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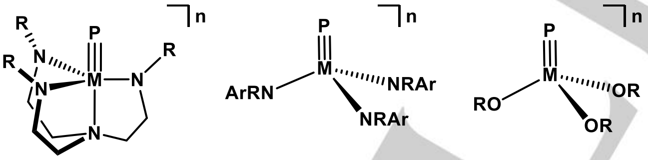
Terminal Molybdenum Phosphides with *d*-Electrons: Radical Character Promotes Coupling Chemistry**

Joshua A. Buss, Paul H. Oyala, and Theodor Agapie*

A terminal Mo phosphide was prepared via group transfer of both P- and Cl-atoms from chloro-substituted dibenzo-7λ^3-phosphanorbornadiene. This compound represents the first structurally characterized terminal transition metal phosphide with valence d electrons. In the tetragonal ligand field, these electrons populate an orbital of d(xy) parentage, an electronic configuration that accommodates both metal d-electrons and a formal M–P triple bond. Single electron oxidation affords a transient open shell terminal phosphide cation with significant spin density on P, as corroborated by CW and pulsed EPR characterization. Facile P–P bond formation occurs from this species via intermolecular phosphide coupling.

Metal phosphides comprise an important and ubiquitous class of solid-state materials with applications as catalysts and semiconductors.[1] In contrast, discrete metal phosphide complexes are rare and their chemistry remains underexplored.[2] Owing to both end-on and side-on reactivity,[2b] rarer still are isolable terminal transition metal phosphides. Indeed, since the initial reports of a P_1 ligand bearing a $M\equiv P$ triple bond two decades ago,[3] only a handful of examples of such a motif have been described (Figure 1).[4] These compounds all display d^0 group 5 and 6 metals in a trigonal coordination environment. Reported herein are the first examples of isolable transition metal complexes with both terminal phosphide ligands and d-electrons.



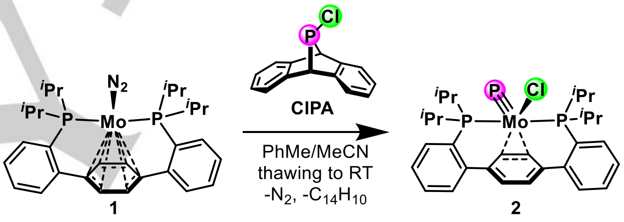
M = W or Mo, n = 0
M = Ta, n = -1

M = W or Mo, n = 0
M = Nb, n = -1

M = W or Mo, n = 0
M = Nb, n = -1

Figure 1. Classes of previously reported terminal phosphide complexes.

In a recent report, we described the ability of a *para*-terphenyl diphosphine supported molybdenum center to undergo a four-electron reductive coupling reaction from a Mo(IV) carbide to afford a Mo(0) dinitrogen adduct.[5] In an effort to access additional Mo≡E complexes, we targeted the reverse of this process—multi-electron oxidative group transfer.[6] Cummins and coworkers have reported a library of dibenzo-7λ^3-phosphanorbornadiene derivatives that undergo anthracene elimination, releasing reactive phosphorous fragments, under mild conditions.[7] With precedent for arene elimination group transfer,[7a-c, 8] these bridgehead phosphinidenes represent promising reagents for the direct and mild installation of M–P multiple bonds.



Scheme 1. Synthesis of terminal phosphide **2**.

Addition of **ClPA** to a thawing solution of molybdenum complex **1** resulted in a color change from red-orange to dark brown over the course of warming to room temperature (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of a reaction mixture aliquot showed complete consumption of **1** (76.4 ppm) and the generation of two new resonances—a broad triplet at 1300.7 ppm and a doublet at 41.3 ppm (^2J(P,P) = 11.1 Hz). The upfield shift of the latter is consistent with a Mo(IV) center;[9] the highly deshielded chemical shift of the former supports the formation of a terminal phosphide.[10]

The structure of **2** was determined by single-crystal X-ray diffraction (XRD), corroborating both the presence of a P_1 ligand and the monomeric nature of the complex (Figure 1). The Mo center adopts a *pseudo*-square pyramidal coordination geometry, with the phosphide in the axial position and the chloride ligand *trans* to an η^2 interaction between Mo and the central arene of the *para*-**P2** ligand. Localization of single- and double-bond character in this arene, an average Mo–C contact of 2.258(1) Å (Table 1), and upfield shifted resonances for these aryl CH groups in both the ^{1}H and ^{13}C{^{1}H} NMR spectra are all consistent with the assigned metal-arene interaction. The short 2.1003(3) Å Mo–P bond distance is in excellent agreement with that of Mo(VI) phosphides,[3-4, 4c-f] supporting a Mo–P triple bond.

Elimination of arenes resulting in group transfer has been employed to deliver a variety of moieties, including N$^-$,[8c, 8d, 8h]

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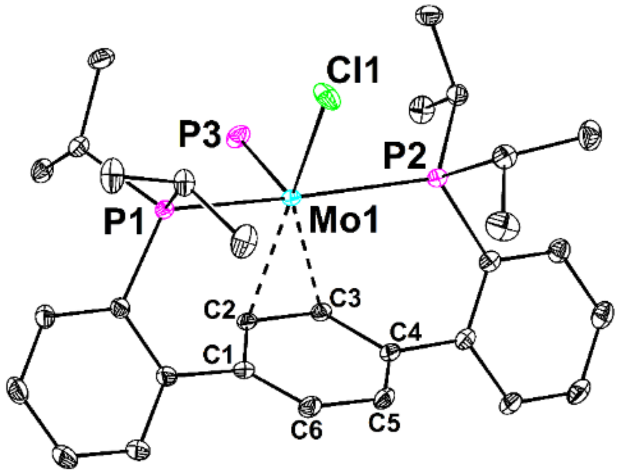


Figure 2. Solid-state structures of **2**. Protons are omitted for clarity. Anisotropic thermal displacement ellipsoids are shown at a 50% probability level.

Table 1. Selected bond metrics [Å] for phosphides **2** and **3**.

	Mo1–P3	Mo1–Cl1	Mo1–C2	Mo1–C3	C2–C3
2	2.1003(3)	2.4358(3)	2.261(1)	2.255(1)	1.433(2)
3	2.092(1)	2.3411(9)	2.465(3)	2.471(3)	1.402(4)

NH,[8b] CH,[8f] NCN,[8e, 8g] O,[8a] PCH,[11] and P$_2$.[7b, 7c] Recently, **ClPA** was employed to transfer P$^+$ to an anionic vanadium nitride to generate the pnictogen-pnictogen linkage in a transient P–N complex.[7a] In line with this strategy, the formation of **2** demonstrates the successful transfer of both P- and Cl-atoms from ClPA, a four-electron process supported by a single metal center. Monometallic four-electron oxidative addition is known, but is limited to the insertion of metal fragments into unsaturated C=O,[12] C=S,[12c] C=N,[12a, 12c] and N=N[13] bonds. Group transfer by elimination of a single arene equivalent more typically results in two-electron processes,[8a, 8d, 8e, 8g, 8h] although four-electron reactivity has been demonstrated when employing two metal centers as group or atom acceptors.[8f] The hapticity change of the metal-arene interaction from η^6 (**1**) to η^2 (**2**) facilitates this multi-electron transformation; the d-orbitals engaging in Mo-arene π-bonding in the low-valent starting material are liberated to form the Mo–P bonds in the product.

The electronic structure of **2**, displaying a Mo(IV) center and two valence d electrons, is of interest, contrasting previously reported C_{3v} d^0 terminal phosphides. Under threefold symmetry, the d orbital splitting varies depending upon both the P-M-L angle and the π-bonding character of the ancillary ligands, with some geometries resulting in orbitals of metal-P π-antibonding character being the lowest energy d-based orbitals.[14] Population of such orbitals would result in destabilization of the M–P interaction.[14] Quantum mechanics studies were employed to interrogate the Mo–P bonding in **2** (Figure 3). Qualitatively, the bonding in C_s symmetric **2** is similar to the vanadyl ion.[15] In *pseudo*-square pyramidal **2**, the HOMO (Figure 3) is of Mo d(xy) parentage and is strictly nonbonding (N.B.) with respect to the phosphide. This MO displays π-backbonding and π-antibonding character with respect to the M-arene and M–Cl interactions, respectively. The bonding between Mo and the phosphide ligand is consistent with a triple bond, involving a σ- (HOMO-4) and two π-bonding interactions (HOMO-1 and HOMO-3). The π-antibonding interactions, displaying Mo d(xz) and d(yz) parentage (HOMO+2 and HOMO+3), are unoccupied. The formal d^2 count is therefore not destabilizing; the valence electrons occupy a N.B. orbital, maintaining a formal M–P bond order of three.

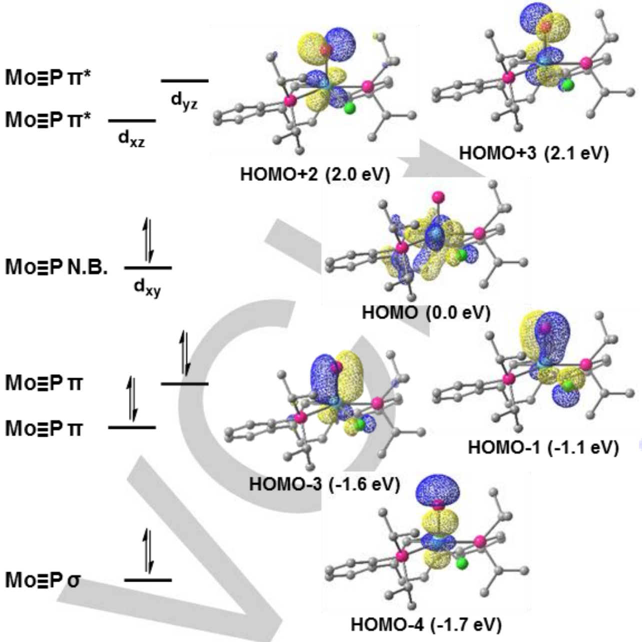


Figure 3. Qualitative MO energy diagram (left) and selected calculated valence MOs (right) depicting the Mo/phosphide bonding in **2**. Isosurfaces are shown at the 0.05 e Å^{-3} level and orbital energies (relative to the HOMO) are provided.

As strictly non-bonding with respect to the phosphide ligand, we anticipated that a single electron oxidation of **2** might afford an open shell phosphide cation. The cyclic voltammogram of **2** in THF displays a one-electron oxidation event at -104 mV vs. Fc/Fc$^+$ (Figure S25). Addition of [Fc][BAr$^F_{24}$] (BAr$^F_{24}$ = B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$) to a thawing 2-MeTHF solution of **2** results in a color change to deep purple upon mixing. The X-band CW EPR spectrum of a glass of this purple solution is consistent with generation of S=1/2 phosphide cation **3** (Scheme 2). The EPR

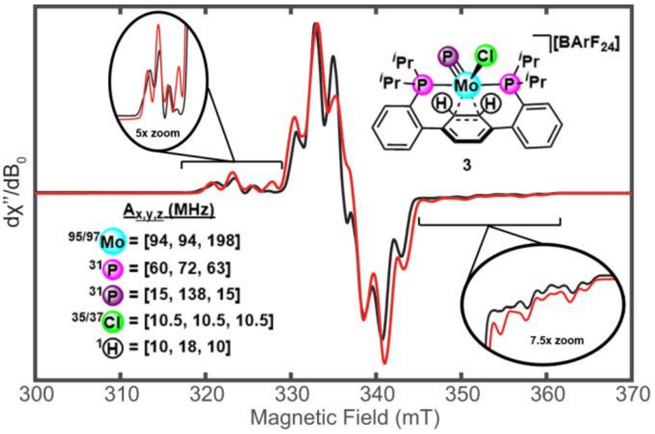
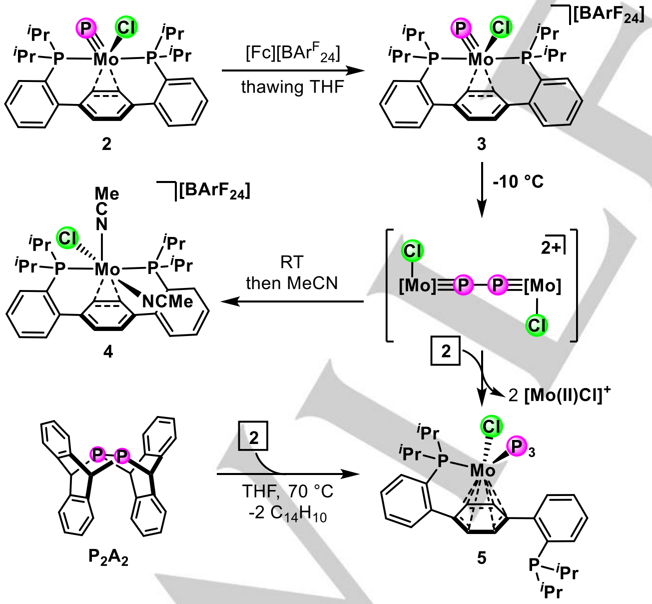


Figure 4. Experimental (black) and simulated (red) X-Band CW EPR spectra of **3** (2Me-THF glass; 77K).

spectrum was satisfactorily fit using a slightly rhombic g tensor with $g_x = 2.0062$, $g_y = 2.0037$, and $g_z = 1.971$ and with hyperfine couplings to $^{95/97}$Mo ($|A_{x,y,z}|$ = [94, 94, 198] MHz), two $^{31}P_{P2}$ ($|A_{x,y,z}|$ = [60, 72, 63] MHz) couplings from the phosphine ligands, and a single highly anisotropic ^{31}P coupling assigned to the phosphide $^{31}P_{Mo\equiv P}$ ($|A_{x,y,z}|$ = [15, 138, 15] MHz) (Figure 4). These parameters were further corroborated by acquisition and analysis of pulse X-band Davies electron nuclear double resonance (ENDOR) spectra and pulse Q-band field swept EPR spectra (see SI). Additional small hyperfine couplings were observed in the Davies ENDOR spectra (see SI) to ^{1}H ($|A_{x,y,z}|$ = [10, 18, 10] MHz), assigned to the two proximal protons from the arene ligand, and $^{35/37}$Cl ($|A_{x,y,z}|$ = [10.5, 10.5, 10.5] MHz). Computationally determined Mulliken spin densities and the large observed hyperfine coupling to $^{95/97}$Mo agree well with primary localization of the unpaired spin on the Mo center. Analysis of the anisotropic component of the phosphide ^{31}P hyperfine coupling[16] indicates appreciable spin density of 0.1-0.14 e^- in a single p-orbital at the terminal phosphide (see SI).

Single crystal XRD confirmed the assignment of cation **3**. The structure of **3** is similar to **2**, with perturbations consistent with the bonding scheme shown in Figure 3. The Mo≡P distance is only slightly contracted at 2.092(1) Å, likely due to the smaller radius for the higher oxidation state Mo(V) center (Table 1). The Mo–Cl and C2–C3 bonds both contract significantly (2.3411(9) and 1.402(4) Å, respectively, Table 1), consistent with a "push-pull" interaction[17] between the π-basic chloride and π-acidic η^2 M-arene interaction. The Mo d(xy) orbital (HOMO of **2**, SOMO of **3**) is bonding with respect to the C2–C3 π*-bond, reflected in the elongation of the Mo–C2 and Mo–C3 distances from **2** to **3**, and consistent with reduction of the Mo-arene bond order upon oxidation.



Scheme 2. Oxidation-induced phosphide coupling.

Though stable in the solid state, warming solutions of **3** above -10 °C results in a color change to red-brown with the concomitant appearance of a singlet at 68 ppm in the ^{31}P{^{1}H} NMR spectrum. The NMR data for this new species in CD_3CN is consistent with a C_s symmetric acetonitrile adduct, confirmed by XRD as chloride cation **4** (Scheme 2). The net three electron reduction of the Mo center and the loss of the ^{31}P signal corresponding to the terminal phosphide ligand is consistent with the formal loss of a P-atom, and suggests intermolecular phosphide coupling as a feasible reaction pathway to generate **4** from **3**; such coupling reactions of transition metal nitrides are known.[8d, 18] Analogous to the formation of **4**, oxidatively induced bimetallic reactions resulting in the formation of new E–E bonds are invoked in both ammonia[18g, 18h] and water[14a] oxidation chemistry.

Hypothesizing that the phosphide ligand converts to diphosphorous (P_2) species,, chemical traps were employed for its detection.[7c, 19] Terminal phosphide complexes themselves have been reported to be efficient P_2 traps, reacting in a one-to-one manner to generate cyclic P_3 products.[19a] Warming THF solutions of **2** and **3** in a 1:2 ratio resulted in a complex ^{31}P{^{1}H} NMR spectrum. Cation **4** was observed, in addition to a species (**5**) with three highly shielded ^{31}P resonances: -155.2 (dd, J = 321.4 and 266.3 Hz), -201.0 (app t, J = 266.1 Hz) and -303.4 (ddd, J = 321.2, 266.6, and 16.4 Hz) ppm. The high field chemical shifts and large scalar coupling constants are consistent with a polyphosphorous ligand bearing at least three P–P bonds.[20] This new phosphorous rich complex could not be prepared in sufficient purity for further characterization. However, it can be prepared independently using an established P_2 source, **P_2A_2**.[7c] Heating **P_2A_2** with complex **2** in THF results in the same high field ^{31}P NMR signature. Establishing the mechanism of formation for **5** requires further experiments; generation of free P_2, direct reaction of **2** with a P–P bonded intermediate (Scheme 2, brackets), or P–P bond formation between **2** and **3** are all possible. Nevertheless, the NMR characteristics of species **5,** generated via any of these potential reactivity manifolds, establishes the ability of **3** to form new P–P bonds via coupling of a terminal phosphide with radical character.

In summary, **ClPA** affords facile transfer of both P- and Cl-atoms to Mo(0) to generate a terminal Mo phosphide. The tetragonal ligand field of the resulting Mo(IV) complex permits a d^2 electron count at Mo and a formal Mo–P triple bond, Oxidation affords, at low temperatures, a paramagnetic Mo(V) phosphide cation with significant radical character on P. Upon warming, phosphide coupling occurs, demonstrating oxidatively induced E–E bond formation from a M≡E precursor.

Keywords: terminal phosphide • group transfer • phosphide coupling • molybdenum complexes • pulse EPR

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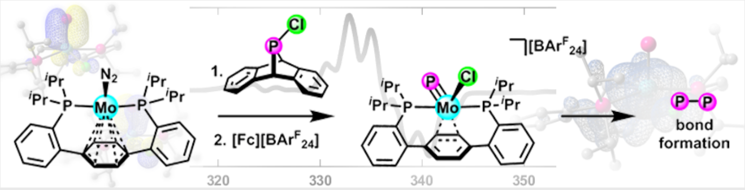

Two P's in a pod: A Mo(IV) terminal phosphide complex is formed via P- and Cl-atom transfer. Single electron oxidation affords a Mo(V) phosphide cation with radical character on Mo and P. This species readily undergoes intermolecular P–P bond formation.

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