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

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Detailed Terms
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[′Bu]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[′Bu]Ar).2 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.3-8 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[CH₂Bu]Ar)3 represents a formidable driving force for phosphorus transfer from niobium to main-group acceptors.11,12

The silylphosphinidene complex, Pr₃SiPNb(N[CH₂Bu]Ar)₃ (2) is formed by the reaction of Pr₃SiOTf (OTf = trifluoromethanesulfonate) and the sodium salt of [PNb(N[CH₂Bu]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). 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[CH₂Bu]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 (1J₂₃ = 655 Hz). These data are consistent with the desired silyldiphosphenido product, [Pr₃SiP=PMo(N[′Bu]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.16 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 ligands 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,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

Unlike nitrogen analogs of 4, such as the silyldiazenido complex Me₃SiNNMo(N[′Bu]Ar)₃ and the azaphosphenido complex MesNPMo(N[′Bu]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[′Bu]Ar)₃ (5), the cyclic phosphinidene trimer (Pr₃SiP)₃ (6), and the phosphinidene tetramer (Pr₃Si)₂P₂Si(Pr₃)₂ (7); the latter two were identified by their ³¹P NMR spectra which were successfully simulated (see Supporting Information).24-25 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 Pr₃SiP=PSiPr₃.
nucleophilic attack at its β-phosphorus, resulting in transfer of the phosphinidene with the tripod-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 diphospheno complex arrived at via O-for-PSiR₃ metathesis involving a terminal phosphorus monoxide ligand. The diphospheno ligand serves as a 3e⁻ donor and its reactivity is distinct from prior examples of 1e⁻ donor diphospheno complexes that are nucleophilic at the α-phosphorus. The electronic structure of diphospheno 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[\text{tBu}]Ar)_3, 1 (Ar = 3,5-Me_2C_6H_3) undergoes an O-for-PSiR metathesis reaction with the niobium phosphinidene complex \textit{t}Pr_3SiPNb(N[CH_2\text{tBu}]Ar)_3, 2, to generate the oxoniobium ONb(N[CH_2\text{tBu}]Ar)_3, 3, and the diphosphenido complex \textit{t}Pr_3SiPPMo(N[\text{tBu}]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[\text{tBu}]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 \textit{t}Pr_3Si=PPh_3.