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

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1021/ja903860k">http://dx.doi.org/10.1021/ja903860k</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Author's final manuscript</td>
</tr>
<tr>
<td>Accessed</td>
<td>Sun Dec 09 05:48:14 EST 2018</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/64726">http://hdl.handle.net/1721.1/64726</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td></td>
</tr>
</tbody>
</table>
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([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 nucelophilic 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.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([CH2Bu]Ar)3 represents a formidable driving force for phosphorus transfer from niobium to main-group acceptors.11,12

The silylphosphinidene complex, Pr3SiNnb(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)º (Figure 1B).13 At 22 ºC, complex 2 reacts with the purple phosphorous 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 (1JPP = 655 Hz). These data are consistent with the desired silyldiphosphenido product, Pr3Si=PSiMo(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)º and 104.46(3)º in analogy to descriptions of daziendeno ligands where the daziendo 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. 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 azaphosphinidene 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 phosphinide tetramer (Pr3Si)2P3SiPr3 (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 terminal phosphide complex 5 and 1 equiv of Pr3Si=P=SiPr3
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 diphenphido 8.

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

Acknowledgement. We thank the US National Science Foundation for support through grant CHE-719157, and Thermophos for a generous donation of funds and supplies.

Supporting Information Available: Full experimental details and spectroscopic data (pdf). Details of X-ray structure determinations (ccif). This material is available free of charge via the Internet at http://pubs.acs.org.

(8); this reactive diphenphido 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 diphenphido 8, we sought to engage it in trapping reactions. Accordingly, complex 4 was warmed to 60 °C in a THF solution of spiro[2.4]hepta-4,6-diene and 2,3-dimethylbutadiene was used instead, the then 1011.

To analyze the bonding in 6, we sought to engage it in trapping reactions. Accordingly, complex 8 was heated to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene, a bent P-P-Si distance, with a nearly linear Mo-P-P angle (163º), a bent P-P-Si distance.

By the many competitive pathways in the reaction mixture.

Acknowledgement. We thank the US National Science Foundation for support through grant CHE-719157, and Thermophos for a generous donation of funds and supplies.

Supporting Information Available: Full experimental details and spectroscopic data (pdf). Details of X-ray structure determinations (ccif). This material is available free of charge via the Internet at http://pubs.acs.org.

(8); this reactive diphenphido 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 diphenphido 8, we sought to engage it in trapping reactions. Accordingly, complex 4 was warmed to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene and the product mixture was analyzed by ¹³P NMR spectroscopy. The [2+4] cycloaddition product of E-diphenphido capture by the organic diene, 9, was observed as a pair of doublets in the ¹³P NMR spectrum (Jₜₚ = 240 Hz) at −112.5 and −117.5 ppm. When 2,3-dimethylbutadiene was used instead, the then C₂-symmetric product, 10, displayed a single ¹³P 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 6, we sought to engage it in trapping reactions. Accordingly, complex 8 was heated to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene, a bent P-P-Si distance, with a nearly linear Mo-P-P angle (163º), a bent P-P-Si distance.

By the many competitive pathways in the reaction mixture.

Acknowledgement. We thank the US National Science Foundation for support through grant CHE-719157, and Thermophos for a generous donation of funds and supplies.

Supporting Information Available: Full experimental details and spectroscopic data (pdf). Details of X-ray structure determinations (ccif). This material is available free of charge via the Internet at http://pubs.acs.org.

(8); this reactive diphenphido 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 diphenphido 8, we sought to engage it in trapping reactions. Accordingly, complex 4 was warmed to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene and the product mixture was analyzed by ¹³P NMR spectroscopy. The [2+4] cycloaddition product of E-diphenphido capture by the organic diene, 9, was observed as a pair of doublets in the ¹³P NMR spectrum (Jₜₚ = 240 Hz) at −112.5 and −117.5 ppm. When 2,3-dimethylbutadiene was used instead, the then C₂-symmetric product, 10, displayed a single ¹³P 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 6, we sought to engage it in trapping reactions. Accordingly, complex 8 was heated to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene, a bent P-P-Si distance, with a nearly linear Mo-P-P angle (163º), a bent P-P-Si distance.

By the many competitive pathways in the reaction mixture.

Acknowledgement. We thank the US National Science Foundation for support through grant CHE-719157, and Thermophos for a generous donation of funds and supplies.

Supporting Information Available: Full experimental details and spectroscopic data (pdf). Details of X-ray structure determinations (ccif). This material is available free of charge via the Internet at http://pubs.acs.org.

(8); this reactive diphenphido 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 diphenphido 8, we sought to engage it in trapping reactions. Accordingly, complex 4 was warmed to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene and the product mixture was analyzed by ¹³P NMR spectroscopy. The [2+4] cycloaddition product of E-diphenphido capture by the organic diene, 9, was observed as a pair of doublets in the ¹³P NMR spectrum (Jₜₚ = 240 Hz) at −112.5 and −117.5 ppm. When 2,3-dimethylbutadiene was used instead, the then C₂-symmetric product, 10, displayed a single ¹³P 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 6, we sought to engage it in trapping reactions. Accordingly, complex 8 was heated to 60 ºC in a THF solution of spiro[2.4]hepta-4,6-diene, a bent P-P-Si distance, with a nearly linear Mo-P-P angle (163º), a bent P-P-Si distance.

By the many competitive pathways in the reaction mixture.
**Abstract:** The terminal phosphorus monoxide complex (OP)Mo(N[tBu]Ar)₃, 1 (Ar = 3,5-Me₂C₆H₃) undergoes an O-for-PSiR₃ metathesis reaction with the niobium phosphinidene complex iPr₃SiPNb(N[CH₂tBu]Ar)₃, 2, to generate the oxoniobium ONb(N[CH₂tBu]Ar)₃, 3, and the diphosphenido complex iPr₃SiPPMo(N[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 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[tBu]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 iPr₃Si=PPh₃.