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Synthesis, Structure, and Reactivities of the Five-Coordinate Molybdenum(0) Mono(acetylene) Complex $[Mo(HC{\equiv}CH)(dppe)_2]$[1]

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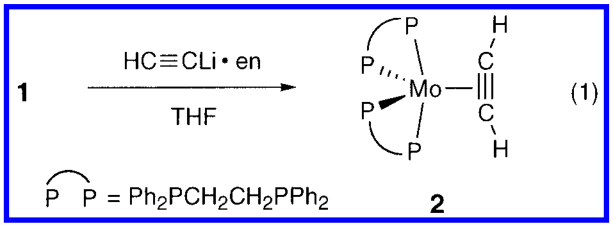
Summary: The reaction of trans-$[Mo(N_2)_2(dppe)_2]$ (**1**; *dppe* = $Ph_2PCH_2CH_2PPh_2$) *with excess amounts of* $HC{\equiv}CLi{\cdot}en$ (*en* = $H_2NCH_2CH_2NH_2$) *afforded the five-coordinate Mo(0) mono(acetylene) complex* $[Mo(HC{\equiv}CH)(dppe)_2]$ (**2**). *Treatment of* **2** *with 2 mol of* $[Cp_2Fe][BF_4]$ (*Cp* = η^5-C_5H_5) *in THF gave the Mo(II) acetylene complex trans-*$[MoF(HC{\equiv}CH)(dppe)_2][BF_4]$, *while that in THF−MeCN followed by anion metathesis with NaOTf (OTf* = OSO_2CF_3) *led to the formation of the metallacyclopropene complex* $[Mo(\eta^3\text{-}CHCHPPh_2CH_2CH_2PPh_2\text{-}C,C',P)(MeCN)_2(dppe)][OTf]_2$.

The chemical bonding and transformation of four-electron-donating alkyne ligands at early-transition-metal centers have been a subject of extensive research activity.[2] A wide variety of six-coordinate d^4 metal (most typically Mo(II) and W(II)) complexes with four-electron-donating alkyne ligands have been synthesized and found to exhibit intriguing reactivities.[2,3] Four-coordinate d^6 complexes of the types $ML(alkyne)_3$[4−8] and $ML_2(alkyne)_2$[9−11] (L = monodentate ligand) have also been reported. In contrast, five-coordinate d^6 mono(alkyne) complexes with the general formula ML_4(alkyne) have been surprisingly scarce; only a few examples, including the chromium complexes $[Cr(CO)_2\{P(OMe)_3\}_2(RC{\equiv}CPh)]$ (R = Ph, H),[12] have been described in the literature. Our extensive studies on low-valent molybdenum and tungsten complexes have demonstrated that the Mo(0) center in the complex *trans*-$[Mo(N_2)_2(dppe)_2]$ (**1**; dppe = $Ph_2PCH_2CH_2PPh_2$) is not only effective for the activation of dinitrogen[13,14] but also provides a unique coordination site to bind and activate various substrates such as dmf (dmf = *N,N*-dimethylformamide),[15] nitriles,[16,17] imines,[18,19] and isocyanides[20] upon dissociation of the dinitrogen ligands. Now we have found that the five-coordinate Mo(0) (d^6) mono(acetylene) complex $[Mo(HC{\equiv}CH)(dppe)_2]$ (**2**) can be derived from complex **1**. Here we describe its synthesis and the structure of complex **2** as well as some chemical properties.

When complex **1** was treated with excess amounts of $HC{\equiv}CLi{\cdot}en$ (10 equiv; en = $H_2NCH_2CH_2NH_2$) in THF at 50 °C for 2 h, a very dark red solution was formed, from which black crystals of complex **2** were obtained in 32% yield after recrystallization (eq 1).[21] At room temperature, a longer reaction time (10 h) was necessary to allow the reaction to go to completion (29% yield). The $^{13}C\{^1H\}$ NMR signal for the acetylene carbons in **2** appears as a triplet (J_{CP} = 15.9 Hz) at δ 171.0, which falls within the region reported for the sp carbons of four-electron-donating alkyne ligands.[3] The $^{31}P\{^1H\}$ NMR spectrum displays two apparent triplets (J_{PP} = 24 Hz), indicating a trigonal-bipyramidal geometry with the acetylene ligand occupying an equatorial position. The resonance for the acetylenic hydrogens appears as a doublet at δ 10.18 due to the coupling to one phosphorus atom ($^3J_{PH}$ = 12.4 Hz) and splits into a broad triplet ($^3J_{PH}$ = 6.0 Hz) upon warming at 90 °C.[22] On the basis of these observations, the acetylene ligand is deduced to take the orientation perpendicular to the equatorial plane.



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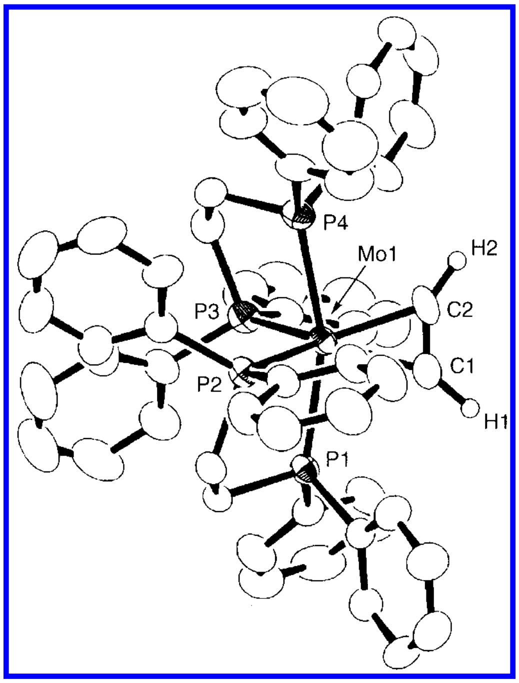

Figure 1. Molecular structure of $\mathbf{2}\cdot C_7H_8$. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Mo(1)−P(1), 2.443(2); Mo(1)−P(2), 2.406(1); Mo(1)−P(3), 2.411(2); Mo(1)−P(4), 2.446(2); Mo(1)−C(1), 2.061(5); Mo(1)−C(2), 2.071(5); C(1)−C(2), 1.265(7); P(1)−Mo(1)−P(4), 161.28(5); P(2)−Mo(1)−P(3), 103.25(5); C(1)−Mo(1)−C(2), 35.7(2); Mo(1)−C(1)−C(2), 72.6(4); Mo(1)−C(2)−C(1), 71.7(3).

The molecular structure of $\mathbf{2}\cdot C_7H_8$ was unambiguously determined by an X-ray diffraction study (Figure 1).[23] In full agreement with the spectral data, complex **2** adopts a distorted-trigonal-bipyramidal structure with the acetylene ligand at an equatorial position. The Mo(1)−C(1)−C(2) and Mo(1)−P(2)−P(3) planes are nearly perpendicular to each other (dihedral angle 86.7°), and the Mo(1)−C(1) (2.061(5) Å) and Mo(1)−C(2) (2.071(5) Å) bond distances are on the high end of the range of Mo−C(four-electron-donating alkyne) distances in accordance with the electron-rich nature of the molybdenum center in **2**.[3] EHMO calculations for the model complex [Mo(HC≡CH)(PH$_3$)$_4$] revealed that the conformer with the acetylene ligand perpendicular to the equatorial plane is more energetically favored than that with the acetylene ligand lying in the equatorial plane, since the former conformation is best suited for both the π-donation from the acetylene $\pi_\perp$ orbital and the π-back-donation from the metal to the acetylene $\pi_{||}^*$ orbital.[12,24]

The formation of complex **2** is of special interest. It has been known that HC≡CLi is in equilibrium with acetylene and LiC≡CLi, and addition of a diamine ligand stabilizes the monolithiated species.[25] Acetylene generated in a low concentration is considered to be required for the production of complex **2** from **1**. In fact, PhC≡CLi as well as internal acetylenes such as bis(trimethylsilyl)acetylene and diphenylacetylene failed to react with **1**. In contrast, it has been reported that the reaction of complex **1** with acetylene gas results in the formation of polyacetylene as the only identified product, while that with other 1-alkynes gives rise to the formation of alkynyl complexes via oxidative addition of the C−H bonds or bis(alkyne) complexes which are regarded as the precursors for the C−H activation.[26,27] No molybdenum complex with a four-electron-donating alkyne ligand was obtained in these reactions. We have also found that the related coordinatively unsaturated species [Mo(CO)(dppe)$_2$], generated in situ from [Mo(CO)(dmf)(dppe)$_2$], readily undergoes oxidative addition of 1-alkynes.[28] Considering the high ability of the electron-rich Mo(0) fragment {Mo(dppe)$_2$} to activate CH bonds, the formation of complex **2** from **1** as the thermally stable product is quite exceptional.

In the cyclic voltammogram, complex **2** showed an irreversible oxidation wave at −0.57 V (vs [Cp$_2$Fe]/[Cp$_2$Fe]$^+$; Cp = η^5-C$_5$H$_5$) in THF, but no reduction wave was observed. Thus, we have investigated the reaction of complex **2** with the oxidant [Cp$_2$Fe][BF$_4$]. The reaction with 2 equiv of [Cp$_2$Fe][BF$_4$] in THF led to the oxidation of the molybdenum center to give the Mo(II) acetylene complex *trans*-[MoF(HC≡CH)(dppe)$_2$][BF$_4$] (**3**) in 82% yield,[21] in which the acetylene ligand behaves as a four-electron donor.[29] Use of 1 equiv of [Cp$_2$Fe][BF$_4$] resulted in the formation of a mixture of **2** and **3**. The reaction of **2** with excess amounts of HBF$_4$·OEt$_2$ also gave **3** in 73% yield along with H$_2$ gas (57% yield).

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(21) Preparation of **2**: **1** (94.9 mg, 0.100 mmol) and HC≡CLi·en (92.1 mg, 1.00 mmol) were dissolved in THF (3 mL), and the mixture was stirred at 50 °C for 2 h. During this period, the color of the solution changed from orange to black. The resulting solution was filtered, and layering the THF solution with hexane afforded a black solid of **2** (29.4 mg, 32% yield). ^{1}H NMR (toluene-d_8): δ 2.21−2.53 (m, 8H, CH$_2$ of dppe), 6.35−7.90 (m, 40H, Ph of dppe), 10.18 (d, 2H, J_{PH} = 12.4 Hz, C$_2$H$_2$). ^{13}C{^{1}H} NMR (C$_4$D$_8$O): δ 171.0 (t, J_{CP} = 15.9 Hz, C$_2$H$_2$). ^{31}P{^{1}H} NMR (C$_4$D$_8$O): δ 95.8 (t, J_{PP} = 24 Hz), 99.1 (t, J_{PP} = 24 Hz). Anal. Calcd for C$_{54}$H$_{50}$MoP$_4$: C, 70.59; H, 5.48. Found: C, 70.38; H, 5.56. Data for the complex $\mathbf{3}\cdot 1.5CH_2Cl_2$ are as follows. ^{1}H NMR (CDCl$_3$): δ 2.77, 2.92 (br, 4H each, CH$_2$ of dppe), 6.75−7.34 (m, 40H, Ph of dppe), 11.49 (s, 2H, C$_2$H$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 225.5 (br, C$_2$H$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.3 (d, J_{PF} = 34 Hz). Anal. Calcd for C$_{55.5}$H$_{53}$BCl$_3$F$_5$MoP$_4$: C, 57.86; H, 4.64. Found: C, 57.98; H, 4.47. Preparation of **4**: to a solution of **2** (139.4 mg, 0.152 mmol) in THF (3 mL) and MeCN (0.3 mL) was added [Cp$_2$Fe][BF$_4$] (82.9 mg, 0.304 mmol) at room temperature, and the mixture was stirred for 3 h at room temperature. During this period, the color of the solution changed from black to dark green. Na[OTf] (261.5 mg, 1.52 mmol) was added to the resultant solution, and the mixture was stirred for a further 2 h at room temperature. Then the mixture was evaporated under vacuum, and the residual green solid was extracted with CH$_2$Cl$_2$. Further recrystallization from MeCN/ether deposited green crystals of **4** (161.9 mg, 82% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 0.70 (s, 3H, MeCN), 2.26 (m, 1H, CHP), 2.46 (s, 3H, MeCN), 1.71−3.73 (m, 8H, CH$_2$ of dppe), 6.75−7.34 (m, 40H, Ph of dppe), 11.36 (br d, 1H, CH, J_{PH} = 29.2 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 14.7 (s), 38.1 (m), 59.4 (m), 72.4 (m). IR (KBr, cm^{-1}): 2313 (w, CN), 2282 (w, CN). Anal. Calcd for C$_{60}$H$_{56}$F$_6$MoN$_2$O$_6$P$_4$S$_2$: C, 55.47; H, 4.34; N, 2.16. Found: C, 55.26; H, 4.36; N, 2.21.

(22) At room temperature, each acetylene proton is considered to have observable coupling only to the axial P atom located roughly *trans* to the acetylene CH, while in the high-temperature limit the two axial P atoms exhibit coupling to the acetylene proton with the averaged *J* values.

(23) Crystals of $\mathbf{2}\cdot C_7H_8$ suitable for X-ray diffraction study were obtained by recrystallization from C$_7$H$_8$/hexane. Crystal data for $\mathbf{2}\cdot C_7H_8$: C$_{61}$H$_{58}$MoP$_4$, M_r = 1010.96, triclinic, space group $P\bar{1}$, a = 12.100(3) Å, b = 13.665(3) Å, c = 17.400(5) Å, α = 72.38(2)°, β = 75.45(2)°, γ = 74.75(2)°, V = 2599(1) Å^3, Z = 2, D_{calcd} = 1.292 g cm^{-3}, $F(000)$ = 1052.00, μ(Mo Kα) = 4.13 cm^{-1}, R = 0.046, R_w = 0.038 for 5279 reflections with $I > 3\sigma(I)$. The acetylenic hydrogen atoms (H(1), H(2)) were found in the final difference Fourier map.

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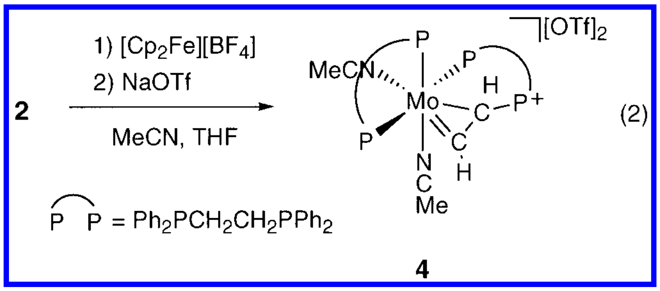
On the other hand, when the oxidation with $[Cp_2Fe][BF_4]$ was carried out in THF−MeCN, nucleophilic attack of a phosphorus atom in dppe ligands on the acetylenic carbon took place to give the novel metallacyclopropene (η^2-vinyl) complex $[Mo(\eta^3\text{-}CHCHPPh_2CH_2CH_2PPh_2\text{-}C,C',P)(MeCN)_2(dppe)][OTf]_2$ (**4**; OTf = OSO_2CF_3) in 82% yield after anion metathesis with NaOTf (eq 2).[21] The ^1H NMR spectrum of **4** exhibited a broad doublet at δ 11.36 (J_{PH} = 29.2 Hz) as well as a multiplet at δ 2.26 assignable to the metallacyclopropene moiety. The molecular structure of **4** was established by X-ray crystallography to confirm the formation of the η^2-vinyl−phosphine ligand (Figure 2).[30] The cation has a distorted-octahedral structure with the two MeCN ligands in mutually *cis* positions. The Mo(1)−C(1) (1.901(9) Å) and Mo(1)−C(2) (2.226(9) Å) distances correspond to a Mo=C double bond and a Mo−C single bond, respectively, and these parameters support the metallacyclopropene structure.[3] Although the formation of metallacyclopropene ligands by direct nucleophilic addition of phosphines and phophites to alkyne ligands has been known for some group 6 alkyne complexes,[31−33] the coupling reaction between a coordinated alkyne and a coordinated phosphine has not been described. Further studies on the reactivities of **2** are now under way.



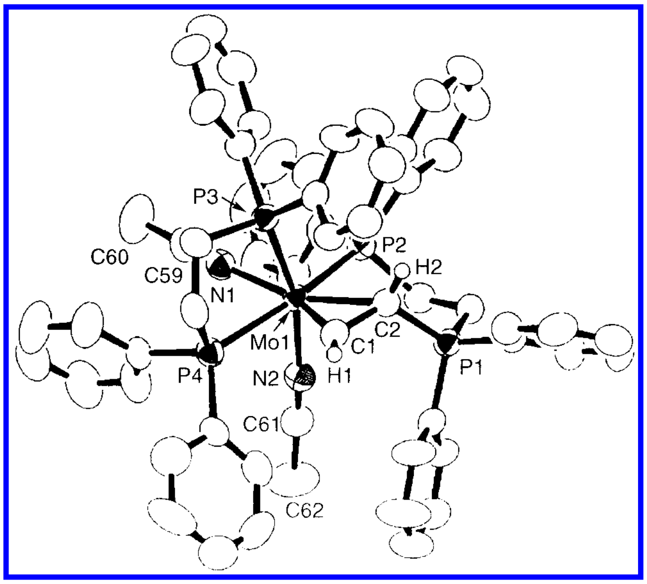


Figure 2. Molecular structure of the cationic part of **4**. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Mo(1)−P(2), 2.546(3); Mo(1)−P(3), 2.473(3); Mo(1)−P(4), 2.500(3); Mo(1)−N(1), 2.200(8); Mo(1)−N(2), 2.181(8); Mo(1)−C(1), 1.901(9); Mo(1)−C(2), 2.226(9); P(1)−C(2), 1.776(8); C(1)−C(2), 1.44(1); C(1)−Mo(1)−C(2), 39.8(3); Mo(1)−C(1)−C(2), 82.4(6); Mo(1)−C(2)−P(1), 123.3(4); Mo(1)−C(2)−C(1), 57.8(5); P(1)−C(2)−C(1), 122.5(7).

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Supporting Information Available: Text giving full experimental procedures and characterization data for the reported complexes and tables giving details of data collection, structure solution, and refinement, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for $\mathbf{2}\cdot C_7H_8$ and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Crystal data for **4**: $C_{60}H_{56}F_6MoN_2O_6P_4S_2$, M_r = 1299.06, monoclinic, space group $P2_1/c$, a = 10.294(5) Å, b = 23.357(7) Å, c = 24.868(6) Å, β = 95.82(4)°, V = 5948(3) Å^3, Z = 4, D_{calcd} = 1.450 g cm^{-3}, $F(000)$ = 2664.00, μ(Mo Kα) = 4.68 cm^{-1}, R = 0.067, R_w = 0.068 for 6567 reflections with $I > 3\sigma(I)$. The hydrogen atoms (H(1), H(2)) of the metallacyclopropene ring were found in the final difference Fourier map.

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