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(NtBu)3 (1, Ar = 3,5-Me2C6H3) is the only example of an isolate terminal phosphorus monoxide complex. 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 nucleophilic at oxygen, as illustrated by its reaction with Cp2ZrMe2 to afford Cp2MeZrOP(Me)Mo(NtBu)Ar). 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. We have recently exploited a versatile niobium terminal phosphide anion as a precursor to a variety of phosphinidene complexes, and the high degree of oxophilicity possessed by the niobium trisanilide fragment Nb(NtBu)3Ar, represents a formidable driving force for phosphorus transfer from niobium to main-group acceptors.

The silylphosphinidene complex, Pr3SiP(Nb(CH3)2Bu)Ar3 (2) is formed by the reaction of Pr3SiOTf (OTf = trifluoromethanesulfonate) and the sodium salt of [P(Nb(NtBu)2Bu)Ar]−. Complex 2 is isolated as an orange solid in 61% yield by crystallization from Et2O and displays a broad 31P 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). At 22 ºC, complex 2 reacts with the purple phosphorus monoxide complex 1 over the course of several minutes to afford the oxoniobium complex, ONb(NCH2Bu)Ar) (3) and one new species (4), identified by 31P, 1H, and 13C NMR spectroscopies (Figure 1A). The 31P 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 (1Jpp = 655 Hz). These data are consistent with the desired silyldiphosphenido product, Pr3SiP=PMo(NtBu)Ar), where the downfield resonance is attributed to the phosphorus atom bound directly to the Mo center. A red-orange single crystal grown from an Et2O solution of the product mixture was subjected to an X-ray diffraction study. 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 dianzenido complexes where the diazenido ligand serves as a 3e− donor. 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 π system. These metrical parameters are in contrast to the few known diphosphenido complexes, 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.

Unlike nitrogen analogs of 4, such as the silyldiazenido complex Me3SiNNMo(NtBu)Ar3 and the azaphosphenido complex MesNPMo(NtBu)Ar3, the diphosphenido complex 4 is not stable in solution for extended periods of time. Over the course of hours to days, or upon heating, complex 4 reacts to form PMo(NtBu)Ar)3 (5), the cyclic phosphinidene trimer (Pr3SiP3) (6), and the phosphinidene tetramer (Pr3Si)2P3P(SiPr3)2 (7); the latter two were identified by their 31P NMR spectra which were successfully simulated (see Supporting Information). Attempts to make analogs of 4 bearing smaller silyl groups (Me3Si, Ph3Si) led to much more rapid formation of the terminal phosphide complex 5 and 1 equiv of Pr3SiP=SiPr3.

Figure 1. (A) The silyldiphosphenido complex 4 and oxoniobium 3 are generated via an O-for-PSiR3 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 (°).
(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 °C in a THF solution of spiro[2.4]hepta-4,6-diene and the product mixture was analyzed by 1H NMR spectroscopy as an equilibrium mixture of 4 and PPh3, the equilibrium constant for this reaction was measured by 31P NMR spectroscopy as Keq = 40-50%.31 By varying the concentration of 4 and PPh3, the equilibrium constant for this reaction was measured by 31P NMR spectroscopy as Keq = 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 PPh3 + Me2SiP=PMo(N[6-Bu]Ar)3 → Me2SiP=PHP + P(MO[N[6-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 PPh3 serves as a model for the bimolecular reaction that forms diphosphene 8.

Herein we have described a molybdenum diphosphene complex arrived at via O-for-PSiR3 metathesis involving a terminal phosphorus monoxide ligand. The diphosphene ligand serves as a 3e donor and its reactivity is distinct from prior examples of 1e donor diphosphene complexes that are nucleophilic at the α phosphorus. The electronic structure of diphosphene 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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Supporting Information Available: Full experimental details and spectroscopic data (pdf). Details of X-ray structure determinations (cif). This material is available free of charge via the Internet at http://pubs.acs.org.
Abstract: The terminal phosphorus monoxide complex (OP)Mo(N\textsubscript{t}Bu\textsubscript{3}Ar)\textsubscript{3}, 1 (Ar = 3,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) undergoes an O-for-PSiR\textsubscript{3} metathesis reaction with the niobium phosphinidene complex iPr\textsubscript{3}SiPNb(N\textsubscript{t}Bu\textsubscript{3}Ar)\textsubscript{3}, 2, to generate the oxoniobium ONb(N\textsubscript{CH\textsubscript{2}tBu\textsubscript{3}Ar})\textsubscript{3}, 3, and the diphosphenido complex iPr\textsubscript{3}SiPPMo(N\textsubscript{t}Bu\textsubscript{3}Ar)\textsubscript{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 3\textit{e}\textsuperscript{-} donor to a formally \textit{d}\textsuperscript{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\textsubscript{t}Bu\textsubscript{3}Ar)\textsubscript{3}, 5, serves as a stable leaving group. Mixtures of 4 and PPh\textsubscript{3} were observed to set up an equilibrium ($K_{eq} = 0.7$) between 4, PPh\textsubscript{3}, and the products of phosphinidene transfer, 5 and iPr\textsubscript{3}Si=P=PPh\textsubscript{3}. 