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

Nicholas A. Piro and Christopher C. Cummins*

Department of Chemistry, 77 Massachusetts Avenue, Room 6-435, Massachusetts Institute of Technology, Cambridge, MA 02139

RECEIVED DATE (automatically inserted by publisher); E-mail: ccummins@mit.edu

First reported in 1997, (OP)Mo(N[^tBu]Ar)₃ (**1**, Ar = 3,5-Me₂C₆H₃) 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 nucleophilic at oxygen, as illustrated by its reaction with Cp₂ZrMe₂ to afford Cp₂MeZrOP(Me)Mo(N[^tBu]Ar)₃.¹ Extending this concept, we speculated that reaction of **1** with a suitable phospho-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 phospho-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 oxophilicity possessed by the niobium trisanilide fragment Nb(N[CH₂^tBu]Ar)₃ represents a formidable driving force for phosphorus transfer from niobium to main-group acceptors.^{11,12}

The silylphosphinidene complex, ^tPr₃SiPNb(N[CH₂^tBu]Ar)₃ (**2**) is formed by the reaction of ^tPr₃SiOTf (OTf = trifluoromethanesulfonate) and the sodium salt of [PNb(N[CH₂^tBu]Ar)₃]⁻. 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).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[CH₂^tBu]Ar)₃ (**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 (¹J_{PP} = 655 Hz). These data are consistent with the desired silyldiphosphenido product, ^tPr₃SiP=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 Et₂O 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

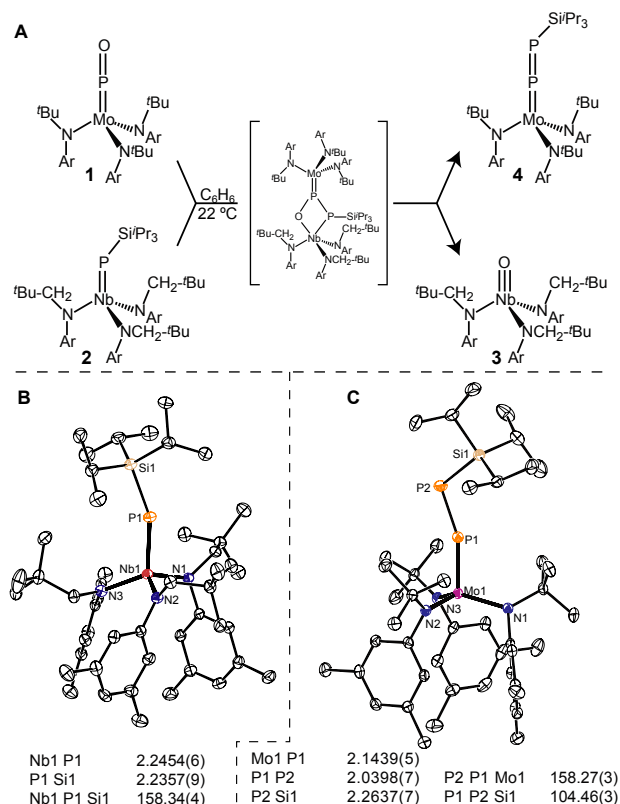
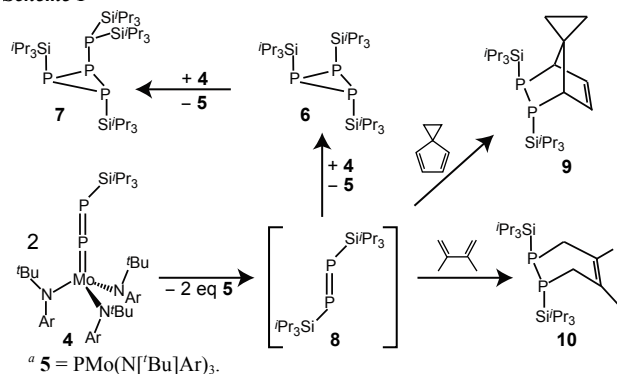


Figure 1. (A) The silyldiphosphenido complex **4** and oxoniobium **3** are generated via an O-for-PSiR₃ metathesis reaction between **1** and **2**. (B and C) ORTEP representations of complexes **2** and **4**, respectively, with 50% probability ellipsoids and selected interatomic distances (Å) and angles (°).

Unlike nitrogen analogs of **4**, such as the silyldiazenido complex Me₃SiNNMo(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 (^tPr₃SiP)₃ (**6**), and the phosphinidene tetramer (^tPr₃Si)₂P₃(Si^tPr₃)₂ (**7**); the latter two were identified by their ³¹P NMR spectra which were successfully simulated (see Supporting Information).²³⁻²⁵ Attempts to make analogs of **4** bearing smaller silyl groups (Me₃Si, Ph₃Si) 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 ^tPr₃SiP=PSi^tPr₃

Scheme 1^a

(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 ³¹P 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 ³¹P 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 ³¹P 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 Me₃SiPPMo(N[ⁱBu]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 (163°), a bent P-P-Si angle (106°), 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*₂₂-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 PPh₃ to form an equilibrium mixture of **4**, **5**, ⁱPr₃SiP=PPh₃, and PPh₃. The phosphoranylidene phosphorane ⁱPr₃SiP=PPh₃ was identified by its ³¹P 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 PPh₃, the equilibrium constant for this reaction was measured by ¹H 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 Δ*E* = 1.5 kcal/mol for the reaction PPh₃ + Me₃SiP=PMo(N[ⁱBu]Ar)₃ → Me₃SiP=PPh₃ + PMo(N[ⁱBu]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**.

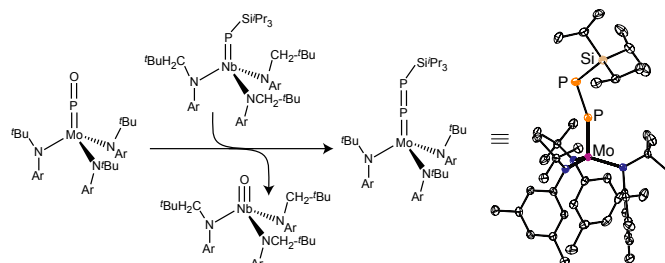
Herein we have described a molybdenum diphosphenido complex arrived at via O-for-PSiR₃ metathesis involving a terminal phosphorus monoxide ligand. The diphosphenido ligand serves as a 3*e*[−] donor and its reactivity is distinct from prior examples of 1*e*[−] donor diphosphenido complexes that are nucleophilic 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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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>.

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- (14) Chemical shielding calculations on the model complex Me₃SiPPMo(N[ⁱBu]Ar)₃ predict the following ³¹P NMR chemical shifts: δ(P_α) = 497 ppm, δ(P_β) = 195 ppm.
- (15) Due to similar solubility properties between oxoniobium **3** and diphosphenido **4**, we have been unable to isolate **4** as a pure substance in quantity.
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TOC Graphic:



Abstract: The terminal phosphorus monoxide complex (OP)Mo(N[^{*t*}Bu]Ar)₃, **1** (Ar = 3,5-Me₂C₆H₃) undergoes an O-for-PSiR₃ metathesis reaction with the niobium phosphinidene complex ^{*i*}Pr₃SiPNb(N[CH₂^{*t*}Bu]Ar)₃, **2**, to generate the oxoniobium ONb(N[CH₂^{*t*}Bu]Ar)₃, **3**, and the diphosphenido complex ^{*i*}Pr₃SiPPMo(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 3 e^- 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 PPh₃ were observed to set up an equilibrium ($K_{eq} = 0.7$) between **4**, PPh₃, and the products of phosphinidene transfer, **5** and ^{*i*}Pr₃SiP=PPh₃.