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Terminal Phosphide and Dinitrogen Molybdenum Compounds Obtained from Pnictide-Bridged Precursors

John-Paul F. Cherry,[†] Frances H. Stephens,[†] Marc J. A. Johnson, Paula L. Diaconescu, and Christopher C. Cummins*

Massachusetts Institute of Technology, Room 2-227, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

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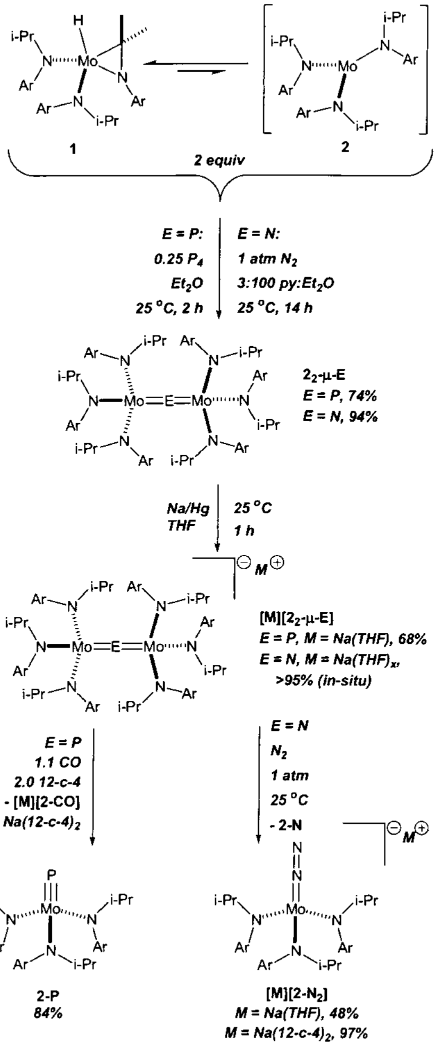
Inspired by recent findings that molybdenum alkylidyne complexes supported by ancillary alkoxide ligands can be prepared by alcoholysis of the corresponding *N-iso*-propylanilide alkylidynes,[1] we selected as synthetic targets two new Mo−ligand multiply bonded compounds supported by removable *N-iso*-propylanilides. Because the successful syntheses of terminal phosphide and dinitrogen compounds proved to be both interesting and challenging, they are communicated in the present report.

Whereas the reaction of white phosphorus with three-coordinate molybdenum compounds supported by *N-tert*-butylanilide ligands has given rise exclusively to the terminal phosphide functionality,[2] it is seen that employing the less sterically hindered fragment Mo(N[*i*-Pr]Ar)$_3$ (**2**, Ar = 3,5-C$_6$H$_3$Me$_2$) leads to a phosphide-bridged product **2_2-μ-P**.[3] Facile combination of the desired PMo(N[*i*-Pr]Ar)$_3$ (**2-P**) with reactive Mo(H)(η^2-Me$_2$C=NAr)(N[*i*-Pr]Ar)$_2$ (**1**) accounts for favorable formation of this bridged phosphide.[4] It was surmised that if **2-P** could be accessed in the absence of **1**, it would be stable and possess synthetic utility. For this reason, a method was sought for splitting dinuclear **2_2-μ-P**. Initially, it was found that nitric oxide was able to effect quantitative bridge cleavage to give equimolar amounts of **2-P** and nitrosyl **2-NO**, but the two possessed similar solubility properties and were therefore difficult to separate. Because **[2-CO]**$^-$ is isoelectronic with **2-NO**, but should be separable from **2-P** because of its negative charge, the one-electron reduction and subsequent carbonylation of **2_2-μ-P** was investigated. Employing sodium amalgam in THF under a nitrogen atmosphere proved to be an effective regimen for high-yield isolation of the sodium salt of the **[2_2-μ-P]**$^-$ anion (Scheme 1).

The red-purple contact ion pair **[Na(THF)][2_2-μ-P]** crystallizes in space group *P*2$_1$/*c* as large blocks from pentane. To stabilize the sodium cation in the solid state, one aryl group flips to interact in a π-fashion with the alkali metal (Figure 1).[5] The Mo−P−Mo bridge is thereby desymmetrized, resulting in modestly different Mo−P distances (2.183(2) and 2.197(2) Å). The Mo−P bond distances in the neutral[6] and anionic species are similar.[7] In both **2_2-μ-P** and **[Na(THF)][2_2-μ-P]**, the Mo−P distances are shorter than those observed for (μ-P)[Mo(N[*t*-Bu]Ph)$_3$]$_2$ (2.2430(6) Å),[8] attributable to steric considerations.

Addition of stoichiometric CO to a THF solution of **[Na(THF)][2_2-μ-P]** at 25 °C effected quantitative cleavage of the phosphide bridge. Because of the ionic nature of **[2-CO]**$^-$, it was easily separated from **2-P** via precipitation and subsequent filtration after the addition of the crown ether 12-c-4 (2 equiv based on Na) to produce **[Na(12-c-4)$_2$][2-CO]**. X-ray quality yellow blocks of **2-P** were found to crystallize from pentane in the space group *P*2$_1$2$_1$2$_1$ (Figure 2). The Mo−P distance of 2.116(3) Å is in close agreement with those observed for previously reported PMo(N-[*t*-Bu]Ar)$_3$ (2.119(4) Å)[2] and PW(NN$_3$) (2.162(4) Å, NN$_3$ = [(RNCH$_2$CH$_2$)$_3$N]).[9] The ^{31}P NMR resonance at δ = 1256 ppm

Scheme 1



[†] First and second named authors contributed equally to this work.

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(6) In the solid-state structure of **2_2-μ-P**, the phosphorus atom lies on a crystallographic inversion center making the Mo−P distances identical (2.2164(4) Å). A subtle Jahn−Teller distortion breaks the symmetry of an otherwise partially occupied doubly degenerate HOMO; one anilide ligand is tilted much further away from the vertical than are the other two, a distortion of approximate C_{2h} symmetry if only core atoms are considered. Further crystallographic information can be found in the Supporting Information.

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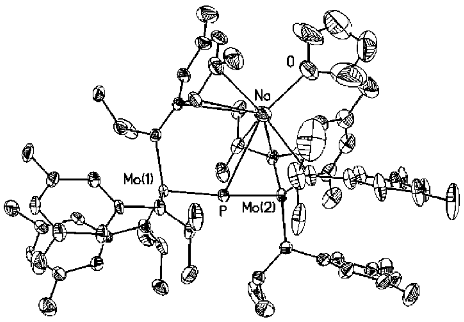

Figure 1. Molecular structure of **[Na(THF)][$\mathbf{2_2}$-$\boldsymbol{\mu}$-P]** (35% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)−P, 2.183(2); Mo(2)−P, 2.197(2); Mo(1)−N(1), 2.051(6); Mo(1)−N(2), 2.017(5); Mo(1)−N(3), 1.970(6); Mo(2)−N(4), 2.059(6); Mo(2)−N(5), 2.059(6); Mo(2)−N(6), 1.959(6); Mo(1)−P−Mo(2), 173.87(10).

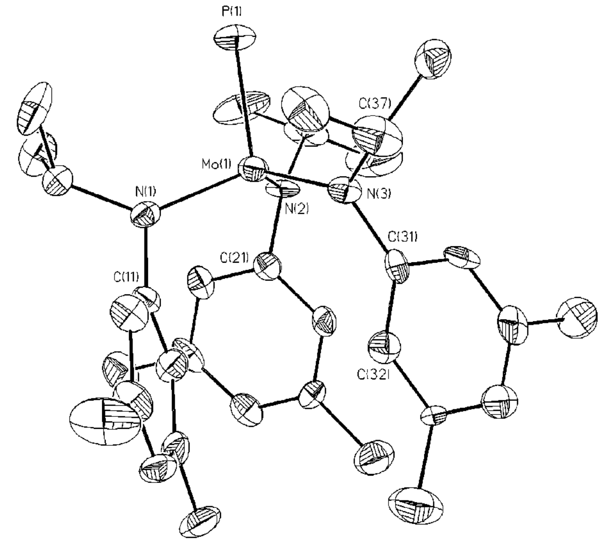

Figure 2. Molecular structure of **2-P** (35% thermal ellipsoids). One of two independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)−P(1), 2.116(3); Mo(1)−N(1), 1.935(9); Mo(1)−N(2), 1.978(10); Mo(1)−N(3), 1.971(10).

for **2-P** is similar to the values of $\delta = 1216$ and 1346 ppm, respectively, for the aforementioned compounds PMo(N[*t*-Bu]Ar)$_3$ and PW(NN$_3$). The origin of such large downfield shifts characteristic of terminal phosphides has been elucidated in detail.[10]

Sodium amalgam reduction of **$\mathbf{2_2}$-$\boldsymbol{\mu}$-N**[11] proceeds with a color change from dark purple to forest green, the latter color being characteristic of **[Na(THF)$_x$][$\mathbf{2_2}$-$\boldsymbol{\mu}$-N]** (Scheme 1).[12] This species (which was not isolated, but rather characterized in situ) was found to react with CO to produce equimolar **[Na(THF)][2-CO]** and **2-N**. In contrast to its phosphorus analogue, **[Na(THF)$_x$][$\mathbf{2_2}$-$\boldsymbol{\mu}$-N]** undergoes a reaction with dinitrogen to produce equimolar **[Na(THF)$_x$][2-N$_2$]** and **2-N**. This discovery provides the only useful protocol to access **[Na(THF)$_x$][2-N$_2$]**, unlike previously described syntheses of the sodium and magnesium salts of [(N$_2$)Mo(N[*t*-Bu]Ar)$_3$]$^-$.[13,14] When carried out with ^{15}N$_2$, this experiment generated exclusively unlabeled **2-N** and **[Na(THF)$_x$][2-^{15}N$_2$]** (^{15}N NMR, $\delta = 401.3$ and 348.8 ppm;[15] these values are similar to those for other dinitrogen anions[13,16]). Additionally, **$\mathbf{2_2}$-$\boldsymbol{\mu}$-^{15}N** is synthesized in 94% yield when **1** is exposed to ^{15}N$_2$[17] and can be reduced under an argon atmosphere to generate **[Na(THF)$_x$][$\mathbf{2_2}$-$\boldsymbol{\mu}$-^{15}N]**. Low temperature (−80 °C) ^{15}N NMR spectroscopy was employed to observe the anionic μ-nitrido resonance at $\delta = 688.7$ ppm. Other μ-^{15}N complexes have been examined by ^{15}N NMR, including the trimers (Cp*MeTa^{15}N)$_3$, $\delta = 528$ and 525 ppm,[18] and {(μ-^{15}N)Nb(N[i-Pr]Ar)$_2$}$_3$, $\delta = 592$ ppm.[13] Addition of N$_2$ (natural isotopic abundance) to a THF-*d*$_8$ solution of **[Na(THF)$_x$][$\mathbf{2_2}$-$\boldsymbol{\mu}$-^{15}N]** produced equimolar **[Na(THF)$_x$][2-N$_2$]** and **2-^{15}N**. The latter compound evinced a ^{15}N NMR signal at 757.7 ppm, in accord with values observed for other *N*-hydrocarbylanilide-supported terminal nitrides NMo(N[R]Ar)$_3$ (R = ^{t}Bu, $\delta = 837.9$ ppm; R = ^{2}Ad, $\delta = 839.8$ ppm)[19] as well as other terminal d^0 nitrides.[20] For synthetic purposes, the separation of **[Na(THF)][2-N$_2$]** from **2-N** was accomplished in 48% yield by crystallization from ether (leaving 52% of **[Na(THF)][2-N$_2$]** and 100% of **2-N** in the mother liquor). Complete separation of the anionic N$_2$-complex from equimolar **2-N** was accomplished by complexation of the cation with the crown ether 12-c-4 (2 equiv per Na) to produce the relatively insoluble **[Na(12-c-4)$_2$][2-N$_2$]** in 97% yield.

The contact ion pair **[Na(THF)$_3$][2-N$_2$]** was found to crystallize with molecular C_3 symmetry (Figure 3). The N(2)−N(3) bond distance was determined to be 1.186(8) Å. While a 3:1 THF/Na ratio was observed for crystals selected freshly from the mother liquor, drying of the crystals under vacuum produced a 1:1 THF/Na ratio as reflected by ^{1}H NMR integration and elemental analysis.

Addition of a stoichiometric amount of methyl tosylate to an ether solution of **[Na(THF)][2-N$_2$]** formed **2-N$_2$Me** in 58% isolated yield as red crystals. Similar molybdenum methyldiazenido complexes prepared with bulkier ligands have been reported.[14,21] Ruby red plates of **2-N$_2$Me** crystallized from

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(7) This is not unexpected, because the electron introduced upon reduction occupies a primarily nonbonding orbital (rather than a Mo−P−Mo bonding orbital). See Supporting Information for results of density functional theory calculations on **[Na(THF)][$\mathbf{2_2}$-$\boldsymbol{\mu}$-P]**.

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(12) Electrochemically, **$\mathbf{2_2}$-$\boldsymbol{\mu}$-N** undergoes a reversible oxidation at −0.9 V and a reversible reduction at −1.9 V (vs Fc/Fc$^+$) in the absence of nitrogen. In the presence of dinitrogen, two irreversible reduction waves (−2.5 and −2.9 V) and a reversible oxidation wave (−0.6 V) were produced.

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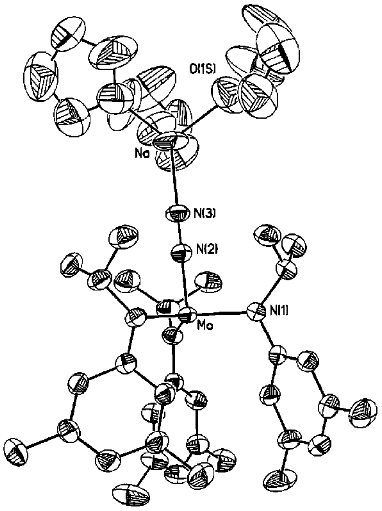

Figure 3. Molecular structure of **[Na(THF)$_3$][2-N$_2$]** (35% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mo−N(2), 1.824(6); N(2)−N(3), 1.186(8); N(3)−Na, 2.196(7); Mo−N(1), 2.023(3); N(1)−Mo−N(2), 95.89(9).

concentrated ether at −25 °C in the space group $P\bar{1}$ (Figure 4). The X-ray crystal structure revealed that in the solid state **2-N$_2$Me** has one *N*-*iso*-propylanilide ligand flipped by 180° relative to the other two ligands.[22] The N(4)−N(5) bond distance is 1.244(3) Å, slightly elongated relative to that of its anionic precursor, yet remaining indicative of an NN bond order of 2.[23] The Mo−N(5)−N(4) angle is 172.5(2)°, and the N(5)−N(4)-C(1) angle is 119.1(2)°.

In summary, reaction of complex **1** with elemental phosphorus or nitrogen smoothly generates pnictogen-atom bridged complexes. The latter undergo smooth one-electron reduction followed by bridge cleavage upon treatment with the π-acids CO or dinitrogen, affording synthetic access to mononuclear derivatives with terminal phosphide or dinitrogen functionality. The new Mo−ligand multiply bonded species presage new manifolds of chemistry because the relatively unhindered *N*-*iso*-propylanilide ligands are protolytically replaceable.

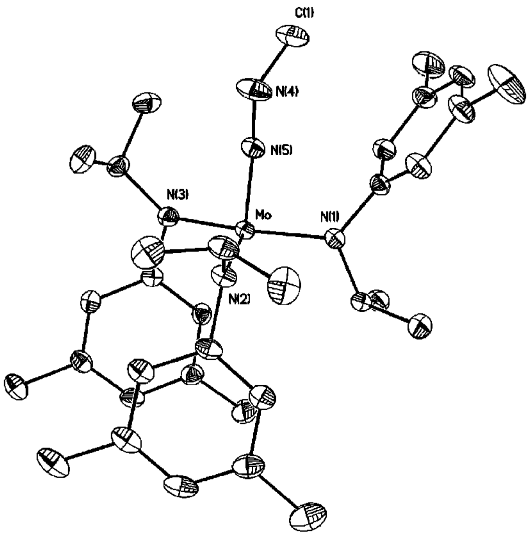

Figure 4. Molecular structure of **2-N$_2$Me** (35% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mo−N(1), 1.981(2); Mo−N(2), 1.936(2); Mo−N(3), 2.013(2); Mo−N(5), 1.760(2); N(5)−N(4), 1.244(3); N(4)−C(1), 1.448(4); N(1)−Mo−N(5), 97.33(9); Mo−N(5)−N(4), 172.5(2); N(5)−N(4)−C(1), 119.1(2).

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Supporting Information Available: Text giving synthetic, spectroscopic, and analytical data for all new compounds and DFT calculations on **[Na(THF)][2$_2$-μ-P]**, and tables giving crystal data, atomic coordinates, structure solution and refinement details, bond lengths and angles, and anisotropic thermal parameters for **2$_2$-μ-P**, **[Na(THF)][2$_2$-μ-P]**, **2-P**, **[Na(THF)$_3$][2-N$_2$]**, and **2-N$_2$Me**. This material is available free of charge via the Internet at http://pubs.acs.org.

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