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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. 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)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. We have recently explored a versatile niobium terminal phosphide anion as a precursor to a variety of phosphinidene complexes9-11 and the high degree of oxophilicity possessed by the niobium trisanilide fragment Nb(N[′Bu]Ar)3 represents a formidable driving force for phosphorus transfer from niobium to main-group acceptors11,12.

The silylphosphinidene complex, [Pr3SiNb(N[′Bu]Ar)3 (2)] is formed by the reaction of Pr3SiOTf (OTf = trifluoromethanesulfonate) and the sodium salt of [P(Nb(N[′Bu]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)º (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(N[′Bu]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 (JPP = 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.13 The molecular structure of the diphosphenido complex (Figure 1C) can be described as “singly bent” (angles at P of 158.27(3)º and 104.46º(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 π system.

Unlike nitrogen analogs of 4, such as the silyldiazenido complex Me2SiNMe2Mo(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)2P3P(SiPr3)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 phospha-Wittig complexes. For example, attempts to make 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 5.

Figure 1. (A) The silyldiphosphenido complex 4 and oxoniobium 3 are generated via an O-for-PSiR 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 (º).

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Scheme 1

This equilibrium reaction suggests that very small relative energies of DFT optimized model complexes revealed a to unity was initially surprising to us, but a comparison of the measured by 1H NMR spectroscopy as 590 Hz) at 30.5 and –263.8 ppm.31 By varying the concentration of 2,3-dimethylbutadiene was used instead, the then observed formation of 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 Me3SiPPMoN\[Bu\]Ar\rangle3 (4m) using the ADF package.9–30 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 π orbitals on the β-phosphorus, respectively. The HOMO can be considered as a back-bond from a reducing, formally σ donating. The LUMO is δ2-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 prior examples of 1 and 2,3-diphenyldiethano-lactam and PPh3, the equilibrium constant for this reaction was evaluated by 31P NMR spectroscopy as κeq = 0.7. This value near 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 Ph3P + Me3SiP=PMo[N\[Bu\]Ar\rangle3 \rightarrow Me3SiP=PPb3 + PMo[N\[Bu\]Ar\rangle3. 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 phosphate 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 diphosphenido 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 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 phosphate 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.

(13) Full crystallographic data are available in cif files as part of the Supporting Information, or from the CCDC under deposition numbers 710581 & 710582. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(14) Chemical shielding calculations on the model complex Me3SiPPMoN\[Bu\]Ar\rangle3, predict the following 31P NMR chemical shifts: δ(P3) = 497 ppm, δ(P1) = 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.
(26) Attempts at quantitative kinetic measurements for this reaction were hindered by the many competitive pathways in the reaction mixture.
(28) The conversion to (Pr3Si)P=CH2 was measured by 31P NMR spectroscopy versus an internal standard and found to be 40-50%.
Abstract: The terminal phosphorus monoxide complex (OP)Mo(N[‘Bu]Ar)₃, 1 (Ar = 3,5-Me₂C₆H₃) undergoes an O-for-PSiR₃ metathesis reaction with the niobium phosphinidene complex ‘Pr₃SiPNb(N[CH₂ ‘Bu]Ar)₃, 2, to generate the oxoniobium ONb(N[CH₂ ‘Bu]Ar)₃, 3, and the diphosphenido complex ‘Pr₃SiPPMo(N[‘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 d² 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[‘Bu]Ar)₃, 5, serves as a stable leaving group. Mixtures of 4 and PPh₃ were observed to set up an equilibrium (Kₑq = 0.7) between 4, PPh₃, and the products of phosphinidene transfer, 5 and ‘Pr₃Si=PPh₃.