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Molybdenum−Phosphorus Triple Bond Stabilization by Ancillary Alkoxide Ligation: Synthesis and Structure of a Terminal Phosphide Tris-1-methylcyclohexanoxide Complex

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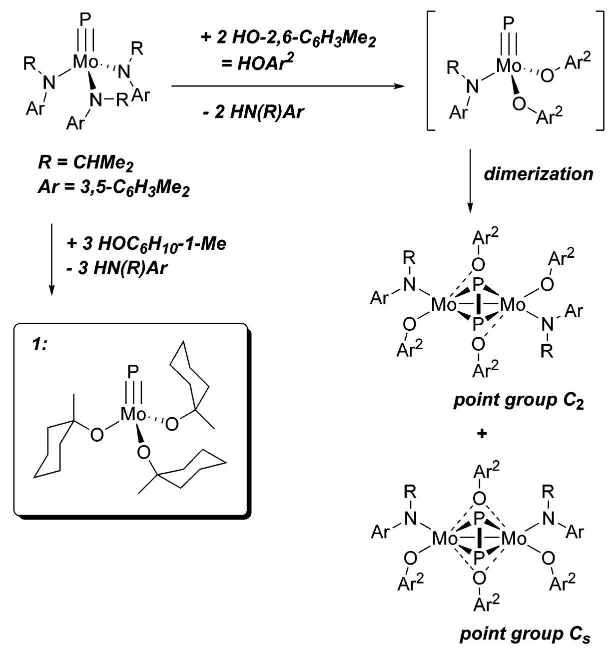
Since the 1995 discovery of kinetically stable terminal phosphide complexes $PMo(N[R]Ar)_3$ ($R = C(CD_3)_2CH_3$; $Ar = 3,5\text{-}C_6H_3Me_2$)[1] and $PM(Me_3SiNCH_2CH_2)_3N$ (M = Mo, W),[2] it has been of interest to determine the extent to which sterically demanding amido ligands are required for terminal MP (M = Mo, W) triple bond protection. Prior to 1995, attempts to generate and observe terminal phosphide complexes had focused on ancillary alkoxide ligation. In Chisholm's 1988 paper on P_4 addition to $W_2(ONp)_6(HNMe_2)$, where Np = CH_2-*t*-Bu, the intermediacy of $PW(ONp)_3$ (not observed) is postulated.[3] In 1999, reinvestigating prior work of Becker,[4−6] Scheer and co-workers studied by NMR the metathesis reaction of $W_2(O\text{-}t\text{-}Bu)_6$ with phosphaalkyne PC-*t*-Bu at low temperature and found a ^{31}P signal at $\delta = 845$ ppm ($^1J_{WP} = 176$ Hz) attributable to the reactive intermediate, $PW(O\text{-}t\text{-}Bu)_3$.[7] While the latter could not be isolated, its stabilization was achieved by in situ $M(CO)_5$ (M = Cr, W) capping of the terminal phosphide; following this strategy, the μ-phosphido complex $(t\text{-}BuO)_3W(\mu\text{-}P)W(CO)_5$ was isolated and structurally characterized. Scheer has extended this methodology to include the synthesis and properties of $(THF)(Ar^2O)_3W(\mu\text{-}P)M(CO)_5$ (M = Cr, Mo; $Ar^2 = 2,6\text{-}C_6H_3Me_2$).[8] Isolable terminal phosphide complexes of the type $PM(OR)_3$ have, to date, remained elusive.

Valuable as well-defined initiators of alkyne metathesis are molybdenum alkylidyne complexes such as $Me_3SiCH_2CMo(O\text{-}Ad)_3$, where Ad = 1-adamantyl, an efficient synthesis of which we devised recently via facile alcoholysis of the amido ligands belonging to the precursor $Me_3SiCH_2CMo(N[i\text{-}Pr]Ar)_3$.[9] With the present work, we adapt this alcoholysis strategy to the synthesis of the first kinetically persistent terminal phosphide complex supported solely by alkoxide ancillary ligation.[10]

From molybdaziridine-hydride $Mo(H)(\eta^2\text{-}Me_2CNAr)(N[i\text{-}Pr]Ar)_2$,[11] a synthon for the reactive molybdenum(III) tris-amide $Mo(N[i\text{-}Pr]Ar)_3$, treatment with P_4 provides phosphide-bridged $(\mu\text{-}P)Mo_2(N[i\text{-}Pr]Ar)_6$. This is followed by reductive carbonylation to cleave the phosphide bridge and produce salt $[Na(12\text{-crown-}4)_2][(OC)Mo(N[i\text{-}Pr]Ar)_3]$ along with neutral, four-coordinate terminal phosphide $PMo(N[i\text{-}Pr]Ar)_3$ in gram quantities and 83% yield.[12] The latter has a characteristic extreme downfield ^{31}P NMR chemical shift of 1256 ppm and has been the subject of an X-ray crystal structure investigation.[12]

^{31}P NMR spectroscopy was used to assess the consequences of $PMo(N[i\text{-}Pr]Ar)_3$ alcoholysis for a variety of commercially available alcohols. In the particular case of 1-methylcyclohexanol, alcoholysis of $PMo(N[i\text{-}Pr]Ar)_3$ provided the kinetically persistent, monomeric, 4-coordinate terminal phosphide complex $PMo(OR)_3$ (**1**, R = 1-methylcyclohexyl, Scheme 1). Complex **1** displays a singlet in the ^{31}P NMR at $\delta = 1130$ ppm and was isolated in 57% yield by recrystallization (pentane, −35 °C) as a yellow crystalline solid. A single-crystal X-ray diffraction study of **1** revealed the molecule's structure as depicted in Figure 1.

Scheme 1. Reaction of $PMo(N[i\text{-}Pr]Ar)_3$ with Alcohols



Important structural parameters for complex **1** include the bond distances (Å) Mo1−P1 = 2.1144(16) and Mo1−O1 = 1.857(2), and the bond angles (deg) P1−Mo−O1 = 107.79(6) and Mo−O1−C11 = 141.92(16). In the crystal, **1** exhibits C_3 molecular symmetry, its Mo−P triple bond vector being coincident with a three-fold axis of the $R\text{-}\bar{3}c$ space group. Interestingly, the Mo−P triple bond distance for **1** is not significantly longer or shorter than distances observed for corresponding phosphides stabilized by bulky amide ligands.[1,2] In this respect, the Mo−P triple bond functional group retains its identity independent of the nature of ancillary supporting ligands. The closest contact from the phosphorus atom of one molecule to the molybdenum atom of another molecule is 6.887 Å, revealing a structure that is not polymeric in the solid state. This is unlike the solid-state structure of $NMo(O[t\text{-}Bu])_3$, which has close contacts (2.844 Å) between the nitrogen from one molecule and the molybdenum of the next.[13]

Use of slightly less bulky alcohols led to slow dimerization of the terminal phosphide unit after alcoholysis. A long-lived ($t_{1/2}$ = ca. 6 h at 20 °C, toluene) terminal phosphide $PMo(OAd)_3$ (**2**) is formed when $PMo(N[i\text{-}Pr]Ar)_3$ is treated with 3 equiv of 1-adamantanol in *n*-pentane. This beige compound has a characteristic ^{31}P NMR shift at $\delta = 1124$ ppm. Over approximately 1 day in

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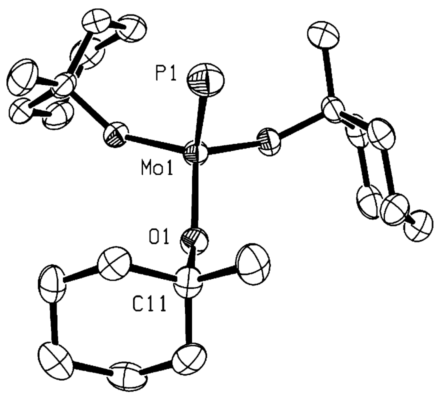

Figure 1. X-ray crystal structure of **1** with ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Mo1−P1, 2.1144(16); Mo1−O1, 1.857(2); O1−C11, 1.456(3); P1−Mo1−O1, 107.79(6); Mo1−O1−C11, 141.92(16).

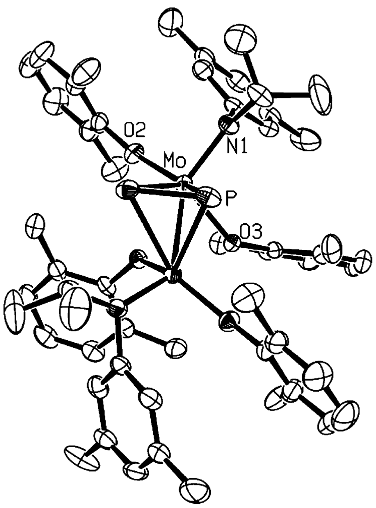

Figure 2. X-ray crystal structure of **[3]$_2$** with ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Mo−P, 2.4951(12); Mo−P′, 2.3926(12); P−P′, 2.086(2); Mo−N1, 1.940(3); Mo−O2, 1.930(3); Mo−O3, 2.005(3); Mo−O3′, 2.339(3); P−Mo−P′, 50.49(6); P−Mo−Mo′, 54.65(3); Mo−P−Mo′, 67.08(3); P−Mo−N1, 84.96(10); P−Mo−O2, 142.05(9); P−Mo−O3, 80.81(8).

toluene solution, **2** cleanly dimerizes to brown [PMo(OAd)$_3$]$_2$ **[2]$_2$** with concomitant appearance of a new ^{31}P NMR signal at $\delta = 188$ ppm.

Rapid dimerization of the MoP unit was observed when 3 equiv of 2,6-dimethylphenol was utilized. Alcoholysis was incomplete, and green-brown [PMo(N[*i*-Pr]Ar)(OAr^2)$_2$]$_2$ was isolated in 51% yield (**[3]$_2$**, Scheme 1). An X-ray diffraction study revealed a slightly skewed tetrahedral Mo_2P_2 core (Mo−P, 2.4951(12) Å; Mo−P′, 2.3926(12) Å) (Figure 2). The P−P distance (2.086(2) Å) is shorter than that in elemental P_4 (2.21 Å) and that in Chisholm's similar tungsten compound W_2(O[*i*-Pr])$_6$(py)(μ-P_2) (2.154(4) Å),[14] but it is slightly longer than that in Scherer's compound [$Mo_2Cp_2(CO)_4$-(μ-P_2)] (2.079(2) Å).[15] A ^{31}P NMR spectrum of **[3]$_2$** in C_6D_6 reveals a mixture of C_s and C_2 isomers in solution. A singlet at $\delta = 235$ ppm can be assigned to the C_2 isomer where both phosphorus atoms are magnetically equivalent, and a pair of doublets centered at $\delta =$ 248 and 238 ppm ($J_{PP} = 366$ Hz) can be assigned to the C_s isomer where the phosphorus atoms are magnetically distinct.

^{31}P NMR chemical shielding calculations were carried out on two model systems, PMo(OH)$_3$ and [PMo(μ-OH)(OH)(NH$_2$)]$_2$, based upon X-ray structural parameters of **1** and **[3]$_2$**.[16] We obtained for the terminal phosphide a calculated chemical shift $\delta = 1141$ ppm, while for the dimer the calculated chemical shift $\delta = 203$ ppm. These values are in good agreement with data for the experimental systems reported herein. The ^{31}P NMR chemical shift for both model compounds is determined exclusively by the paramagnetic shielding term, σ_{para},[17] as the diamagnetic contribution (σ_{dia}) is invariant at ca. 965 ppm, and the spin−orbit term (σ_{so}) is no larger than ca. 20 ppm.[18]

Formation of the Mo_2P_2 core via terminal phosphide dimerization is a process of great interest as well as potential mechanistic complexity. Chisholm's recent theoretical study of a related process involving breakup of isolobal $M_2(CH)_2$ (M = Mo, W) alkoxide-supported cores may be consulted for considerable insight.[19]

Acknowledgment. On the occasion of his 50th birthday, the authors do hereby dedicate this paper to Prof. Philip P. Power. The authors are grateful to the NSF (CHE-9988806) for funding.

Supporting Information Available: Text giving experimental details and tables of bond lengths and angles, fractional coordinates, and anisotropic thermal parameters for the structures of PMo(OMeCy)$_3$ and [PMo(N[*i*-Pr]Ar)(OAr^2)$_2$]$_2$; text giving experimental details for PMo(OAd)$_3$; text describing theoretical methods and results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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