3$. The phosphoranylidene phosphorane ^{i}Pr$_3$SiP=PPh$_3$ was identified by its ^{31}P NMR spectrum, which exhibits two sharp doublets (J_{PP} = 590 Hz) at 30.5 and –263.8 ppm.[31] By varying the concentration of **5** and PPh$_3$, the equilibrium constant for this reaction was measured by ^{1}H NMR spectroscopy as K_{eq} = 0.7. This value near to unity was initially surprising to us, but a comparison of the relative energies of DFT optimized model complexes revealed a very small ΔE = 1.5 kcal/mol for the reaction PPh$_3$ + Me$_3$SiP=PMo(N[^{t}Bu]Ar)$_3$ → Me$_3$SiP=PPh$_3$ + PMo(N[^{t}Bu]Ar)$_3$. This equilibrium reaction suggests that **4** is susceptible to

nucleophilic attack at its β-phosphorus, resulting in transfer of the phosphinidene with the triply-bonded molybdenum terminal phosphide **5** serving as a leaving group. In this sense, the reaction between **4** and PPh$_3$ serves as a model for the bimolecular reaction that forms diphosphene **8**.

Herein we have described a molybdenum diphosphenido complex arrived at via O-for-PSiR$_3$ metathesis involving a terminal phosphorus monoxide ligand. The diphosphenido ligand serves as a $3e^-$ donor and its reactivity is distinct from prior examples of $1e^-$ donor diphosphenido complexes that are nucleophilic at the α phosphorus. The electronic structure of diphosphenido complex **4** is unusual and confers upon it the reactivity of a potent phosphinidene source with terminal phosphide **5** serving as a stable leaving group.

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(14) Chemical shielding calculations on the model complex Me$_3$SiPPMo(N[^{t}Bu]Ar)$_3$ predict the following ^{31}P NMR chemical shifts: δ(P$_α$) = 497 ppm, δ(P$_β$) = 195 ppm.
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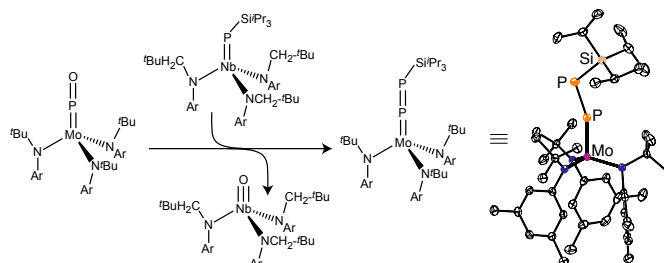
Abstract: The terminal phosphorus monoxide complex (OP)Mo(N[^{t}Bu]Ar)$_3$, **1** (Ar = 3,5-Me$_2$C$_6$H$_3$) undergoes an O-for-PSiR$_3$ metathesis reaction with the niobium phosphinidene complex ^{i}Pr$_3$SiPNb(N[CH$_2$^{t}Bu]Ar)$_3$, **2**, to generate the oxoniobium ONb(N[CH$_2$^{t}Bu]Ar)$_3$, **3**, and the diphosphenido complex ^{i}Pr$_3$SiPPMo(N[^{t}Bu]Ar)$_3$, **4.** The structure of **4**, as determined by X-ray crystallography, contains a singly-bent diphosphenido moiety, suggesting that the diphosphenido ligand serves as a $3e^-$ donor to a formally d^2 metal center. This bonding characterization was supported by DFT calculations, and is unique among known diphosphenido complexes. Diphosphenido **4** was found to react over time to produce products consistent with a bimolecular degradation pathway where the terminal phosphide complex PMo(N[^{t}Bu]Ar)$_3$, **5**, serves as a stable leaving group. Mixtures of **4** and PPh$_3$ were observed to set up an equilibrium (K_{eq} = 0.7) between **4**, PPh$_3$, and the products of phosphinidene transfer, **5** and ^{i}Pr$_3$SiP=PPh$_3$.