J|A|C|S
COMMUNICATIONS

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, Massachusetts 02139

Received May 12, 2009; E-mail: ccummins@mit.edu

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 oxophilicity 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]

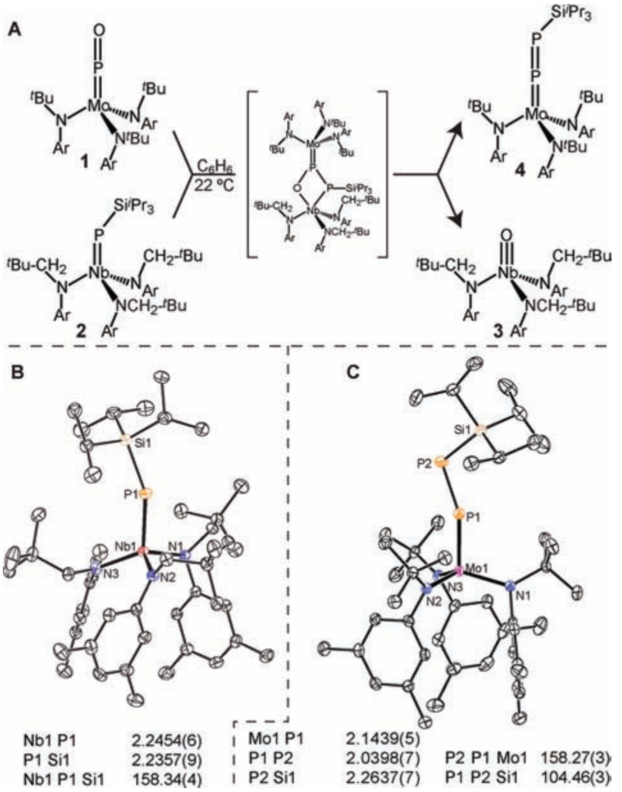
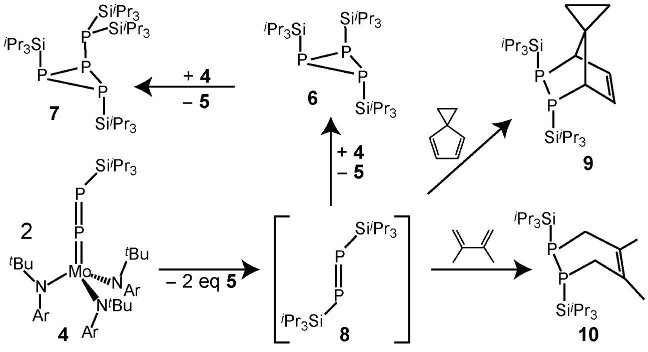


Figure 1. (A) Silyldiphosphenido complex **4** and oxoniobium complex **3** are generated via an O-for-$PSiR_3$ metathesis reaction between **1** and **2**. (B and C) ORTEP representations of complexes **2** and **4**, respectively, with 50% probability ellipsoids and selected interatomic distances (Å)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

Unlike nitrogen analogues 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 analogues 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

10.1021/ja903860k CCC: $40.75

Scheme 1^a



^{a} **5** = PMo(N[^{t}Bu]Ar)$_3$.

of the phosphinidene unit of a fourth equivalent of **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 ^{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 (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 a 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.

Acknowledgment. We thank the U.S. National Science Foundation for support through Grant CHE-719157 and Thermphos for a generous donation of funds and supplies.

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.

References

(1) Johnson, M. J. A.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1523–1524.
(2) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445–451.
(3) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756–759.
(4) Masuda, J. D.; Jantunen, K. C.; Ozerov, O. V.; Noonan, K. J. T.; Gates, D. P.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 2408–2409.
(5) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921.
(6) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170–10171.
(7) Cossairt, B. M.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 8863–8866.
(8) Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210*, 181–201.
(9) Figueroa, J. S.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 984–988.
(10) Piro, N. A.; Figueroa, J. S.; McKellar, J. T.; Cummins, C. C. *Science* **2006**, *313*, 1276–1279.
(11) Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916–13917.
(12) Piro, N. A.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2008**, *48*, 934–938.
(13) Full crystallographic data are available in cif files as part of the Supporting Information, or from the CCDC under deposition numbers 7710581 and 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 Me$_3$SiPPMo(N[^{t}Bu]Ar)$_3$ predict the following ^{31}P NMR chemical shifts: $\delta(P_\alpha)$ = 497 ppm, $\delta(P_\beta)$ = 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.
(16) DuBois, D. L.; Hoffmann, R. *Nov. J. Chim.* **1977**, *1*, 479.
(17) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110–114.
(18) Jutzi, P.; Meyer, U. *Chem. Ber.* **1988**, *121*, 559–560.
(19) Weber, L.; Kirchhoff, R.; Boese, R.; Stammler, H. G.; Neumann, B. *Organometallics* **1993**, *12*, 731–737.
(20) Weber, L.; Frebel, M.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1010–1011.
(21) Weber, L.; Meine, G.; Niederprüm, N.; Boese, R. *Organometallics* **1987**, *6*, 1989–1991.
(22) Peters, J. C.; Cherry, J.-P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10053–10067.
(23) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042–2044.
(24) Baudler, M.; Makowka, B. *Z. Anorg. Allg. Chem.* **1985**, *528*, 7–21.
(25) Goerlich, J. R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 173–176.
(26) Attempts at quantitative kinetic measurements for this reaction were hindered by the many competitive pathways in the reaction mixture.
(27) Weber, L. *Chem. Rev.* **1992**, *92*, 1839–1906.
(28) The conversion to $(^i\text{Pr}_3\text{Si})_2\text{P}_2\text{C}_6\text{H}_{10}$ was measured by ^{31}P NMR spectroscopy versus an internal standard and found to be 40−50%.
(29) Baerends, E. J. et al. *ADF, ADF 2007. 01*; Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 2007 (http://www.scm.com).
(30) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.
(31) Smith, R. C.; Shah, S.; Protasiewicz, J. D. *J. Organomet. Chem.* **2002**, *646*, 255–261.

JA903860K