4934 *Organometallics* **2002,** *21,* 4934−4938

The Combination of Organometallic $\{Mo(\eta^3\text{-allyl})(CO)_2(phen)\}$ Fragments and Hard Aquo and Hydroxo Ligands: Controlled Synthesis and Structural Characterization

Dolores Morales, M. Elena Navarro Clemente,† Julio Pérez,* Lucía Riera, and Víctor Riera

Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC,
33071 Oviedo, Spain

Daniel Miguel

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid,
47071 Valladolid, Spain

Received May 13, 2002

The reaction of $[Mo(\eta^3\text{-}C_3H_4\text{-Me-2})Cl(CO)_2(phen)]$ with $NaBAr'_4$ ($Ar' = 3,5$-bis(trifluoromethyl)phenyl) and H_2O allowed the isolation of the aquo complex $[Mo(\eta^3\text{-}C_3H_4\text{-Me-2})(OH_2)(CO)_2(phen)]BAr'_4\cdot 2Et_2O$ (**1**). Deprotonation of **1** afforded a neutral monomeric hydroxo compound isolated as $[\{Mo(\eta^3\text{-}C_3H_4\text{-Me-2})(OH)(CO)_2(phen)\}_2(\mu\text{-}H_2O)]$ (**2**), which could be also obtained by reaction of $[Mo(\eta^3\text{-}C_3H_4\text{-Me-2})Cl(CO)_2(phen)]$ with KOH in a biphasic CH_2Cl_2/H_2O medium. The reaction of **1** and **2** afforded the binuclear hydroxo-bridged compound $[\{Mo(\eta^3\text{-}C_3H_4\text{-Me-2})(CO)_2(phen)\}_2(\mu\text{-}OH)]BAr'_4$ (**3b**) via nucleophilic substitution of water by the hydroxo ligand.

Introduction

Hard aquo and hydroxo ligands are prominent in classical coordination chemistry due to the hard nature of the metal fragments and to the widespread use of water as solvent. In the organometallic chemistry of transition metal fragments in low oxidation state, on the other hand, complexes with these ligands are relatively rare.[1] Complexes with ligands both hard (aquo, hydroxo) and soft (carbonyl and allyl are the ones relevant to the work described here) bound to the same metal center represent a borderline situation between Werner-type complexes and organometallic compounds. We have recently reported the synthesis and preliminary reactivity studies of the new alkoxo complexes $[Mo(\eta^3\text{-allyl})(OR)(CO)_2(N{-}N)]$ ($N{-}N$ = bipyridine or phenanthroline).[2] As a continuation of these studies, we sought to prepare the analogous hydroxo derivatives.[3] Examples of complexes containing $\{Mo(\eta^3\text{-allyl})(CO)_2\}$ fragments bridged by hydroxo groups are known;[4] however, monometallic compounds of this kind have not been reported. In fact, and despite the extensive studies conducted on the chemistry of Mo(II) carbonyl compounds,[5] mononuclear hydroxo complexes remain unknown, and the first mononuclear organometallic compound of Mo(II) (without carbonyls) containing a terminal hydroxo ligand, namely, $[Mo(\eta^5\text{-}C_5H_5)(OH)(PMe_3)_2]$, has been reported only recently.[6] On the other hand, in a recent exploration of the catalytic activity of the Lewis-acidic fragment $\{Mo(\eta^3\text{-allyl})(CO)_2(phen)\}^+$ (phen = 1,10-phenanthroline) we found evidence suggesting the

---

* Correspondence author. E-mail: japm@sauron.quimica.uniovi.es.

† Permanent address: ESIQIE-IPN, Edificio 6, 6217 UPALM, D.F., Mexico.

(1) Metal aquo complexes: (a) Hung, Y.; Kung, W.-J.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457. (b) Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Burgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358. (c) Raab, K.; Olgemoeller, B.; Schloter, K.; Beck, W. J. *J. Organomet. Chem.* **1981,** *214*, 81. (d) Laurenczy, G.; Helm, L.; Ludi, A.; Merbach, A. *Helv. Chim. Acta* **1991**, *74*, 1236. (e) Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramblich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1994**, 2815. (f) Funaioli, T.; Cavazza, C.; Marchetti, F.; Fachinetti, G. *Inorg. Chem.* **1999**, *38*, 3361. (g) Crane, T. W.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **2000**, *39*, 1081, and references therein. Metal hydroxo complexes: See ref 1g and: (h) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (i) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895. (j) Grushin, V. V.; Alper, H. *Organometallics* **1996**, *15*, 5242. (k) Tahmassebi, S. K.; McNeil, W. S.; Mayer, J. M. *Organometallics* **1997**, *16*, 5342. (l) Boncella, J. M.; Eve, T. M.; Rickman, B.; Abboud, K. A. *Polyhedron* **1998**, *17*, 725. (m) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6826. (n) Poli, R.; Quadrelli, E. A. *New J. Chem.* **1998**, *22*, 435. (o) MacGregor, S. A.; MacQueen, D. *Inorg. Chem.* **1999**, *38*, 4868. (p) Li, J. J.; Li, W.; James, A. J.; Holbert, T.; Sharp, T. P.; Sharp, P. R. *Inorg. Chem.* **1999**, *38*, 1563. For a rare example of chromium(0) hydroxo carbonyl complexes see: McNeese, T. J.; Mueller, T. E.; Wierda, D. A.; Darensbourg, D. J.; Delord, T. J. *Inorg. Chem.* **1985**, *24*, 3465.

(2) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1750.

(3) For a recent review containing hydroxo compounds see: Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44.

(4) (a) Murdoch, H. D.; Henzi, R. *J. Organomet. Chem.* **1966**, *5*, 552. (b) Prout, K.; Couldwell, M. C. *Acta Crystallogr.* **1977**, *B33*, 2146. (c) Breakell, K. R.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 139. (d) Lush, S.-F.; Wang, S.-H.; Lee, G.-H.; Peng, S.-M.; Wang, S.-L.; Liu, R.-S. *Organometallics* **1990**, *9*, 1862. (e) Borgmann, C.; Limberg, C.; Kaifer, E.; Pritzkow, H.; Zsolnai, L. *J. Organomet. Chem.* **1999**, *580*, 214. (f) Balzarek, C.; Weakley, T. J. R.; Kuo, L. Y.; Tyler, D. R. *Organometallics* **2000**, *19*, 2927. (g) Borgmann, C.; Limberg, C.; Cunskis, S.; Kircher, P. *Eur. J. Inorg. Chem.* **2001**, 349.

(5) Baker, P. K. *Adv. Organomet. Chem.* **1995**, *40*, 45

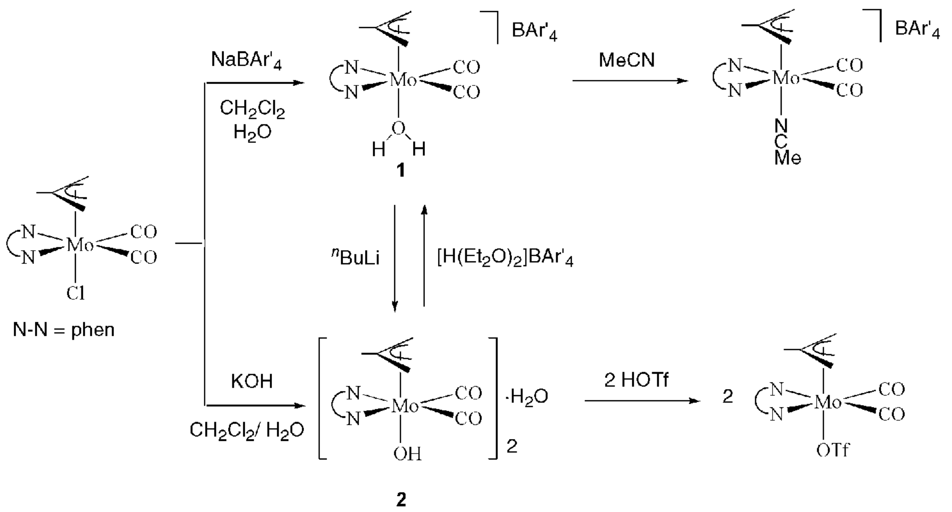
(6) (a) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A. *Chem. Commun.* **1997**, 889. (b) Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Quadrelli, E. A. *J. Chem. Soc., Dalton Trans.* **1999**, 497.

10.1021/om0203882 CCC: $22.00 © 2002 American Chemical Society
Publication on Web 10/17/2002

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 17, 2002 on http://pubs.acs.org | doi: 10.1021/om0203882

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 17, 2002 on http://pubs.acs.org | doi: 10.1021/om0203882

Scheme 1



intervention of an aquo complex.[7] The ionization of the labile bis(nitrile) compound [Mo(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$] in water to give a putative cationic aquo complex has been previously noted.[8] In organotransition metal chemistry, where water is often excluded, and, in particular, in the chemistry of molybdenum carbonyl compounds, hydroxo and aquo complexes are obtained fortuitously in most cases.[1i] The results of our search of a simple and rational approach to the synthesis of {Mo(η^3-allyl)(CO)$_2$} complexes with aquo and hydroxo ligands are summarized in what follows.

Results and Discussion

As previously reported, the reaction of [Mo(η^3-C_3H_5)(OTf)(CO)$_2$(phen)] with NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[9] in CH_2Cl_2 leads (through abstraction of triflate as NaOTf, insoluble in CH_2Cl_2) to solutions of cationic species that could include [Mo(η^3-C_3H_5)(OH$_2$)(CO)$_2$(phen)]BAr′$_4$.[7] Repeated attempts to isolate crystalline solids from these solutions were unsuccessful. However, we were pleased to find that upon addition of water (3 equiv) to solutions obtained similarly from the methallyl complex [Mo(η^3-C_3H_4-Me-2)Cl(CO)$_2$(phen)],[10] red crystals of [Mo(η^3-C_3H_4-Me-2)(OH$_2$)(CO)$_2$(phen)]BAr′$_4$·2Et$_2$O (**1**) could be obtained (see Scheme 1) upon crystallization from Et$_2$O/hexane mixtures.[11] The IR of a CH_2Cl_2 solution of these crystals was identical to that of the mother solutions. ^{1}H NMR examination of CD_2Cl_2 solutions obtained from the crystals showed a multitude of signals that could not be assigned, in agreement with extreme lability of the water ligand. When excess water was added to the NMR tube, a single species could be observed, corresponding to the aquo complex **1**. The addition of equimolar (with respect to Mo) amounts of MeCN to these solutions yielded instantaneously the compound [Mo(η^3-C_3H_4-Me-2)(NCMe)(CO)$_2$(phen)]BAr′$_4$ (see Experimental Section), confirming the high lability of the aquo ligand.

Recrystallization from Et$_2$O/hexane afforded single crystals of **1**, one of which was used for an X-ray diffraction analysis. The crystal was found to be thermally unstable due to loss of solvent; as a result, the quality of the data is limited. The results of the structure determination are displayed in Figure 1. The cation of **1** consists of a {Mo(η^3-C_3H_4-Me-2)(CO)$_2$(phen)}$^+$ moiety with a geometry resembling that found in related neutral complexes,[12] with a water molecule coordinated trans to the allyl group (Figure 1a). The coordinated water molecule makes two strong hydrogen bonds with two molecules of diethyl ether, as indicated by the distances O(3)−O(90) = 2.603(8) Å and O(3)−O(95) = 2.707(9) Å (Figure 1b).

Treatment of THF solutions of **1** with strong bases (BuLi or K[N(SiMe$_3$)$_2$]) led to IR ν_{CO} values considerably lower than those of **1**, suggesting deprotonation to give a neutral hydroxo complex. A simple method to prepare this complex was sought. The reaction of [Mo(η^3-C_3H_4-Me-2)Cl(CO)$_2$(phen)] with KOH in a biphasic CH_2Cl_2/H$_2$O system afforded the targeted hydroxo complex (Scheme 1), isolated as the hemihydrate [{Mo(η^3-C_3H_4-Me-2)(OH)(CO)$_2$(phen)}$_2$(μ-H$_2$O)] (**2**), the structure of which was determinated by single-crystal X-ray diffraction (Figure 2). Its IR was identical to that obtained by deprotonation of **1**. The IR ν_{CO} wavenumber values of **2** are close to those of related alkoxides [Mo(η^3-C_3H_5)(OR)(CO)$_2$(phen)].[2] A difference between both types of compounds is the high solubility of **2** in Et$_2$O, due to hydrogen bond interactions (the methoxo complex [Mo(η^3-C_3H_5)(OMe)(CO)$_2$(phen)] has a very small solubility in Et$_2$O). The presence of the hydroxo ligand is shown by the medium-intensity IR absorption at 3628 cm^{-1}, and a broad signal at 1.61 ppm is assigned to exchange-averaged hydroxo ligand and free water. The first coordination sphere in **2** is similar to that found in the complex [Mo(η^3-C_3H_5)(OMe)(CO)$_2$(phen)].[2] As it is shown in Figure 2, the unligated water molecule centered at

---

(7) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Corzo-Suárez, R.; García-Granda, S.; Miguel, D. *Organometallics* **2002**, *21*, 1540.

(8) Brisdon, B. J.; Cartwright, M.; Hodson, A. G. *J. Organomet. Chem.* **1984**, *277*, 85.

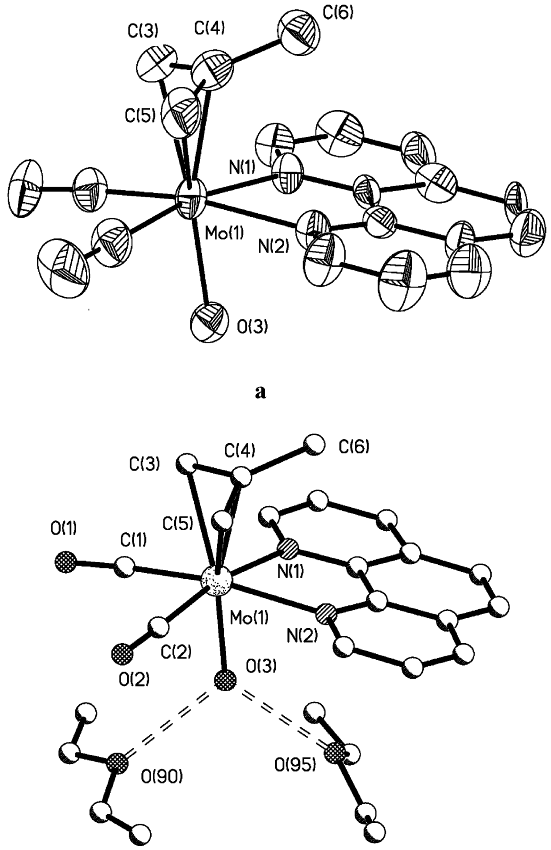
(9) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(10) Powell, P. *J. Organomet. Chem.* **1977**, *129*, 175.

(11) Note that while starting from the more labile triflato complex was necessary for the generation of cationic complexes of the η^3-C_3H_5 derivative, when the more electron-rich methallyl complex was used, chloride abstration with NaBAr′$_4$ was possible, saving the preparation of the triflato complex.

(12) Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E. *Organometallics* **2002**, *21*, 1622.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 17, 2002 on http://pubs.acs.org | doi: 10.1021/om0203882



a

b

Figure 1. (a) Thermal ellipsoid (30% probability) plot of the {Mo(η^3-C_3H_4-Me-2)(OH_2)$(CO)_2$(phen)}$^+$ cation of **1** with hydrogen atoms omitted for clarity. (b) Structure of a **1** unit. Selected bond lengths (Å) and angles (deg): Mo(1)−O(3) 2.196(7), O(3)−O(90) 2.603(8), O(3)−O(95) 2.707(9); O(90)−O(3)−O(95) 104.2(5).

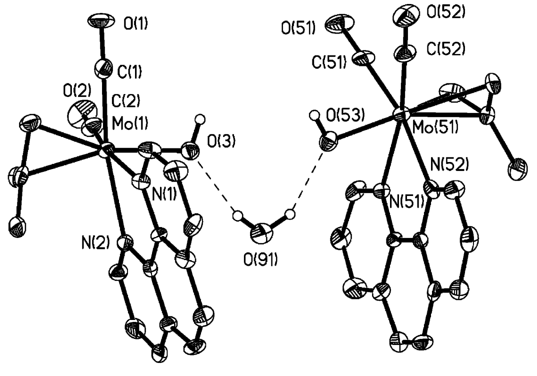


Figure 2. Thermal ellipsoid (30% probability) plot of **2**. Selected bond lengths (Å): Mo(1)−O(3) 2.055(5), Mo(51)−O(53) 2.065(5), O(3)−O(91) 2.736(9), O(91)−O(53) 2.835(8).

O(91) participates in two hydrogen bonds, making contacts of 2.736(9) and 2.835(8) Å with the hydroxy oxygen atoms O(3) and O(53), respectively, of two [Mo(η^3-C_3H_4-Me-2)(OH)$(CO)_2$(phen)] molecules, acting as donor in both hydrogen bonds.[13]

The preparation of **2** takes 24 h at room temperature with good stirring. Starting from the more labile triflato complex [Mo(η^3-C_3H_4-Me-2)(OTf)$(CO)_2$(phen)][7] did not appreciably shorten this period. Thus, the long duration of the reaction was attributed to its heterogeneous nature. Accordingly, the synthesis of related alkoxo complexes in homogeneous media is completed in minutes.[2]

Protonation of **2** with HOTf afforded [Mo(η^3-C_3H_4-Me-2)(OTf)$(CO)_2$(phen)], pressumably via protonation of the OH ligand followed by displacement of the resulting aquo ligand by the triflate anion. On the other hand, when the acid [H$(Et_2O)_2$]BAr′$_4$[9] with less coordinating anion was used, the protonation of **2** regenerated **1** (see Experimental Section).

The reaction of equimolar amounts of **1** and **2** did not lead to a simple mixture of **1** and **2** through H^+ transfer; rather, it afforded the binuclear cationic complex [{Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)}$_2$(μ-OH)]BAr′$_4$ (**3b**) (Scheme 2) through water substitution by the nucleophilic hydroxo ligand. While this kind of reaction, termed olation,[14] is believed to be common in condensation of acidic aquo cations, no precedents involving isolated aquo and hydroxo organometallic compounds are known to us. The resulting cationic complex was isolated as BAr′$_4$ salt and characterized by spectroscopy and X-ray diffraction (Figure 3) for the allyl derivative (**3a**). The cation consists of two identical {Mo(η^3-C_3H_5)$(CO)_2$(phen)} fragments, similar to those present in **1** and **2**, bridged by a single OH ligand. Formation of **3b** was also found to occur upon addition of half the stoichiometric amount of BuLi to THF solutions of **1**. A search for an alternative synthesis starting from a simple precursor revealed that complex **3a** can be conveniently prepared by reaction of [Mo(η^3-C_3H_5)(OTf)$(CO)_2$(phen)] with KOH in anhydrous THF, as detailed in the Experimental Section. A major difference between the synthetic routes to the terminal **2** and bridged **3a**,**b** hydroxo complexes is the presence of water in the former. We speculate that, under these conditions, the chloride substitution is effected by water rather than by hydroxide anion. The resulting aquo complex would then be deprotonated in the basic medium, yielding the terminal hydroxo complex **2**. Since the proton transfer is expected to be much faster than the aquation step, significant concentrations of the aquo complex would not build up, explaining why it was not detected in the IR monitoring of the reaction. On the other hand, working in water-free THF, hydroxide would substitute the chloride ligand. The resulting neutral hydroxo complex is highly soluble in THF, and as its concentration grows, it becomes competitive with free hydroxide ion (whose concentration in THF is low) as a nucleophile (through the nondissociated OH ligand) toward the remaining chloro complex, yielding the observed OH-bridged product.

Although compounds with OH bridges between {Mo(η^3-C_3H_5)$(CO)_2$} fragments are known,[4] **3a**,**b** are the first complexes with a hydroxo group as a single bridge between two molybdenum fragments. The Mo−O−Mo angle in **3a** (145.3(4)°) is, as expected, larger than in species with several OH bridges[4b,e−f] and similar to the Mo−Cl−Mo angle (134.0(1)°) in [{Mo(η^3-C_3H_5)$(CO)_2$(bipy)}$_2$(μ-Cl)]BF_4.[15] Further aspects of the reactivity of complexes **1**−**3** are under investigation in this laboratory.

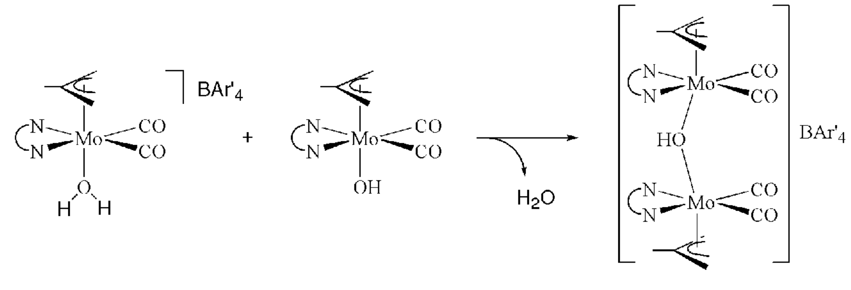
---

[13] In this context, donor means the group that formally bears the hydrogen atom.

[14] Jolivet, J. P. *Metal Oxide Chemistry and Synthesis. From Solution to Solid State;* Wiley: Chichester, 2000; p 53.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 17, 2002 on http://pubs.acs.org | doi: 10.1021/om0203882

Scheme 2



3b

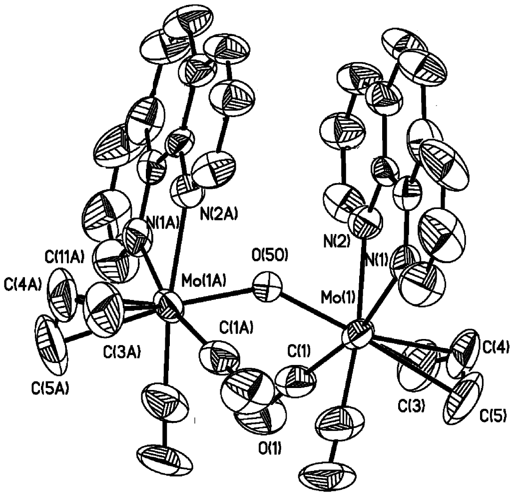


Figure 3. Thermal ellipsoid (30% probability) plot of the [{Mo(η^3-C_3H_5)(CO)$_2$(phen)}$_2$(μ-OH)]$^+$ cation of **3a** with hydrogen atoms omitted for clarity.

Experimental Section

General Procedures. All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were distilled from Na (hexane), Na/benzophenone (tetrahydrofuran), and CaH_2 (CH_2Cl_2). CD_2Cl_2 was dried over molecular sieves (4 Å) and stored over Na_2CO_3 in Young tubes in the dark. Elemental analyses were obtained using a Perkin-Elmer 240-B microanalyzer. The IR and NMR spectra were recorded on Perkin-Elmer FT 1720-X (over the range 2200−1600 cm^{-1}) and Bruker AC-200 (or AC-300) spectrometers, respectively, using TMS as internal reference for the NMR spectra. [MoCl(η^3-C_3H_4-(CH_3)-2)(CO)$_2$(phen)][10] was prepared according to literature procedures.

Atom labelings for the allyl, phenanthroline, and BAr′$_4$ groups are given in Scheme 3.

Crystal Structure Determination for Compounds 1, 2, and 3a. General Description. The crystals of **1**, **2**, and **3a** were measured on a Bruker AXS SMART 1000 diffractometer. Raw frame data were integrated with the SAINT[16] program. The structure was solved by direct methods with SHELXTL.[17] All non-hydrogen atoms were refined anisotropically. All calculations and graphics were made with SHELXTL.

Synthesis of [Mo(η^3-C_3H_4-Me-2)(OH_2)(CO)$_2$(phen)]BAr′$_4$·2Et$_2$O (1). CH_2Cl_2 (15 mL) was added to a mixture of [Mo(η^3-C_3H_4-Me-2)Cl(CO)$_2$(phen)] (0.03 g, 0.07 mmol) and NaBAr′$_4$ [9] (0.06 g, 0.07 mmol). After 15 min stirring, water (4 μL, 0.22 mmol) was added to the red solution. After 30 min stirring, the solution was filtered through diatomaceous earth. In vacuo concentration to 2 mL followed by addition of hexane (15 mL) while stirring afforded a red precipitate that was dried in vacuo. The dry solid was dissolved in diethyl ether (5 mL), and hexane (15 mL) was layered. Slow diffusion at −20 °C gave red-orange crystals of **1**. The crystals were found to be stable at room temperature under nitrogen for several days. However, decomposition, showed by darkening and a decrease in the intensity of the reflections, was observed when a single crystal was subjected to a structure determination by X-ray diffraction. When an NMR sample was prepared by dissolving these crystals in CD_2Cl_2, the spectrum showed broad, noninformative signals. However, addition of water (5 μL) to the sample led to a well-resolved spectrum given below. Yield: 0.05 g, 60%. Anal. Calcd for $C_{58}H_{49}BF_{24}MoN_2O_5$: C, 49.17; H, 3.48; N, 1.98. Found: C, 49.44; H, 3.54; N, 2.12. IR (CH_2Cl_2): 1959, 1879 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 9.29 [dd ($J_{H2,3}$ = 4.8, $J_{H2,4}$ = 1.6), 2H, $H_{2,9}$], 8.58 [dd ($J_{H4,3}$ = 7.9 Hz, $J_{H4,5}$ = 1.2 Hz), 2H, $H_{4,7}$], 7.98 [s, 2H, $H_{5,6}$], 7.93 [dd, 2H, $H_{3,8}$], 7.71 [m, 8H, H_o], 7.50 [m, 8H, H_p], 6.23 [s, 2H, H_2O], 3.37 [q (J = 7.09), 8H, Et_2O], 3.14 [s, 2H, H_s], 1.44 [s, 2H, H_a], 1.08 [t (J = 6.9), 12H, Et_2O], 0.68 [s, 3H, η^3-C_3H_4(CH_3)-2].

Synthesis of [{Mo(η^3-C_3H_4-Me-2)(OH)(CO)$_2$(phen)}$_2$(μ-H_2O)] (2). A solution of KOH (0.1 g, excess) in H_2O (0.5 mL) was added to a solution of [Mo(η^3-C_3H_4-Me-2)Cl(CO)$_2$(phen)] (0.03 g, 0.07 mmol) in CH_2Cl_2 (10 mL). After stirring for 24 h, the mixture was cooled to −78 °C and the organic phase was separated from the ice formed using filtration through a cannula tipped with filter paper. The filtered solution was concentrated in vacuo evaporation to a volume of 5 mL, layered with hexane, and placed at −30°C, affording red needles of **2**, one of which was used for the structure determination by X-ray diffraction. Yield: 0.03 g, 90%. Anal. Calcd for $C_{18}H_{16}MoN_2O_3$·0.5H_2O: C, 52.31; H, 4.14; N, 6.78. Found: C, 52.20; H, 4.40; N, 7.11. IR (THF): 1929, 1843 (ν_{CO}); (KBr): 3628 (ν_{OH}). ^{1}H NMR (CD_2Cl_2): 9.11 [dd ($J_{H2,3}$ = 5.1, $J_{H2,4}$ = 1.6), 4H, $H_{2,9}$], 8.46 [dd ($J_{H4,3}$ = 8.2 Hz, $J_{H4,5}$ = 1.6 Hz), 4H, $H_{4,7}$], 7.93 [s, 4H, $H_{5,6}$], 7.80 [dd, 4H, $H_{3,8}$], 2.98 [s, 4H, H_s], 1.61 [s br, 4H, H_2O and OH], 1.27 [s, 4H, H_a], 0.84 [s, 6H, η^3-C_3H_4(CH_3)-2].

Synthesis of [{Mo(η^3-C_3H_5)(CO)$_2$(phen)}$_2$(μ-OH)]BAr′$_4$ (3a). KOH (0.1 g, excess) was added to a solution of [Mo(η^3-C_3H_5)(OTf)(CO)$_2$(phen)][7] (0.10 g, 0.19 mmol) in THF (20 mL), and the mixture was stirred for 20 h. The garnet solution was filtered through paper-tipped cannula to eliminate the excess of KOH and evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (10 mL), and NaBAr′$_4$ (0.17 g, 0.19 mmol) was added, causing the precipitation of a white solid. After stirring for 15 min the mixture was filtered through diatomaceous earth, and the solution was concentrated in vacuo and precipitated with hexane, affording a red microcrystalline solid, which was dried in vacuo. Yield: 0.11 g, 73%. Single crystals suitable for an X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of **3a** in CH_2Cl_2 at −20 °C. Anal. Calcd for $C_{66}H_{39}BF_{24}Mo_2N_4O_5$: C, 48.73; H, 2.42; N, 3.44. Found: C, 48.98; H, 2.40; N, 3.49. IR (CH_2Cl_2): 1964,

---

[15] Curtis, M. D.; Fotinos, N. A. *J. Organomet. Chem.* **1984**, *272*, 43.

[16] SAINT+, SAX area detector integration program, Version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

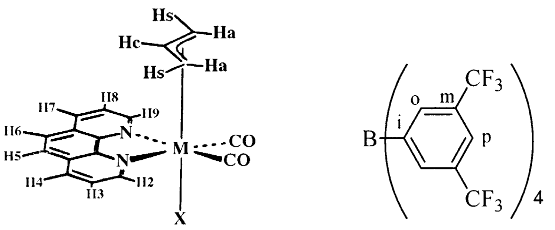
[17] Sheldrick, G. M. *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data*, Version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on October 17, 2002 on http://pubs.acs.org | doi: 10.1021/om0203882

Table 1. Crystal Data and Refinement Details for Complexes 1, 2, and 3b

	1	**2**	**3b**
formula	$C_{58}H_{47}BF_{24}MoN_2O_5$	$C_{18}H_{17}MoN_2O_{3.50}$	$C_{66}H_{38}BF_{24}Mo_2N_4O_7$
fw	1414.73	413.28	1657.69
cryst syst	monoclinic	triclinic	tetragonal
space group	$P2(1)/n$	$P\bar{1}$	$P\bar{4}c2$
a, Å	13.035(2)	11.125(7)	18.0819(6)
b, Å	13.655(3)	12.985(8)	18.0819(6)
c, Å	36.631(7)	13.782(9)	21.5706(10)
α, deg	90	106.383(12)	90
β, deg	99.132(4)	110.452(12)	90
γ, deg	90	99.849(12)	90
V, Å^3	6438(2)	1707.4(19)	7052(5)
Z	4	4	4
T, K	293(2)	299(2)	293(2)
D_c, g cm^{-3}	1.460	1.608	1.561
$F(000)$	2848	836	3292
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst size, mm	0.14 × 0.15 × 0.20	0.02 × 0.06 × 0.31	0.10 × 0.10 × 0.10
μ, mm^{-1}	0.319	0.790	0.473
scan range, deg	$1.13 \leq \theta \leq 23.28$	$1.70 \leq \theta \leq 23.40$	$1.13 \leq \theta \leq 23.26$
abs corr	SADABS	SADABS	SADABS
no. of reflns measd	28 177	7675	31 382
no. of ind reflns	9264	4925	5073
no. of data/restraints/params	9264/0/825	4925/0/449	5073/0/475
goodness-of-fit on F^2	0.983	0.947	1.019
R_1/R_{w2} [$I > 2\sigma(I)$]	0.0944/0.2168	0.0518/0.0704	0.0588/0.1321
R_1/R_{w2} (all data)	0.1972/0.2682	0.1068/0.0789	0.0997/0.1557

Scheme 3



1946, 1879, 1869 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 8.88 [dd ($J_{H2,3}$ = 5.0 Hz, $J_{H2,4}$ = 1.5), 4H, $H_{2,9}$], 8.21 [dd ($J_{H4,3}$ = 8.2), 4H, $H_{4,7}$], 7.75 [m, 8H, H−C$_o$], 7.66 [s, 4H, $H_{5,6}$], 7.57 [m, 8H, 4H-C$_p$ and 4H of phen $H_{3,8}$], 3.14 [d ($J_{Hs,c}$ = 6.5), 4H, H$_s$], 2.78 [m, 2H, H$_c$], 1.33 [d ($J_{Ha,c}$ = 9.3), 4H, H$_a$], −2.47 [s, 1H, OH]. **3a** is also obtained by reaction of the aquo complex **1** with half the stoichiometric amount of ^{n}BuLi in THF, as evidenced by the spectra of the resulting crude product. However, this method was not further studied.

Synthesis of [{Mo(η^3-C_3H_4-Me-2)(CO)$_2$(phen)}$_2$(μ-OH)]-BAr′$_4$ (3b). This compound can be prepared as described for **3a**. The following method is an alternative. CH_2Cl_2 (10 mL) was added to a mixture of **1** (0.05 g, 0.035 mmol) and **2** (0.02 g, 0.035 mmol), and the brown solution was stirred for 5 min, concentrated in vacuo to a volume of 2 mL, layered with hexane, and placed at −30 °C, affording brown-orange crystals, which were dried in vacuo. Yield: 0.05 g, 86%. Anal. Calcd for $C_{68}H_{43}BF_{24}Mo_2N_4O_5$: C, 49.35; H, 2.62; N, 3.38. Found: C, 49.52; H, 2.58; N, 3.41. IR (CH_2Cl_2): 1962 (sh), 1951, 1878 (sh), 1868 (ν_{CO}); KBr: 3700 (ν_{OH}). ^{1}H NMR (CD_2Cl_2): 8.86 [dd ($J_{H2,3}$ = 4.9, $J_{H2,4}$ = 1.5), 4H, $H_{2,9}$], 8.21 [dd ($J_{H4,3}$ = 8.2 Hz, $J_{H4,5}$ = 1.5 Hz), 4H, $H_{4,7}$], 7.76 [m, 8H, H$_o$], 7.65 [s, 4H, $H_{5,6}$], 7.59 [dd, 4H, $H_{3,8}$], 7.55 [m, 8H, H$_p$], 2.95 [s, 4H, H$_s$], 1.32 [s, 4H, H$_a$], 0.53 [s, 6H, η^3-C_3H_4(CH_3)-2], −2.62 [s br, 1H, OH].

Synthesis of [Mo(η^3-C_3H_4-Me-2)(NCMe)(CO)$_2$(phen)]-BAr′$_4$. CH_2Cl_2 (15 mL) was added to a mixture of [Mo(η^3-C_3H_4-Me-2)Cl(CO)$_2$(phen)] (0.05 g, 0.12 mmol) and NaBAr′$_4$ (0.10 g, 0.12 mmol). MeCN (0.5 mL) was added to the red solution. After 10 min stirring, the solution was filtered through diatomaceous earth, concentrated in vacuo to 2 mL, layered with hexane (15 mL), and placed at −20 °C, affording orange crystals. Yield: 0.105 g, 70%. Anal. Calcd for $C_{52}H_{30}BF_{24}MoN_3O_2$: C, 48.36; H, 2.34; N, 3.25. Found: C, 48.57; H, 2.52; N, 3.39. IR (CH_2Cl_2): 1965, 1885 (ν_{CO}). ^{1}H NMR ($CDCl_3$): 9.15 [dd ($J_{H2,3}$ = 5.1, $J_{H2,4}$ = 1.6), 2H, $H_{2,9}$], 8.38 [dd ($J_{H4,3}$ = 8.2 Hz, $J_{H4,5}$ = 1.6 Hz), 2H, $H_{4,7}$], 7.82 [dd, 2H, $H_{3,8}$], 7.75 [s, 2H, $H_{5,6}$], 7.71 [m, 8H, H$_o$], 7.50 [m, 8H, H$_p$], 3.24 [s, 2H, H$_s$], 1.89 [s, 3H, CH_3CN], 1.74 [s, 2H, H$_a$], 1.29 [s, 3H, η^3-C_3H_4(CH_3)-2].

Protonation of 2 with [H(Et$_2$O)$_2$]BAr′$_4$. A mixture of **2** (0.02 g, 0.05 mmol) and [H(Et$_2$O)$_2$]BAr′$_4$ (0.05 g, 0.05 mmol) was charged in a 5 mm NMR tube in the drybox. The tube was stoppered with a rubber septum and taken out of the box. CD_2Cl_2 (0.5 mL) was injected, causing the immediate dissolution of the solids. A ^{1}H NMR spectrum showed the formation of compound **1**. Unlike when crystals of **1** are dissolved in CD_2Cl_2 (see text) in the ^{1}H NMR spectrum obtained as described above, the signals of compound **1** can be clearly observed. We attribute this difference to the presence of some adventitious water in the extremely hygroscopic [H(Et$_2$O)$_2$]BAr′$_4$ compound.

Acknowledgment. We thank Ministerio de Ciencia y Tecnología (Projects MCT-00-BQU2000-0220, PB97-0470-C02-01) and Principado de Asturias (PR-01-GE−7) for support, and predoctoral (L.R.) and postdoctoral (D.M.) scholarships. M.E.N.C. thanks PCI-AL.E-2002, AECI (Spain), and IPN (Mexico) for a visiting professorship.

Supporting Information Available: General description of crystal structure determination for compounds **1**, **2**, and **3a**. Tables giving positional and thermal parameters and bond distances and bond angles for **1**, **2**, and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0203882