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A Triply Bonded Dimolybdenum Hydride Complex with Acid, Base and Radical Activity

Celedonio M. Alvarez,[†] M. Angeles Alvarez,[†] M. Esther García,[†] Alberto Ramos,[†] Miguel A. Ruiz,*[,†] Maurizio Lanfranchi,[‡] and Antonio Tiripicchio[‡]

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universitá di Parma, Parco Area delle Scienze 17/A, I-43100 Parma, Italy

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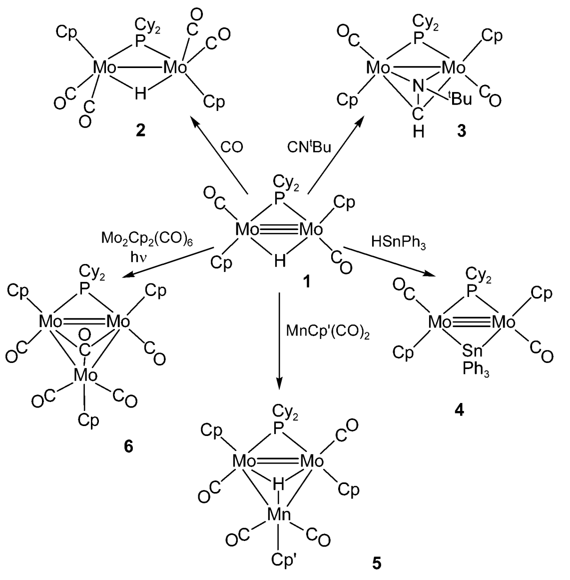
Summary: The triply bonded complex [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2$] (Cp = η^5-C_5H_5) reacts readily at room temperature with a great variety of simple molecules, resulting in diverse processes, as illustrated by its reactions with CO (addition), CN^{t}Bu (insertion), and $HSnPh_3$ (H_2 elimination). This unsaturated hydride also easily incorporates 17e [$MoCp(CO)_3$] or 16e [$MnCp'(CO)_2$] metal fragments to give 46e heterometallic clusters (Cp′ = η^5-C_5H_4Me).

Organometallic compounds having hydride ligands across metal−metal bonds of formal order (BO) higher than 1 are usually very active species which react under mild conditions with a great variety of molecules to give products that cannot be prepared through other routes. This is well illustrated by the rich chemistry developed around the complexes [$Os_3(\mu\text{-}H)_2(CO)_{10}$],[1] [$Re_2(\mu\text{-}H)_2(CO)_8$],[2] and [$Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)$][3] ($L_2$ = $(EtO)_2POP(OEt)_2$, $Ph_2PCH_2PPh_2$), all of which display an unsaturated $M_2(\mu\text{-}H)_2$ moiety with a formal BO = 2. Recently, we reported the synthesis of the 30e hydride [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2$] (**1**; Cp = η^5-C_5H_5),[4] for which a formal BO = 3 can be formulated according to the effective atomic number rule. Precedents for this triply bonded complex are limited to the monocarbonyls [$M_2Cp_2^*(\mu\text{-}H)_2(\mu\text{-}CO)$] (Cp* = C_5Me_5; M = Ru,[5a,b] Os[5c]) and the cations [$W_2Cp_2(\mu\text{-}H)(CO)_2(\mu\text{-}R_2PCH_2PR_2)$]$^+$ (R = Me, Ph),[6] the chemistry of which has not been yet explored. A formal BO = 3 can also be formulated for the polyhydride compounds [$M_2Cp^*_2(\mu\text{-}H)_4$] (M = Fe, Ru), which are also highly unsaturated and reactive molecules.[7] According to theoretical calculations, however, the degree of direct M−M interaction is very low in the latter polyhydride dimers,[8a] as was also calculated for those compounds having a doubly bonded $M_2(\mu\text{-}H)_2$ moiety.[8b] The situation is clearly different in the case of compound **1**, where the number of hydride atoms is lower than the formal BO. Thus, it is expected that a considerable electron density remains at the intermetallic region in this unsaturated compound, which should provide it with a significant electron-donor ability. As will be shown, this preliminary study on the reactivity of compound **1** reveals that, in addition to the acidic behavior expected from an unsaturated molecule, compound **1** can also act as an electron donor and a radical trap, thus allowing for the rational synthesis of heterometallic clusters (Scheme 1).

Scheme 1



Experimental evidence for the presence of a strong direct Mo−Mo interaction in **1** comes from its short intermetallic separation (2.528(2) Å; Figure 1),[9] which

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* To whom correspondence should be addressed. E-mail: mara@fq.uniovi.es.

[†] Universidad de Oviedo.

[‡] Universitá di Parma.

(1) (a) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859. (b) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

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(9) X-ray data for **1**: dark brown crystals, monoclinic (*C*2/*c*), a = 35.081(12) Å, b = 8.798(3) Å, c = 16.104(6) Å, β = 103.27(2)°, V = 4838(3) Å^3, T = 293 K, Z = 8, R = 0.0585 (observed data with $I > 2\sigma(I)$), GOF = 0.874.

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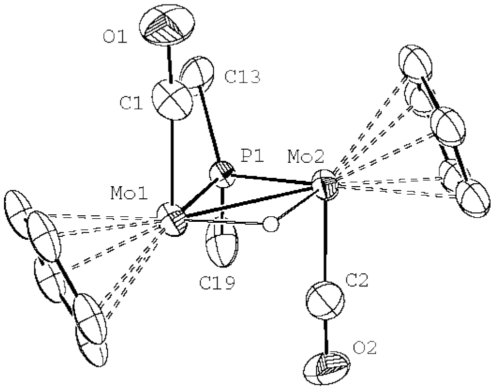

Figure 1. ORTEP diagram of compound **1**, with H atoms and Cy groups omitted for clarity, except the C^1 atoms and the hydride ligand. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.528(2), Mo(1)−P(1) = 2.382(3), Mo(2)−P(1) = 2.386(3), Mo(1)−C(1) = 1.918(14), Mo(2)−C(2) = 1.901(7); C(1)−Mo(1)−Mo(2) = 79.7(4), C(2)−Mo(2)−Mo(1) = 80.1(2).

is comparable to the value found for the unbridged triple bond in $[Mo_2Cp_2(CO)_4]$ (2.4477(12) Å)[10a] and is ca. 0.7 Å shorter than the values found for saturated $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PR}_2)(CO)_4]$ complexes having the same types of bridging ligands.[10b] As expected for a triply bonded complex, compound **1** reacts rapidly with simple ligands such as CO and phosphines to give the corresponding electron-precise derivatives, e.g. $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_4]$ (**2**),[11] from **1** and CO (Scheme 1).

Compound **1** reacts at room temperature with 1-alkynes or isocyanides to give insertion products. In the latter reaction, insertion occurs specifically to give a formimidoyl ligand (HCNR). An X-ray analysis on the ${}^tBu$ derivative **3** (Figure 2)[12,13] revealed that the HCNR ligand displays an unusual[14] $\mu\text{-}\eta,\kappa{:}\,\eta,\kappa$ coordination mode which makes it a 5e donor, thus yielding a 34e count for the complex. In agreement with this, the Mo−Mo and C−N lengths have values close to the expected figures for the corresponding single bonds.

Compound **1** reacts at room temperature with simple molecules having E−H bonds (E = S, P, Sn, etc.), this resulting in the intermolecular elimination of H_2 and replacement of the hydride ligand by the E fragment. In this way, new unsaturated molecules inaccessible through conventional routes can be prepared. For example, the reaction of **1** with $HSnPh_3$ gives selectively $[Mo_2Cp_2(\mu\text{-SnPh}_3)(\mu\text{-PCy}_2)(CO)_2]$ (**4**),[15] which is the first complex displaying a stannyl group bridging two metal atoms. The closest precedents for **4** are the clusters $[Pt_3(\mu\text{-Ph}_2PCH_2PPh_2)_3(\mu_3\text{-SnMe}_2X)]PF_6$ (X = H, $OPOF_2$),[16] where the stannyl group bridges the metal triangle. Compound **4** is formally a 30e species, which is consistent with its short Mo(1)−Mo(2) distance (2.5743(7) Å; Figure 3),[17] only ca. 0.05 Å longer than that in **1**, and also consistent with its chemical behavior (rapid addition of ligands), currently under study.

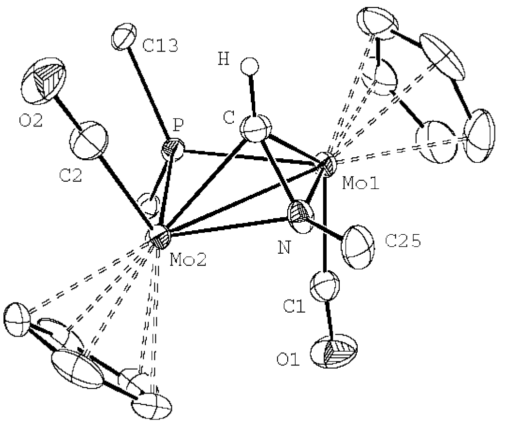

Figure 2. ORTEP diagram of compound **3**, with H atoms, Cy, and ${}^tBu$ groups omitted for clarity, except the C^1 atoms and formimidoyl H atom. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.883(2), Mo(1)−P = 2.416(2), Mo(2)−P = 2.436(2), Mo(1)−C(1) = 1.959(6), Mo(1)−C = 2.101(6), Mo(1)−N = 2.187(4), Mo(2)−C(2) = 1.914(6), Mo(2)−C = 2.115(6), Mo(2)−N = 2.157(4), C−N = 1.388(7); C(1)−Mo(1)−Mo(2) = 80.4(2), C(2)−Mo(2)−Mo(1) = 111.5(2).

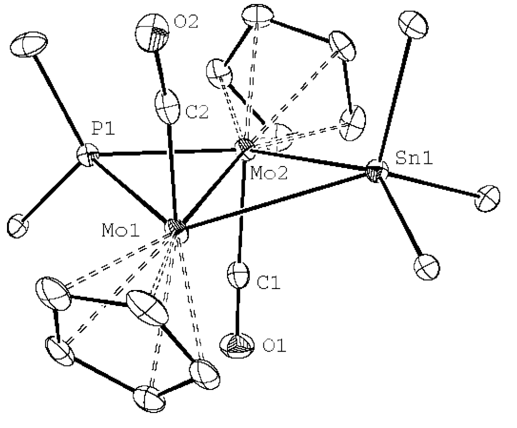

Figure 3. ORTEP diagram of compound **4**, with H atoms and Cy and Ph rings omitted for clarity, except the C^1 atoms. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.5743(7), Mo(1)−P(1) = 2.385(1), Mo(2)−P(1) = 2.368(1), Mo(1)−Sn(1) = 2.9139(7), Mo(2)−Sn(1) = 2.9244(7), Mo(1)−C(2) = 1.946(6), Mo(2)−C(1) = 1.922(5); C(1)−Mo(2)−Mo(1) = 71.2(2), C(2)−Mo(1)−Mo(2) = 90.50(14).

Compound **1** is also very reactive toward different metal fragments, which makes it an useful intermediate in the synthesis of heterometallic clusters. Two main reaction pathways have been discovered so far, both

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(11) García, M. E.; Riera, V.; Ruiz, M. A.; Rueda, M. T.; Sáez, D. *Organometallics* **2002**, *21*, 5515.

(12) Selected spectroscopic data for **3**: $\nu(CO)$ (CH_2Cl_2) 1851(m, sh), 1823 (vs) cm^{-1}; ${}^{31}P\{{}^1H\}$ NMR (CD_2Cl_2) δ 155.2 ppm; ${}^1H$ NMR (CD_2Cl_2) δ 3.72 ppm (d, $J_{HP} = 1.5$ Hz, 1H, HCN); ${}^{13}C\{{}^1H\}$ NMR (C_6D_6) δ 63.6 ppm (d, $J_{CP} = 33$, HCN).

(13) X-ray data for **3**: yellow-orange crystals, triclinic ($P\bar{1}$), a = 10.100(6) Å, b = 11.745(7) Å, c = 13.815(9) Å, α = 105.90(2)°, β = 98.26(2)°, γ = 107.56(2)°, V = 1456.2(15) $Å^3$, T = 293 K, Z = 2, R = 0.0578 (observed data with $I > 2\sigma(I)$), GOF = 1.072.

(14) We have found only one previous example of this coordination mode, in a ditantalum complex: Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **1997**, *36*, 896.

(15) Selected spectroscopic data for **4**: $\nu(CO)$ (CH_2Cl_2) 1864 (m), 1809 (vs) cm^{-1}; ${}^{31}P\{{}^1H\}$ NMR (CD_2Cl_2) δ 248.6 ppm (s, $J_{^{117}SnP} \approx J_{^{119}SnP} = 86$).

(16) (a) Douglas, G.; Jennings, M. C.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1989**, 159. (b) Jennings, M. C.; Schoettel, G.; Roy, S.; Puddephatt, R. J. *Organometallics* **1991**, *10*, 580.

(17) X-ray data for **4**: dark brown crystals, triclinic ($P\bar{1}$), a = 8.974(2) Å, b = 12.207(3) Å, c = 17.457(4) Å, α = 94.374(4)°, β = 97.325(4)°, γ = 95.911(4)°, V = 1878.9(8) $Å^3$, T = 120 K, Z = 2, R = 0.0387 (observed data with $I > 2\sigma(I)$), GOF = 1.077.

leading to unsaturated 46e trinuclear clusters. The first one involves the addition of 16e metal fragments to give unusual hydrido-bridged derivatives; e.g., **1** and [MnCp′(CO)$_2$(THF)] (Cp′ = C_5H_4Me) give [MnMo$_2$-(μ_3-H)(μ-PCy$_2$)(CO)$_4$] (**5**),[18] thus illustrating the electron-donor ability of the unsaturated hydride complex **1**. Incidentally, we note that compound **5** seems to be the first reported Mo$_2$Mn cluster with an electron count of 46.[19] The second reaction pathway involves the replacement of the bridging hydride in **1** by a photogenerated 17e metal fragment, as found in the reaction of **1** with [Mo$_2$Cp$_2$(CO)$_6$] under visible light irradiation to give [Mo$_3$Cp$_3$(μ-PCy$_2$)(μ_3-CO)(CO)$_4$] (**6**).[20] Similar reactions can be used to incorporate transition metals such as W, Re, Ru, or Co and are currently under study. An X-ray analysis of **6** revealed the presence of a near-isosceles Mo$_3$ triangle with the shorter edge bridged by the PCy$_2$ group (Figure 4).[21] The intermetallic distances are indicative of the presence of rather localized single (Mo(3)−Mo(2) and Mo(3)−Mo(1)) and double bonds (Mo(1)−Mo(2)) for this 46e cluster, which also displays an asymmetric triply bridging carbonyl ligand.

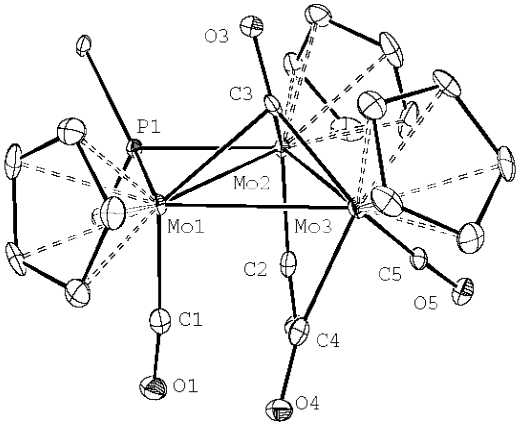

Figure 4. ORTEP diagram of compound **6**, with H atoms and Cy rings omitted for clarity, except the C^1 atoms. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.7428(12), Mo(1)−Mo(3) = 3.0846(11), Mo(2)−Mo(3) = 3.0935(10), Mo(1)−P(1) = 2.399(2), Mo(2)−P(1) = 2.398(2), Mo(3)−C(3) = 2.042(6), Mo(3)−C(5) = 1.966(6), Mo(1)−C(3) = 2.275(6), Mo(2)−C(3) = 2.197(6); Mo(3)−C(3)−O(3) = 139.9(5).

In summary, we have shown that the triply bonded hydride complex **1** has a remarkably versatile chemical behavior and reacts at room temperature with a great variety of molecules to give derivatives that are not accessible by conventional routes. This includes the rational design of unsaturated heterometallic clusters and the synthesis of complexes promoting unusual coordination modes for simple organic molecules.

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Supporting Information Available: Text and tables giving experimental procedures, spectroscopic data for new compounds, and crystallographic data for compounds **1**, **3**, **4,** and **6**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Selected spectroscopic data for **5**: ν(CO) (CH$_2$Cl$_2$) 1915 (vs), 1875 (m, sh), 1851 (s), 1833 (m, sh) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 167.5 ppm; ^{1}H NMR (C$_6$D$_6$) δ 5.13 (s, 10H, Cp), 4.28 (s, 1H, C$_5$H$_4$), 4.19 (s, 2H, C$_5$H$_4$), 4.13 (s, 1H, C$_5$H$_4$), −15.82 (s, 1H, μ-H) ppm.

[19] We are only aware of one other compound displaying a Mo$_2$Mn triangle, it being electron precise: Adams, R. D.; Kwon, O. S. *Inorg. Chem.* **2003**, *42*, 6175.

[20] Selected spectroscopic data for **6**: ν(CO) (CH$_2$Cl$_2$) 1954 (vs), 1915 (m), 1890 (m), 1866 (m), 1814 (w) cm^{-1}; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 178.3 ppm; ^{1}H NMR (CDCl$_3$) δ 5.31 (s, 5H, Cp), 5.07 (s, 10H, Cp) ppm.

[21] X-ray data for **6**: black crystals, monoclinic ($P2_1/n$), a = 9.704(3) Å, b = 22.494(6) Å, c = 14.465(4) Å, β = 109.17(3)°, V = 2982.4(15) Å^3, T = 120 K, Z = 4, R = 0.0514 (observed data with $I > 2\sigma(I)$), GOF = 1.12.