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Molybdenum Complexes with Linked Cycloheptatrienyl–Phenolate Ligands

Matthias Tamm,* Thomas Bannenberg, and Bernd Dressel

Anorganisch-Chemisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany

Roland Fröhlich[†] and Christiane Holst[†]

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstrasse 40, D-48149 Münster, Germany

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The tropylium salt (2-hydroxy-3,5-dimethylphenyl)cycloheptatrienylium tetrafluoroborate (**3**) has been synthesized in three steps from THP-protected 2,4-dimethylphenol and tropylium tetrafluoroborate, $(C_7H_7)BF_4$. In CH_2Cl_2 solution, the unexpected formation of tricyclic 2,4-dimethylbenzo[*b*]cyclohepta[*d*]furanylium tetrafluoroborate (**5**) has been observed, which must have formed from **3** by loss of H_2. **5** was characterized by an X-ray crystal structure determination and could independently be synthesized by treatment of **3** with $NaHCO_3$ to give 2,4-dimethylbenzo[*b*]cyclohepta[*d*]furan (**4**) followed by acidification with $HBF_4 \cdot Et_2O$. The arene transfer reaction of **3** with [(η-*p*-xylene)$Mo(CO)_3$] furnished the cycloheptatrienyl complex $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(CO)_3]BF_4$ (**6**), which could be converted into the chiral chelate complexes $[(\overline{OC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6})Mo(CO)(PR_3)]$ (**9a**, R = Ph; **9b**, R = *c*-C_6H_{11}; **9c**, *i*-Pr) by subsequent treatment with NaI, PR_3, and NaH. The linked cycloheptatienyl–phenolate ligand in **9a** could be protonated at the coordinated oxygen atom employing $HBF_4 \cdot Et_2O$ to yield $[(\overline{HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6})Mo(CO)(PPh_3)]BF_4$ (**10**). In **10**, the appended phenol group is coordinated in a hemilabile fashion, which allowed the introduction of 2,6-dimethylphenyl isocyanide and CO and formation of complexes $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(CO)(PPh_3)L]BF_4$ (**11**, L = XyNC; **12**, L = CO). On thermal reaction of $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(CO)_2I]$ (**7**) with dppe, the addition of the diphosphine was observed together with the simultaneous formation of the molydenum–oxygen bond to yield $[(\overline{OC_6H_2Me_2\text{-}\eta^3\text{-}C_7H_6})Mo(CO)_2(dppe)]$ (**13**), in which the cycloheptatrienyl ring has reduced its hapticity from seven to three. The pseudooctahedral complex **13** exhibits an interesting fluxional behavior in solution, which has been studied by means of variable-temperature ^{31}P and ^1H NMR spectroscopy. A $\eta^3 \rightarrow \eta^7$ hapticity reversion could be achieved by UV irradiation of a solution of **13** in THF to give the electron-rich complex $[(\overline{OC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6})Mo(dppe)]$ (**14**). **14** was readily oxidized with ferrocenium hexafluorophosphate, and the resulting paramagnetic monocationic complex **15** has been studied by means of ESR spectroscopy and X-ray diffraction. In addition, the X-ray crystal structures of complexes **9a**, **10**$\cdot 2CH_2Cl_2$, **12**, and **13** are reported.

Introduction

η-Cyclopentadienyl complexes, (η-C_5R_5)M, as well as η-arene complexes, (η-C_6R_6)M, are among the most important classes of compounds in organotransition metal chemistry.[1] In particular, the widespread use of cyclopentadienyls as organometallic ligands is due to the large number of ring-substituted cyclopentadienes, which have been synthesized since the serendipitous synthesis and discovery of ferrocene. Succesive replacement of hydrogen atoms by alkyl or aryl substituents alters the steric and electronic properties of the

* To whom correspondence should be addressed. E-mail: mtamm@uni-muenster.de.

[†] X-ray crystal structure determinations.

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Cp ring and gives rise to increased steric bulk, solubility, and stability of the resulting complexes.[2] Numerous routes to ring-substituted Cp derivatives are known to date, and stable cyclopentadienyl complexes of almost any element have been synthesized. It has recently been estimated that about 80% of all organometallic compounds of the transition metals are cyclopentadienyl complexes.[2a] Consequently, cyclopentadienyl complexes are nowadays ubiquitous and indispensable in research areas such as homogeneous catalysis,[3] organic synthesis,[4] and materials science.[5] In contrast, η-cycloheptatrienyl−transition metal complexes, (η-C_7R_7)M, have been much less thoroughly studied, and with a few exceptions, the use of cycloheptatrienyl ligands had been confined to the parent C_7H_7 system.[6] Only recently, we have been able to report on the syntheses and properties of the first heptamethylcycloheptatrienyl (CHT*) complexes[7] and of complexes derived from sterically demanding tropylium salts of the type (1,3,5-$C_7H_4R_3$)BF_4 (R = *tert*-butyl, $SiMe_3$).[8]

Another concept, which has been extremely successful, in particular in cyclopentadienyl chemistry, is ligand functionalization, whereby an additional coordinating site is linked to the periphery of the five-membered ring via a suitable bridging moiety. This prospering area has produced a large number of novel cyclopentadienyl ligands bearing pendant N-,[9,10] O-,[11] P-, As-, and S-donor groups.[12] If properly designed, these ligands can coordinate to a transition metal center in a chelating $\eta^5:\eta^1$ fashion, and several of these complexes have played a key role in homogeneous catalysis as so-called constraint-geometry catalyst systems.[3] In organometallic cycloheptatrienyl chemistry on the other hand, ligand functionalization is an almost unknown concept. To the best of our knowledge, no complexes with donor-functionalized cycloheptatrienyl ligands coordinating in a chelating $\eta^7:\eta^1$ fashion have been reported to date, whereas a few examples are known, in which the functional group is directly attached to the seven-membered ring only allowing the cycloheptatrienyl ligand to bridge two different metal centers.[13−15] For instance, lithiation of [(η-C_7H_7)Ti(η-C_5H_5)] with *n*-BuLi occurs preferentially at the seven-membered ring,[13] and the consecutive reaction with chlorodiphenylphosphine allows the selective functionalization of the cycloheptatrienyl ring to yield [(η^7-$C_7H_6PPh_2$)Ti(η-C_5H_5)], which has been used as a monodentate phosphine ligand forming bimetallic complexes.[14] Dimetalation of [(η-C_7H_7)Ti(η-C_5H_5)] can also be achieved, and the reaction with $ClPR_2$ (R = Me, Ph) produces [(η^7-$C_7H_6PR_2$)Ti(η^5-$C_5H_4PR_2$)], which can react with various metal carbonyls to produce a series of complexes with the bifunctionalized sandwich unit acting as a chelating or bridging diphosphine ligand.[15] In this respect, bimetallic sesquifulvalene derivatives can also be regarded as complexes containing cyclopentadienyl-functionalized cycloheptatrienyl ligands, and various complexes have been reported, in which the five- and seven-membered rings are coordinated in a bridging μ-$\eta^7:\eta^5$-mode.[16,17]

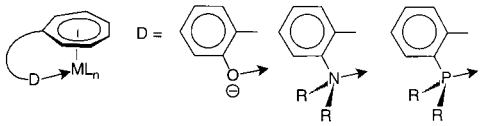

Figure 1. Cycloheptatrienyl complexes bearing pendant O-, N-, and P-donors.

We have recently started to apply the concept of ligand functionalization to cycloheptatrienyl transition metal chemistry and have already studied cycloheptatrienyl complexes bearing pendant phenolate, amine, and phosphine donor groups (Figure 1). The reasons for our interest in the development of such ligand systems are the following: First, donor functionalization can in general lead to the formation of chelate complexes of significantly enhanced stability, which can allow the preparation and isolation of complexes of previously unknown structural types and reactivities. As for instance, as coordination of the cycloheptatrienyl ring to a transition metal center is often much more difficult than the introduction of a cyclopentadienyl group, the donor group can serve as a *Trojan horse*, which binds to a metal first

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followed by the formation of the metal−carbon bonds. Second, some of the donor groups might only coordinate in a labile fashion or could be converted into hemilabile groups, which offers the possibility to reversibly provide free coordination sites for other molecules or substrates. With this contribution, we introduce for the first time the preparation of complexes containing such functionalized cycloheptatrienyl ligands and wish to report on the syntheses of a series of molybdenum complexes containing linked cycloheptatrienyl−phenolate ligands, which are capable to bind to the metal center in a chelating $\eta^7:\eta^1$-fashion (Figure 1). The *ortho*-phenylene moiety had been chosen as the bridging unit between the seven-memberd ring and the *O*-donor group, as it will lead to the formation of complexes with a very rigid, C_s symmetric ligand backbone and will additionally allow to alter their steric and electronic properties via modification of the aryl fragment.

Results and Discussion

Ligand Synthesis. Although several phenolate-functionalized cyclopentadienyl systems are known,[11] we are only aware of two related cyclopentadienyl complexes, in which the phenolate group is directly attached to the five-membered ring via its *ortho*-carbon atom.[18,19] For instance, Marks and co-workers have obtained the ligand precursor 2-(tetramethylcyclopentadienyl)-4-methylphenol by the reaction of 2-bromo-4-methylphenol with 2 equiv of *n*-butyllithium followed by addition of 2,3,4,5-tetramethyl-2-cyclopentenone.[18] Similarly, one should be able to obtain related cycloheptatriene phenol ligand precursors such as **2** by addition of a phenol derivative lithiated in the 2-position to the tropylium cation $C_7H_7^+$.[20] The reaction of doubly lithiated 2-bromo-4-methylphenol with $(C_7H_7)BF_4$, however, did not result in a clean reaction, presumably due to the fact that O-alkylation of the phenol competed with the expected C-alkylation reaction. Therefore, the starting material 2,4-dimethylphenol was treated with 3,4-dihydro-*2H*-pyran in the presence of a catalytic amount of iodotrimethylsilane to obtain the tetrahydopyranyl ether **1**.[21] *Ortho*-lithiation was achieved by the reaction of **1** with *n*-butyllithium in hexane in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), whereby the intermediate lithium salt is probably stabilized by intramolecular coordination of the THP oxygen atom (Scheme 1).[22] The addition of $(C_7H_7)BF_4$ yields, after acid-catalyzed cleavage of the THP protecting group,[23] the ligand precursor 2-(cyclohepta-2,4,6-trienyl)-4,6-dimethylphenol (**2**) as a stable colorless oil in large quantities.

As we have recently developed a method for the quantitative complexation of tropylium salts via an arene exchange reaction,[8] the cycloheptatriene **2** was not used as a ligand but was converted into the tropylium salt **3** by hydride abstraction using triphenylcarbenium tetrafluoroborate, $(Ph_3C)BF_4$. (2-Hydroxy-3,5-dimethylphenyl)cycloheptatrienylium tetrafluoroborate (**3**) was obtained as a red crystalline solid, which is stable under ambient conditions. If **3** is kept in CH_2Cl_2 solution for prolonged periods of time, however, slow formation of the tetrafluoroborate salt **5** is observed, which contains the tricyclic 2,4-dimethylbenzo[*b*]cyclohepta[*d*]-furanylium cation. The molecular structure of this cation is depicted in Figure 2. The cation is almost perfectly planar, and the mean and maximum deviations from the best plane containing all atoms C1−C15 and O are 0.012 and −0.036 Å (for C13), respectively. The bond distances and angles in the six- and seven-membered rings are all in agreement with those expected for a nearly undistorted aromatic systems (Table 1), and the structure of the cation is best presented by the Lewis formula shown in Scheme 1.

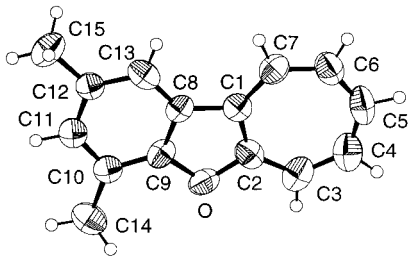
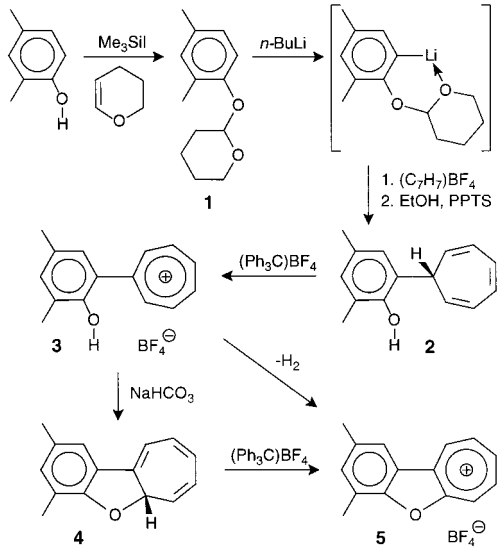


Figure 2. DIAMOND drawing of the cation in **5** with thermal ellipsoids drawn at 50% probability.

Scheme 1



5 must have formed by H_2 elimination from **3**. H_2 can also be removed succesively as a proton and a hydride via deprotonation of **3** with $NaHCO_3$ to give the neutraly charged 2,4-dimethylbenzo[*b*]cyclohepta[*d*]furan (**4**) followed by hydride abstraction to give the tricyclic furanylium salt **5**.[24] Increasing the nucleophilicity of the donor atom generally

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Table 1. Selected Bond Distances (Å) and Angles (deg) for **5**, **9a**, **10**·$2CH_2Cl_2$, **12**, **13**, and **15**

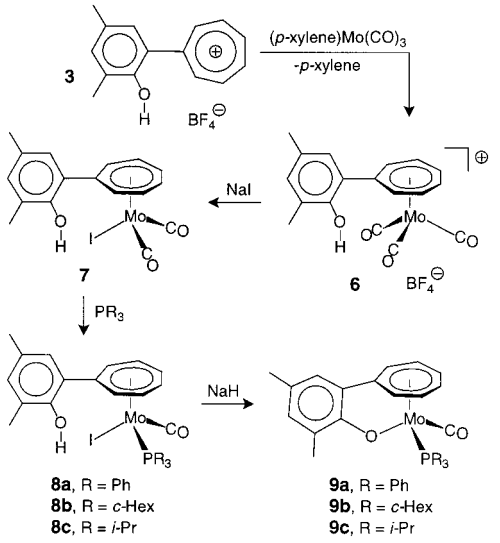
	5	9a	10·$2CH_2Cl_2$	12	13	15
C1−C2	1.402(12)	1.407(3)	1.409(12)	1.412(4)	1.453(3)	1.418(9)
C2−C3	1.381(12)	1.410(4)	1.363(14)	1.409(4)	1.341(3)	1.402(9)
C3−C4	1.365(13)	1.406(4)	1.404(13)	1.413(4)	1.435(4)	1.411(10)
C4−C5	1.386(14)	1.399(4)	1.426(13)	1.390(4)	1.341(4)	1.396(11)
C5−C6	1.390(14)	1.408(4)	1.403(14)	1.424(4)	1.448(4)	1.431(11)
C6−C7	1.378(12)	1.396(3)	1.404(12)	1.393(4)	1.407(3)	1.369(9)
C1−C7	1.394(12)	1.422(3)	1.422(11)	1.434(3)	1.430(3)	1.453(10)
C1−C8	1.441(12)	1.486(3)	1.494(13)	1.505(4)	1.493(3)	1.488(9)
Mo−C1		2.226(2)	2.221(8)	2.355(2)	2.393(2)	2.203(6)
Mo−C2		2.286(2)	2.259(8)	2.343(2)		2.274(6)
Mo−C3		2.287(3)	2.288(8)	2.307(2)		2.270(7)
Mo−C4		2.313(3)	2.295(8)	2.357(3)		2.327(7)
Mo−C5		2.300(2)	2.297(8)	2.331(3)		2.287(7)
Mo−C6		2.315(2)	2.312(8)	2.343(3)	2.455(2)	2.292(7)
Mo−C7		2.237(2)	2.305(7)	2.344(3)	2.221(2)	2.288(7)
Mo−O1		2.114(2)	2.255(6)		2.1662(15)	2.039(4)
Mo−C16		1.993(3)	2.032(9)	2.013(3)	1.965(2)	
Mo−C17				2.013(3)	1.960(2)	
Mo−P1		2.5045(7)	2.510(2)	2.5069(6)	2.5813(7)	2.5440(18)
Mo−P2					2.5117(7)	2.5430(18)
C16−O2		1.146(3)	1.128(10)	1.135(3)	1.155(3)	
C17−O3				1.139(3)	1.156(3)	
Mo−C16−O2		174.9(2)	177.4(8)	179.1(3)	173.2(2)	
Mo−C17−O3				178.4(3)	175.8(2)	
(C1C7)−(C8−C13)[a]		84.4	84.6	42.8		78.4

[a] Interplanar angle.

prevents the isolation of stable tropylium salts such as **3**, and immediate ring closure by intramolecular nucleophilic attack on the seven-membered ring is observed upon hydride abstraction from amine- and phosphine-functionalized cycloheptatrienes to give polycyclic ammonium or phosphonium salts, respectively.[25] Accordingly, we had difficulties in isolating the analogous tropylium salt (2-hydroxy-3,5-di-*tert*-butylphenyl)cycloheptatrienylium tetrafluoroborate in pure form, as the introduction of *tert*-butyl groups to the 3,5-positions of the aryl substituent greatly enhances the nucleophilicity of the phenol oxygen atom leading to the instantaneous formation of 2,4-di-*tert*-butylbenzo[*b*]cyclohepta[*d*]furanylium tetrafluoroborate.

Preparation and Reactions of Monophosphine Complexes of the Type [($OC_6H_2Me_2$-η^7-C_7H_6)Mo(CO)(PR_3)] (R = Ph, *c*-C_6H_{11}, *i*-Pr). As mentioned above, we have recently developed a high-yielding protocol for the direct complexation of the cations in substituted tropylium salts by an arene exchange reaction using [(η-*p*-xylene)$Mo(CO)_3$].[8] Accordingly, treatment of a THF/CH_2Cl_2 solution of the tropylium tetrafluoroborate **3** with a slight excess of [(η-*p*-xylene)$Mo(CO)_3$] leads to an instantaneous color change from yellow to brown-red and furnishes the cycloheptatrienyl complex [($HOC_6H_2Me_2$-η^7-C_7H_6)$Mo(CO)_3$]BF_4 (**6**) in good yield after stirring for about 1 h (Scheme 2). Air-stable **6** is obtained as a yellow-brown, crystalline solid after precipitation with diethyl ether. Due to coordination of the seven-membered ring to the $Mo(CO)_3$ fragment, the ^1H and ^{13}C NMR spectra of **6** exhibit a pronounced high-field shift for the resonances of the ring carbon and hydrogen atoms, respectively, in comparison with the resonances found for the uncoordinated cation in **3**. Deprotonation at this stage

Scheme 2



does not lead to intramolecular CO-substitution and formation of a chelate complex [($OC_6H_2Me_2$-η^7-C_7H_6)$Mo(CO)_2$]. Instead, the spectroscopic characterization of the reaction mixture obtained upon treatment of **6** with various bases indicates the formation of the furan−cycloheptatriene complex [(η^6-**4**)$Mo(CO)_3$] by intramolecular nucleophilic attack of the phenolate oxygen atom at the seven-membered ring; as in **6,** the cycloheptatrienyl ring rather than the metal center represents the most electrophilic center of the molecule. Therefore, one has to substitute CO for more electron-rich or less π-accepting ligands, respectively, to reduce the electrophilicity of the seven-membered ring by strong metal-to-ligand back-bonding. Treatment of **6** with NaI results in the formation of uncharged [($HOC_6H_2Me_2$-η^7-C_7H_6)Mo-$(CO)_2$I] (**7**).[26] Substitution of CO by iodide leaves the metal center in **7** more electron-rich, thus leading to an increase

(25) Tamm, M.; Bannenberg, T.; Baum, K.; Dressel, B. Unpublished results.

in back-bonding to the remaining carbonyl groups as well as to the cycloheptatrienyl ligand as indicated by shifting the CO stretching frequencies to lower wavenumbers and by shifting the ^{1}H and ^{13}C NMR resonances of the ring hydrogen and carbon atoms to higher field in comparison with **6**.

It has previously been demonstrated that monophospine complexes of the type [(η-C_7H_7)M(CO)X(PR_3)] (M = Mo, W; X = halide) allow the introduction of various nucleophiles by halide substitution reactions, whereas the reaction of the dicarbonyl analogues [(η-C_7H_7)M($CO)_2$X] with organolithium or Grignard reagents generally leads to complexes of significantly lower stability.[27] Therefore, [($HOC_6H_2Me_2$-η^7-C_7H_6)Mo($CO)_2$I] (**7**) was treated with a small excess of PR_3 (R = Ph, *c*-C_6H_{11}, *i*-Pr) in toluene at elevated temperature leading to the direct, high-yield formation of [($HOC_6H_2Me_2$-η^7-C_7H_6)Mo(CO)I(PR_3)] (**8**). Complexes **8** can be used without further purification, and their reaction with NaH furnishes the red-brown chelate complexes [($OC_6H_2Me_2$-η^7-C_7H_6)Mo(CO)(PR_3)] (**9a**, R = Ph; **9b**, R = *c*-C_6H_{11}; **9c**, R = *i*-Pr) by intramolecular substitution of iodide by the appended phenolate group (Scheme 2). Due to chelation by the linked cycloheptatrienyl−phenolate ligand, complexes **9** seem to be significantly more stable than related halide or alkyl complexes, and chromatographic purification is possible under ambient conditions using alumina (4% H_2O).

In **9a**−**c**, the pseodotetrahedrally coordinated molybdenum centers have four different ligands each, and the complexes are thus obtained as a racemic mixture of two enantiomers. As these three new representatives of so-called "chiral-at-metal" half-sandwich compounds[28] are all configurationally stable, the diastereotopic cycloheptatrienyl hydrogen atoms give rise to six different resonances in their ^{1}H NMR spectra. This portion of the 600 MHz spectrum of **9b** is shown in Figure 3. Accordingly, seven ^{13}C NMR resonances are observed for the C_7H_6 carbon atoms (Figure 3). The assignment of all ^{1}H and ^{13}C NMR resonances in **9b** is supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). The ^{13}CO carbonyl resonances in **9a,b** are observed as doublets at 239.4 ($^2J_{C,P}$ = 17 Hz) and 245.3 ppm ($^2J_{C,P}$ = 18 Hz) (**9c** decomposed during data aquisition overnight). In addition, one single ^{31}P NMR resonance is observed for each complex **9a**−**c** at 38.6, 34.9, and 40.6 ppm, respectively. As expected, the IR spectra of all complexes **9** exhibit one CO absorption, which decreases going from **9a** (1932 cm^{-1}) to **9b** (1920 cm^{-1}) and **9c** (1919 cm^{-1}), as significantly enhanced metal-to-ligand π-back-bonding occurs in **9b,c** due to the stronger electron-release capability of the tricyclohexyl and triisopropyl phosphine ligands compared to triphenyl phosphine in **9a**.

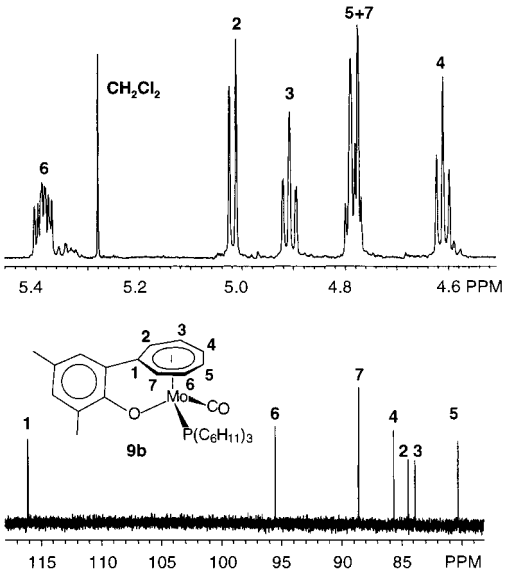


Figure 3. Selected parts of the ^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR spectra (151 MHz), $CDCl_3$) of **9b**.

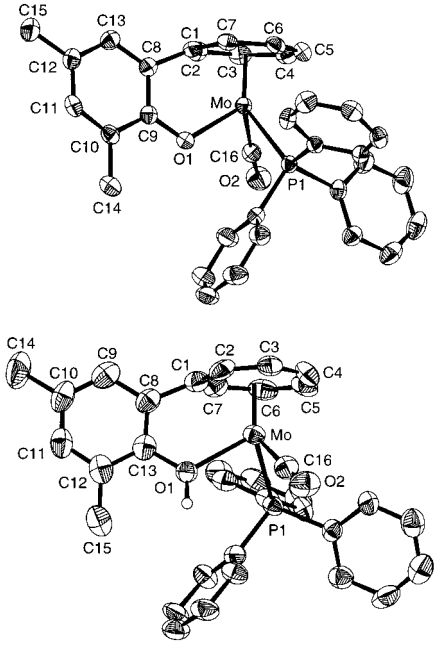


Figure 4. DIAMOND drawing of **9a** (top) and of the cation in **10**·$2CH_2Cl_2$ (bottom) with thermal ellipsoids drawn at the 50% probability.

To unambiguously confirm the formation of chelate complexes, a single-crystal of **9a** was subjected to X-ray diffraction analysis, and the molecular structure of one enantiomer in **9a** is depicted in Figure 4 (top). One recognizes that the CHT−phenolate ligand does indeed act as a chelate ligand with almost perfectly perpendicularly oriented six- and seven-membered rings (interplanar angle of 84.4°). The molybdenum atom is η^7-coordinated with the shortest bond to C1 (2.226(2) Å) and the longest bond to the neighboring C7 (2.327(2) Å) (Table 1), with the latter being slightly enlongated probably due to steric interaction with the PPh_3 ligand. No significant deviation from planarity can be observed for the seven-membered ring in **6**, and the mean and maximum deviations from the least-squares plane (C1−C7) are 0.032 and −0.068 Å (for C1), respectively. To allow

(26) (a) Roberts, A.; Whiteley, M. W. *J. Organomet. Chem.* **1993**, *458*, 131. (b) Hoch, G.; Panter, R.; Ziegler, M. L. *Z. Naturforsch.* **1976**, *31b*, 294.
(27) (a) Grime, R. W.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 1671. (b) Schwed, E.; Hund, H.-U.; Bosch, W.; Berke, H. *Helv. Chim. Acta* **1991**, *74*, 189.
(28) (a) Brunner, H. *Eur. J. Inorg. Chem.* **2001**, 905. (b) Brunner, H. *Angew. Chem.* **1999**, *111*, 1248; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1194.

chelate formation, the six-membered ring has to bend down toward the metal center, and the angle between the C1−C8 axis and the seven-membered ring deviates by 21.8° from a perfectly coplanar orientation.

To activate complexes **9** for subsequent reactions with organic substrates, we sought for their protonation, which might convert the tightly bound phenolate group into a loosely coordinated, hemilabile phenol. In fact, the treatment of a solution of **9a** in dichloromethane with etheral HBF_4 at low temperature affords $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(CO)(PPh_3)]BF_4$ (**10**), which precipitates from the reaction mixture as a light green crystalline solid. Single crystals could be obtained by recrystallization from dichloromethane/diethyl ether allowing us to establish the molecular structure of **10** by an X-ray crystal structure determination. **10** crystallizes in the chiral space group *Cc*, and the single crystal used in the diffraction experiment does only contain the enantiomer shown in Figure 4 (bottom). The proton at O1 could not be located by X-ray diffraction. No significant structural changes are observed for the cycloheptatrienyl−phenolate ligand in comparison with the molecular structure of neutraly charged **9a** except for the Mo−O-bond, which lengthens upon protonation (2.221(8) versus 2.1136(16) Å) (Table 1). The impact on the Mo−C−O bond distances is also almost negligible, and the lengthening of the Mo−C16 bond (2.032(9) versus 1.993(3) Å) together with the shortening of the C16−O2 bond (1.128(10) versus 1.146(3) Å) indicate only a slight increase in back-bonding to the carbonyl ligand. The conversion of the phenolate ligand into a hemilabile phenol ligand is actually best elucidated spectroscopically by comparison of the NMR spectra of **9a** and **10**. The cycloheptatrienyl proton portion of the ^{1}H NMR spectrum of **10** again exhibits six different resonances, which are shifted to lower field and reveal a significant line-broadening due to dynamic behavior of the weakly coordinated phenol group. In addition, protonation results in deshielding of the phosphorus atom in **10**, and the corresponding resonance at 47.7 ppm is observed 9 ppm downfield from the resonance in **9a**. It should be noted, however, that the resonance for the OH proton could not be detected by NMR spectroscopy.

Further evidence for a protonation at the phenolate oxygen atom stems from the reactivity of **10**, as substitution of the loosely bound phenol group should easily allow the introduction of various nucleophiles. In fact, the reaction of **10** with 2,6-dimethylphenyl isocyanide in dichloromethane results in an immediate color change from green to red and affords a dark red crystalline solid after precipitation with diethyl ether. All analytical and spectroscopic data are in agreement with coordination of the isocyanide to the molybdenum center and indicate the formation of $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(CO)(PPh_3)(CNC_6H_3Me_2)]BF_4$ (**11**) (Scheme 3). Consequently, the ^{13}C NMR spectrum exhibits a Mo*C*N resonance at 171.2 ppm together with the Mo*C*O resonance at 222.4 ppm, and the CN and CO IR stretching absorptions are observed at 2111 and 1966 cm^{-1}, respectively. The force constant for the CN bond can be calculated according to the method of Cotton[29] giving k(CN) = 1697 N/m, which indicates that the isocyanide is sufficiently stabilized by d → π* back-bonding toward an intramolecular addition of the phenolic OH group, and hence, **10** shows no tendency for carbene formation.[30]

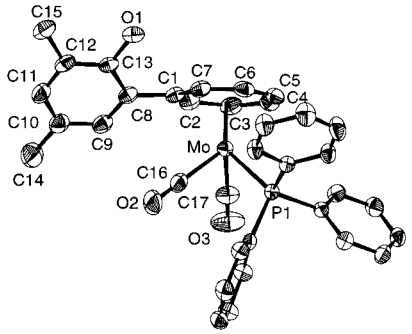
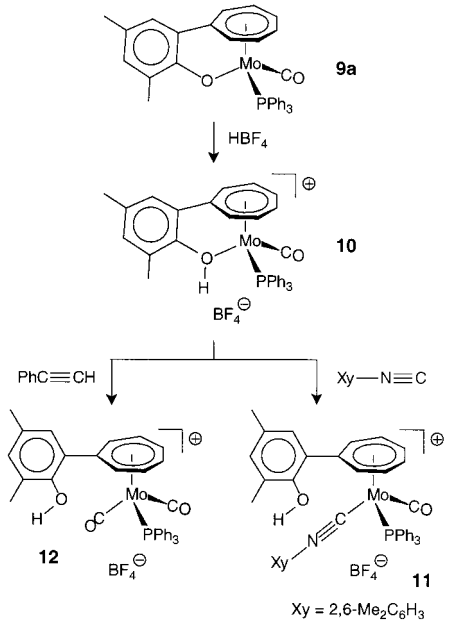


Figure 5. DIAMOND drawing of **12** with thermal ellipsoids drawn at 50% probability.

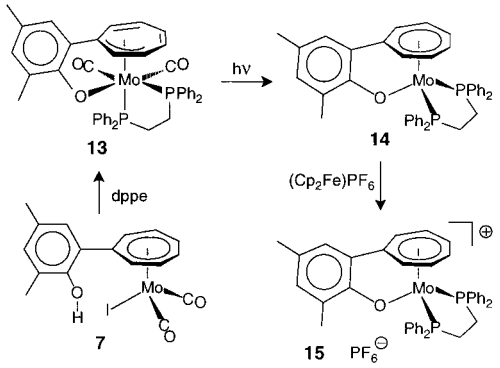
Scheme 3



On the other hand, activation of alkynes appeared to be a feasible goal, as the resulting vinylidene complexes should be more susceptible to intramolecular reaction with the OH group.[31] Treatment of **10** with alkynes such as phenylacetylene, however, did neither result in vinylidene nor in carbene formation. Instead, also in the presence of other alkynes, we have repeatedly isolated the dicarbonyl complex $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(CO)_2(PPh_3)]$ (**12**) (Scheme 3), which could be characterized by X-ray diffraction analysis. The molecular structure of the cation in **12** is shown in Figure 5, and important structural features are summarized in Table 1. In contrast to the perpendicular orientation of the six- and seven-membered rings in **9a** and **10**, the six-membered ring in **12** adopts an orientation, which deviates by 42.8° from a coplanar arrangement with the cycloheptatrienyl plane. Due to the unperturbed coordination of the nonchelating cyclo-

(29) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.
(30) (a) Hahn, F. E.; Tamm, M. *Organometallics* **1995**, *14*, 2597. (b) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175.
(31) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

Scheme 4



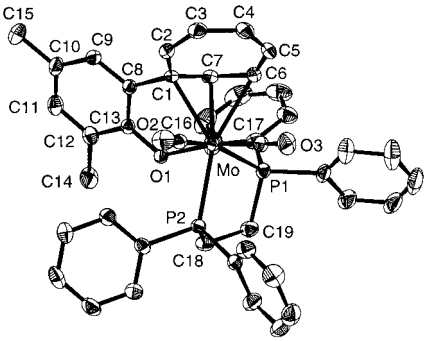


Figure 6. DIAMOND drawing of **13** with thermal ellipsoids drawn at 50% probability.

heptatrienyl-phenol ligand, the Mo−C(C_7 ring) bond distances exhibit less variation and are slightly elongated on average in comparison to those found in the chelate complexes **9a** and **10**. The formation of **12** remains unclear at this stage, and **12** could have formed by an intermolecular CO scrambling process or by hydrolytic cleavage of an intermediate vinylidene ligand. Additional experiments, e.g. including the use of ^{13}C labeled alkynes, have to be carried out to further elucidate the reaction mechanism.

Preparation and Characterization of Diphosphine Complexes [(OC$_6$H$_2$Me$_2$-η^3-C$_7$H$_6$)Mo(CO)$_2$(dppe)] (13) and [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(dppe)] (14). The failure in alkyne activation lead to our assumption that a metal center having a stronger electron-release capability should be better suited to stabilize a vinylidene intermediate, and in fact, Whiteley and co-workers have reported several vinylidene complexes of the molybdenum auxiliary [(η-C_7H_7)Mo(dppe)]$^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[32] Therefore, we have studied the thermal reaction of [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)$_2$I] (**7**) with dppe in toluene, which turned out to be quite surprising (Scheme 4). Rather than substituting both CO groups, the diphosphine adds to the molybdenum center forcing the cycloheptatrienyl ring to reduce its hapticity from seven to three. Similar $\eta^7 \rightarrow \eta^3$ hapticity interconversions in cycloheptatrienylmolybdenum and -tungsten complexes have been reported in the literature.[33] Simultaneously, the molydenum−oxygen bond is formed with loss of hydrogen iodide. The resulting complex [(OC$_6$H$_2$Me$_2$-η^3-C$_7$H$_6$)Mo(CO)$_2$(dppe)] (**13**) is exceptionally stable, is highly crystalline, and can easily be isolated by column chromatography. Single crystals could be obtained from acetone solution, and the result of the X-ray diffraction analysis is shown in Figure 6. The coordination geometry is best described as pseudooctahedral with the assumption that the cycloheptatrienyl ring, which is bound in an allylic η^3-fashion via C1, C7, and C6, occupies one coordination site. The bond lengths C2−C3 (1.341(3) Å) and C4−C5 (1.341(4) Å) are significantly shorter than the remaining intra-ring bond distances and clearly correspond to C(sp^2)−C(sp^2) double bonds. On the basis of previous studies,[33] the ligand arrangement observed here concurs with the expected geometric isomer, in which the two CO ligands are located cis to each other and trans to the phenolate oxygen atom and to one of the phosphorus atoms, respectively.

As one can see from the two presentations in Figure 7, two different stereoisomers, the Λ- and the Δ-isomer, exist for the chiral complex **13**. Although inequivalence of the two phosphorus atoms must be expected for this configuration, the ^{31}P NMR spectrum exhibits only one resonance at room temperature revealing a rapid intramolecular rearrangement, which interconverts the two isomers. This rearrangement can be explained by means of a trigonal twist process involving rotation of the triangular face formed by the oxygen and the two phosphorus atoms with respect to the face formed by the cycloheptatrienyl ring and the two carbonyl groups. To fully complete the enantiomerization process between the Λ- and Δ-isomers, a simultaneous rearrangement of the trihapto-bonded cycloheptatrienyl ring must be operative, whereby the metal center shifts from the carbon atoms C1, C7, and C6 to C1, C2, and C3, presumably by two consecutive 1,2-shifts via an intermediate coordination of C1, C2, and C7.[34] A variable-temperature ^{31}P NMR study reveals coalescence of the original broad singlet to a broad doublet at about −19 °C (Figure 7), and line-shape analysis allows one to estimate the barrier of rearrangement to about 12 kcal/mol (or 50 kJ/mol).[35] This activation barrier agrees well with values obtained for related allylic species;[36] it should be noted, however, that cycloheptatrienyl complexes such as [(η^3-C_7H_7)MoI(CO)$_2$(dppe)] show coalescence at elevated temperatures in the range from +8 to +45 °C.[33c]

(32) (a) Beddoes, R. L.; Grime, R. W.; Hussain, Z. I.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1996**, 3893. (b) Beddoes, R. L.; Bitcon, C.; Grime, R. W.; Ricalton, A.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1995**, 2873. (c) Adams, J. S.; Bitcon, C. Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1987**, 3049.

(33) (a) Beddoes, R. L.; Hussain, Z. I.; Roberts, A.; Barraclough, C. R.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1996**, 3629. (b) Breeze, R.; Plant, M. S.; Ricalton, A.; Sutton, D. J., Whiteley, M. W. *J. Organomet. Chem.* **1988**, *356*, 343. (c) Brown, R. A.; Salasiah, E.; Friend, J.; Hill, J. M.; Whiteley, M. W. *J. Organomet. Chem.* **1988**, *339*, 283. (d) Breeze, R.; Salasiah, E.; Whiteley, M. W. *J. Organomet. Chem.* **1986**, *302*, 371.

(34) Faller, J. W. *Inorg. Chem.* **1969**, *8*, 767.

(35) The following approximate equation was used for the calculation of $\Delta G^{\ddagger}$: $\Delta G^{\ddagger} = 4.57T_c(9.97 + \log(T_c/\Delta\nu))$ (cal/mol) with $T_c = 254$ K and $\Delta\nu = 67.9$ Hz according to: Günther, H. *NMR Spectroscopy*; Georg Thieme Verlag: Stuttgart, Germany, 1973; p 248.

(36) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.

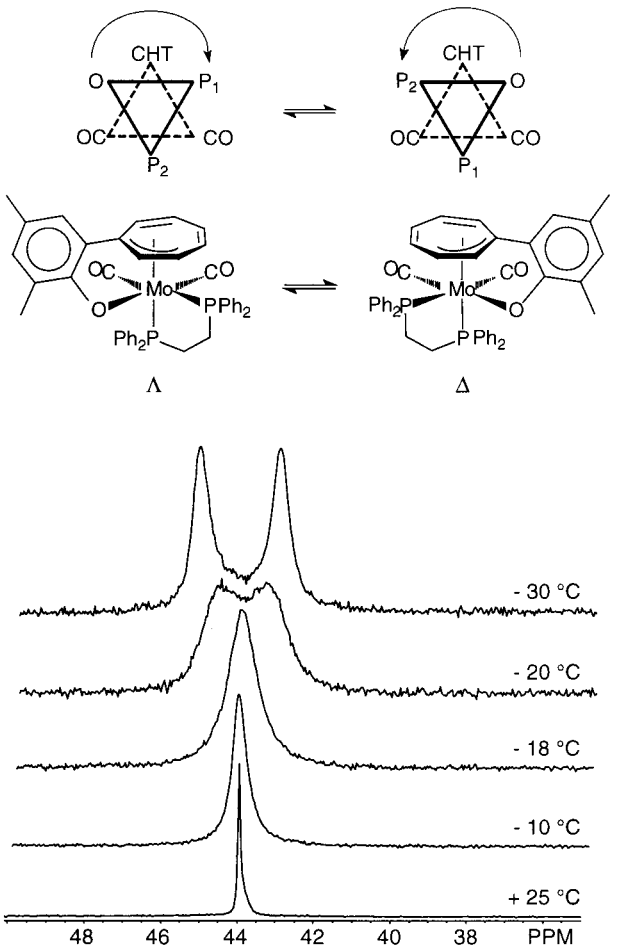


Figure 7. Variable-temperature ^{31}P NMR study and fluxional behavior of **13**.

At room temperature, the ^{1}H NMR spectrum of **13** exhibits three broad resonances for the cycloheptatrienyl CH resonances in a 2:2:2 ratio as expected for a C_s symmetric arrangement indicating that the two dynamic processes described above render the environment of the diastereotopic protons at C2/C7, C3/C6, and C4/C5 equivalent. A low-temperature 600 MHz NMR study at −80 °C allows one to completely freeze out the fluxional behavior of **13**, and six discrete resonances attributable to the C_7H_6 protons can be observed. The most striking feature of the spectrum depicted in Figure 8 is the high-field position of one of these resonances at 1.06 ppm. In agreement with the solid-state structure, this signal can be assigned to the metal-coordinated *ortho*-CH group (C7 in Figure 6), since this proton penetrates the shielding region of the anisotropy cone of one of the dppe phenyl groups, which leads to the observed high-field shift.

As mentioned above, the noncoordinated part of the trihapto-bonded cycloheptatrienyl ring contains two double bonds positioned on top of the two carbonyl groups, which should be easily removable by intramolecular CO substitution. In fact, this intramolecular $\eta^3 \rightarrow \eta^7$ hapticity reversion is readily achieved by UV irridation.[37] The resulting complex

(37) Green, M. L. H.; Ng, D. K. P. *J. Chem. Soc., Dalton Trans.* **1993**, 17.

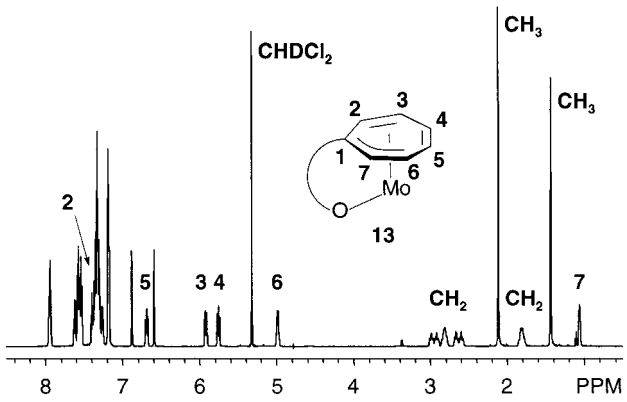


Figure 8. ^{1}H NMR spectrum of **13** (600 MHz, $CDCl_3$, T = 193 K).

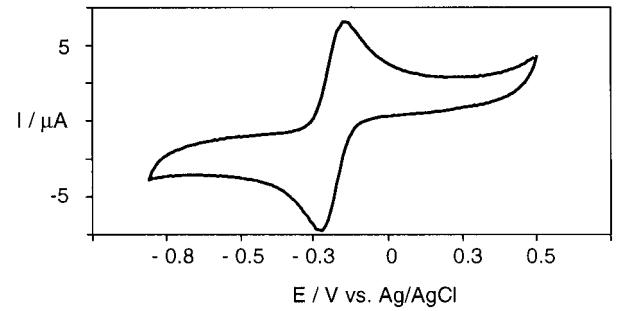


Figure 9. Cyclic voltammetric trace for **14** (T = 298 K, υ = 100 mV/s).

[(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(dppe)] (**14**) is isolated as dark green, air-sensitive compound. The ^{1}H NMR spectrum exhibits three C_7H_6 resonances at 5.02, 4.12, and 3.73 ppm giving clear evidence for the formation of a C_s symmetric complex. Whereas the two phosphorus nuclei in **14** give rise to a single ^{31}P NMR resonance at 57.8 ppm, the sensitivity of **14** defied our efforts to properly characterize it by ^{13}C NMR spectroscopy. A cyclic voltammetric study (Figure 9) reveals the electron-richness of **14** and affords a redox potential of $E° = -190$ mV for a reversible one-electron oxidation. As the potential for the ferrocene/ferrocenium couple is observed at +480 mV under identical conditions, the corresponding 17-electron radical cation [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(dppe)]$^+$ should easily be accessible by chemical oxidation with ferrocenium salts. Consequently, the addition of [Fe(η-C$_5$H$_5$)$_2$]PF$_6$ to a solution of **14** in dichloromethane produced an intensely colored solution, which afforded moderate yields of air-stable [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(dppe)]PF$_6$ (**15**) (Scheme 4).

15 is readily characterized by elemental analysis, X-ray diffraction, and EPR spectroscopy, and Figure 10 shows an ORTEP presentation of the cation in **15**. Compared to the molecular structure of **9a** (vide supra), the bond lengths and angles about the metal center do not change significantly, and oxidation of molybdenum is only marginally reflected by a slight shortening of the Mo−O and Mo−C(C_7 ring) bond distances (Table 1). Again, the molybdenum atom is symmetrically η^7-coordinated with the shortest bond to C1 (2.203(6) Å) and the longest bond to C4 (2.327(7) Å), and

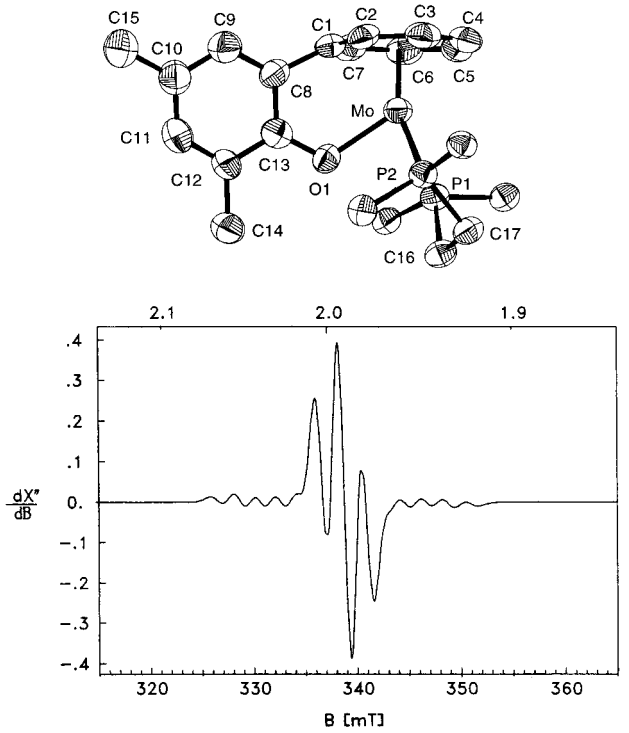


Figure 10. DIAMOND drawing of the cation in **15** with thermal ellipsoids drawn at 50% probability (top, only the *ipso*-carbon atoms of the PPh_2 groups are shown) and X-band EPR spectrum of **15** (bottom).

the planar seven-membered ring exhibits a mean and maximum deviation from the least-squares plane including C1−C7 of 0.032 and −0.068 Å (for C1), respectively. Finally, the paramagnetic chararacter of the monocation in **15** can be confirmed by its X-band EPR spectrum at 240 K in fluid dichloromethane (Figure 10), which reveals a hyperfine structure assignable to coupling of the unpaired electron with two equivalent ^{31}P and with the ^{95}Mo and ^{97}Mo nuclei. The *g* factor of 1.99 compares well with those reported for related compounds such as $[(\eta\text{-}C_7H_7)MoX(dppe)]^+$ (X = alkynyl;[32c] X = Cl, Br[38a]) and $[(\eta\text{-}C_7H_7)MoX\{P(OMe)_3\}]^+$.[38b]

As mentioned above, we have sought for the synthesis of a complex containing an electron-rich metal center to obtain better results in alkyne activation and in the stabilization of potential vinylidene intermediates as compared to the failure of employing the phenol complex **10** (vide supra; Scheme 3). The treatment of **14** with etheral HBF_4, however, did not result in protonation of the phenolate oxygen atom and in the formation of a diamagnetic phenol complex **14**·HBF_4, $[(HOC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(dppe)]BF_4$. Instead, we have exclusively observed oxidation of **14** together with evolution of a gas (presumably dihydrogen) and the formation of the paramagnetic phenolate complex $[(OC_6H_2Me_2\text{-}\eta^7\text{-}C_7H_6)Mo(dppe)]BF_4$ (**15**), which is not suprising taking into account the cathodic potential determined by cyclic voltammetry for the reversible oxidation of **14** (vide supra). Therefore at this stage, we have not continued to pursue the activation of the cycloheptatrienyl−phenolate complexes **9** and **14** reported herein.

(38) (a) Green, M. L. H.; Pardy, R. B. A. *Polyhedron* **1985**, *4*, 1035. (b) Bitcon, C.; Breeze, R.; Miller, P. F.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *364*, 181.

Conclusion

With this contribution, chelate complexes of functionalized cycloheptatrienyl ligands bearing pendant donor groups have been reported for the first time, and we have presented a high-yielding protocol for the synthesis of a series of molybdenum complexes containing linked cycloheptatrienyl-phenolate ligands. These complexes are archetypal for the new class of donor-functionalized cycloheptatrienyl complexes, which will emerge from our laboratory soon. The development of stable cycloheptatrienyl chelate complexes of molybdenum could be particularly useful for catalytic C−C bond forming reactions in view of the extensive chemistry of analogous ruthenium complexes of the type $[(\eta\text{-}C_5Me_5)RuL_2X]$.[39] In fact, the similarity between the isoelectronic fragments $[(\eta\text{-}C_7H_7)Mo]$ and $[(\eta\text{-}C_5Me_5)Ru]$ has been demonstrated several times,[6] and we are currently pursuing a general study on the possibility to replace ruthenium catalysts by analogous but much cheaper molybdenum systems.

In addition, the phenolate complexes introduced here offer the possibility to study their application in heterolytic dihydrogen cleavage, in which the Mo−OAr unit is converted into Mo−H and H−OAr upon H_2 uptake. Dihydrogen is thereby cleaved into a hydridic hydrogen atom at the metal center and into a protic hydrogen atom on the phenol group, which remains attached to the seven-membered ring and could thus form an intramolecular ArO−H···H−Mo bond.[40] Related cyclopentadienylruthenium complexes featuring dihydrogen cleavage have been reported in the literature.[41] Simultaneous or succesive transfer of H^- and H^+ onto an organic substrate then regenerates the phenolate complex. Tuning of the electronic properties of the molybdenum center by ligand variation as shown in this paper together with the modification of the aryl fragment will allow one to adjust the basicity of the Mo−H group as well as the acidity of the ArO−H moiety according to the requirements of these reactions.

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. Tropylium tetrafluoroborate,[42] triphenylcarbenium tetrafluoroborate,[43] and $[(\eta\text{-}p\text{-}xylene)Mo(CO)_3]$[44] were prepared according to published procedures.

(39) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067.
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Preparation of 2-(2,4-Dimethylphenoxy)tetrahydropyran (1). 2,4-Dimethylphenol (10.0 g, 82 mmol) and 3,4-dihydro-*2H*-pyran (18.6 g, 221 mmol) were dissolved in dry dichloromethane (120 mL). A catalytic amount of iodotrimethylsilane (0.1 mL) was added, and the reaction mixture was stirred at ambient temperature for 1 h. After evaporation of the solvent, the oily residue was purified chromatographically on deactivated silica (4% H_2O). Elution with petroleum ether/ethyl acetate (10:1) afforded **1** as a colorless oil. Yield: 11.4 g (67%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.92 (m, 3H, C*H*), 5.33 (dd, 1H, C*H*O$_2$), 3.88 (m, 1H, OC*H*$_2$), 3.57 (m, 1H, OC*H*$_2$), 2.23 (s, 3H, C*H*$_3$), 2.22 (s, 3H, C*H*$_3$), 2.04−1.81 (m, 3H, C*H*$_2$), 1.67−1.59 (m, 3H, C*H*$_2$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 152.8 (C_6 ring: *C*O), 131.2 (C_6 ring: *C*H + *C*CH$_3$), 130.3 (C_6 ring: *C*CH$_3$), 126.9, 114,1 (C_6 ring: *C*H), 96.2 (*C*HO$_2$), 61.8, 30.5, 25.2 (*C*H$_2$), 20.3 (*C*H$_3$), 18.9 (*C*H$_2$), 16.0 (*C*H$_3$). MS (EI) [*m*/*z* (%)]: 206 (12) [M$^+$], 122 (100) [($C_6H_3Me_2OH$)$^+$], 85 (28) [(C_5H_9O)$^+$]. Anal. Calcd for $C_{13}H_{18}O_2$ (M_r = 206.28): C, 75.69; H, 8.80. Found: C, 75.42; H, 8.90.

Preparation of 2-(Cyclohepta-2,4,6-trienyl)-4,6-dimethylphenol (2). A solution of *n*-butyllithium (26.5 mL of a 2.5 M solution in hexane, 66 mmol) is treated with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.9 mL, 6 mmol). THF (3 mL) and **1** (11.37 g, 55 mmol) were consecutively added dropwise to the reaction mixture at 0 °C. After the mixture was stirring for 12 h at ambient temperature, THF (80 mL) was added. The resulting solution was cooled to −78 °C and treated with solid (C_7H_7)BF_4 (9.80 g, 55 mmol). Stirring was continued for 2 h at room temperature, and the solvent was removed in vacuo. After the addition of water, the product was extracted with diethyl ether (3 × 50 mL), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography on alumina (4% H_2O) with petroleum ether/ethyl acetate (40:1) afforded the tetrahydropyranyl ether of **2** as a colorless oil. Yield: 10.10 g (62%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.14 (s, 1H, C_6 ring: C*H*), 6.91 (s, 1H, C_6 ring: C*H*), 6.71 (m, 2H, C_7 ring: C*H*), 6.22 (m, 2H, C_7 ring: C*H*), 5.36 (dd, 1H, C_7 ring: C*H*), 5.25 (dd, 1H, C_7 ring: C*H*), 4.66 (t, 1H, C*H*O$_2$), 3.91 (m, 1H, OC*H*$_2$), 3.40 (m, 1H, OC*H*$_2$), 3.15 (t, 1H, C_7 ring: C*H*), 2.31 (s, 3H, C*H*$_3$), 2.30 (s, 3H, C*H*$_3$), 1.69 (m, 3H, C*H*$_2$), 1.46 (m, 3H, C*H*$_2$). MS (EI) [*m*/*z* (%)]: 296 (3) [M$^+$], 212 (100) [(M −C_5H_9O + H)$^+$], 85 (47) [(C_5H_9O)$^+$]. Anal. Calcd for $C_{20}H_{24}O_2$ (M_r = 296.41): C, 81.04; H, 8.16. Found: C, 80.52; H, 8.72.

To remove the THP group, a 10 g (34 mmol) portion of the compound obtained as described above was dissolved in 96% ethanol (150 mL), and the solution was treated with a catalytic amount (850 mg) of pyrdinium tosylate (PPTS) and heated to 55 °C for 3 h. Evaporation of the solvent and purification by column chromatography on silica (4% H_2O) with petroleum ether/ethyl acetate (20:1) afforded the phenol **2** as a yellowish viscous oil. Yield: 6.06 g (84%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.98 (s, 1H, C_6 ring: C*H*), 6.88 (s, 1H, C_6 ring: C*H*), 6.73 (m, 2H, C_7 ring: C*H*), 6.27 (m, 2H, C_7 ring: C*H*), 5.44 (dd, 2H, C_7 ring: C*H*), 4.62 (s, 1H, O*H*), 2.89 (t, 1H, C_7 ring: C*H*), 2.26 (s, 3H, C*H*$_3$), 2.22 (s, 3H, C*H*$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 148.4 (*C*OH), 129.8 (C_7 ring: *C*H), 128.6 (C_6 ring: *C*H), 128.3 (C_6 ring: *C*-2), 126.9 (*C*CH$_3$), 125.3 (C_6 ring: *C*H), 124.1, 123.8 (C_7 ring: *C*H), 122.5 (C_6–Ring: *C*CH$_3$), 39.0 (C_7 ring: *C*-1), 19.3, 14.6 (*C*H$_3$). MS (EI) [*m*/*z* (%)]: 212 (100) [M$^+$], 197 (34) [(M − CH$_3$)$^+$], 91 (15) [(C_7H_7)$^+$]. Anal. Calcd for $C_{15}H_{16}O$ (M_r = 212.29): C, 84.86; H, 7.59. Found: C, 83.45; H, 7.61.

Preparation of (2-Hydroxy-3,5-dimethylphenyl)cycloheptatrienylium Tetrafluoroborate (3). A solution of the cycloheptatriene **2** (2.0 g, 9.4 mmol) in CH_2Cl_2 (30 mL) was treated with (Ph_3C)BF_4 (2.80 g, 8.5 mmol), and the reaction mixture was stirred for 90 min at ambient temperature. After the solution volume was reduced to about 5 mL, diethyl ether (100 mL) was added to precipitate **3** as an orange-red crystalline solid, which was collected by filtration and dried in vacuo. Yield: 1.83 g (72%). ^{1}H NMR (600 MHz, CD_3CN): δ 9.30 (dm, 2H, C_7 ring: C*H*), 9.01 (m, 4H, C_7 ring: C*H*), 7.26 (s, 1H, C_6 ring: C*H*), 7.21 (s, 1H, C_6 ring: C*H*), 6.85 (s, 1H, O*H*), 2.32 (s, 3H, C*H*$_3$), 2.30 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, CD_3CN): δ 168.4 (*C*OH), 155.7, 153.1, 152.6 (C_7 ring: *C*H), 150.4 (C_7 ring: *C*-1), 136.7 (C_6 ring: *C*H), 131.8 (C_6 ring: *C*CH$_3$), 130.4 (C_6 ring: *C*H), 127.5 (C_6 ring: *C*-1), 126.7 (C_6 ring: *C*CH$_3$), 19.7, 16.2 (*C*H$_3$). MS (ESI) [*m*/*z* (%)]: 211 (100) [M$^+$]. Anal. Calcd for $C_{15}H_{15}BF_4O$ (M_r = 298.09): C, 60.44; H, 5.07. Found: C, 59.92; H, 4.87.

Preparation of 2,4-Dimethylbenzo[*b*]cyclohepta[*d*]furan (4). In a separatory funnel, the tropylium salt **3** (1.5 g, 5.0 mmol) was treated with 300 mL of a saturated solution of $NaHCO_3$ in water. A clear solution was obtained, and the product was isolated by extraction with diethyl ether (3 × 50 mL). After drying of the combined extracts over $MgSO_4$, the solvent was evaporated to afford **4** as a yellowish oil. Yield: 0.960 g (91%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.03 (s, 1H, C_6 ring: C*H*), 6.86 (s, 1H, C_6 ring: C*H*), 6.59 (m, 1H, C_7 ring: C*H*), 6.40 (m, 1H, C_7 ring: C*H*), 6.04 (m, 1H, C_7 ring: C*H*), 5.38 (m, 1H, C_7 ring: C*H*), 5.04 (d, 1H, C_7 ring: C*H*), 2.26 (s, 3H, C*H*$_3$), 2.24 (s, 3H, C*H*$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 161.1 (C_6 ring: *C*O), 136.4 (quart-*C*), 132.5, 130.4 (*C*H), 130.1 (quart-*C*), 128.5 (*C*H), 123.8 (quart-*C*), 122.3 (*C*H), 119.9 (quart-*C*), 119.3, 119.1, 110.2 (*C*H), 83.0 (C_7-ring: *C*HO), 20.7, 14.9 (*C*H$_3$).

Preparation of 2,4-Dimethylbenzo[*b*]cyclohepta[*d*]furanylium Tetrafluoroborate (5). A solution of the furan **4** (690 mg, 3.3 mmol) in CH_2Cl_2 (25 mL) was treated with (Ph_3C)BF_4 (980 g, 2.9 mmol), and the reaction mixture was stirred for 90 min at ambient temperature. After reduction of the solution volume to about 5 mL, diethyl ether (50 mL) was added to precipitate **5** as a yellow crystalline solid, which was collected by filtration and dried in vacuo. Yield: 720 mg (84%). ^{1}H NMR (600 MHz, CD_3CN): δ 9.71 (m, 1H, C_7 ring: C*H*), 9.32 (m, 1H, C_7 ring: C*H*), 9.02 (m, 3H, C_7 ring: C*H*), 8.19 (s, 1H, C_6 ring: C*H*), 7.75 (s, 1H, C_6 ring: C*H*), 2.66 (s, 3H, C*H*$_3$), 2.56 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 168.3 (C_6 ring: *C*O), 157.4 (C_7 ring: *C*O), 149.1 (C_7 ring: *C*H), 146.6 (C_7 ring: *C*-1), 146.4, 145.7, 143.3 (C_7 ring: *C*H), 139.6 (C_6 ring: *C*H), 138.2 (C_6 ring: *C*CH$_3$), 136.5 (C_7 ring: *C*H), 123.9 (C_6 ring: *C*CH$_3$), 123.2 (C_6 ring: *C*-1), 121.1 (C_6 ring: *C*H), 20.8, 14.2 (*C*H$_3$). Anal. Calcd for $C_{15}H_{13}BF_4O$ (M_r = 296.07): C, 60.85; H, 4.43. Found: C, 60.75; H, 4.21.

Preparation of Tricarbonyl[(2-hydroxy-3,5-dimethylphenyl)-cycloheptatrienyl]molybdenum Tetrafluoroboarate (6), [(HOC_6-H_2Me$_2$-η^7-C_7H_6)Mo(CO)$_3$]BF_4. The tropylium salt **3** (1.0 g, 3.4 mmol) was dissolved a mixture of CH_2Cl_2 (40 mL) and THF (30 mL) and treated with [(η-*p*-xylene)Mo(CO)$_3$]. After being stirred for 1 h under ambient conditions, the solution was reduced in volume to about 10 mL, and diethyl ether was added to precipitate **6**, which was isolated as a yellow-brown solid after filtration. Yield: 1.19 g (74%). ^{1}H NMR (200 MHz, acetone-d_6): δ 8.16 (s, 1H, O*H*), 7.24 (s, 1H, C_6 ring: C*H*), 7.10 (s, 1H, C_6 ring: C*H*), 6.72 (m, 2H, C_7 ring: C*H*), 6.57 (s, 4H, C_7 ring: C*H*), 2.28 (s, 3H, C*H*$_3$), 2,24 (s, 3H, C*H*$_3$). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 208.8 (Mo*C*O), 150.9 (*C*OH), 134.8 (C_6 ring: *C*H), 130.9 (C_6 ring: *C*-1), 130.5 (C_6 ring: *C*H), 126.8, 124,7 (C_6 ring: *C*CH$_3$), 120.3 (C_7 ring: *C*-1), 104.3, 101.5, 100.2 (C_7 ring: *C*H), 20.4, 16.8 (*C*H$_3$). IR (CH_2Cl_2): ν(CO) 2074, 2025 cm^{-1}. Anal. Calcd for

$C_{18}H_{15}BF_4MoO_4$ (M_r = 478.07): C, 45.22; H, 3.16. Found: C, 44.16; H, 3.29.

Preparation of Dicarbonyl[(2-hydroxy-3,5-dimethylphenyl)-cycloheptatrienyl]iodomolybdenum (7), [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)-Mo(CO)$_2$I]. NaI (3.37 g, 23 mmol) was added to a solution of **6** (4.3 g, 9 mmol) in acetone (60 mL), and the reaction mixture was stirred overnight. The solvent was removed in vacuo, and the product was extracted with CH_2Cl_2 (20 mL). After filtration over Celite, the solvent was evaporated to afford **7** as a green solid, which could be purified by recrystallization from diethyl ether/dichloromethane. Yield: 3.40 g (77%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.10 (s, 1H, C$_6$ ring: C*H*), 7.00 (s, 1H, C$_6$ ring: C*H*), 5.79 (d, 2H, C$_7$ ring: C*H*), 5.60 (m, 2H, C$_7$ ring: C*H*), 5.45 (m, 2H, C$_7$ ring: C*H*), 5.27 (s, 1H, O*H*), 2.28 (s, 6H, CH_3). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 213.0 (Mo*C*O), 148.8 (*C*OH), 132.5 (C$_6$ ring: *C*H), 130.0 (C$_6$ ring: *C*-1), 129.8 (C$_6$ ring: *C*H), 125.4, 124,7 (C$_6$ ring: *C*CH$_3$), 111.7 (C$_7$–Ring: *C*-1), 95.7, 94.1, 93.3 (C$_7$ ring: *C*H), 20.4, 16.2 (*C*H$_3$). IR (CH_2Cl_2): ν(CO) 2016, 1970 cm^{-1}. Anal. Calcd for $C_{17}H_{15}MoO_3I$ (M_r = 490.15): C, 41.65; H, 3.08. Found: C, 42.48; H, 3.12.

General Procedure for the Preparation of [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)I(PR$_3$)] (8a, R = Ph; 8b, R = *c*-C$_6$H$_{11}$; 8c, *i*-Pr) and of [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)(PR$_3$)] (9a, R = Ph; 9b, R = *c*-C$_6$H$_{11}$; 9c, *i*-Pr). A solution of 7 (4.9 g, 10 mmol) in toluene (60 mL) was treated with the appropriate phosphine (10.5 mmol), and the reaction mixture was heated to 90 °C for 3 h. After evaporation of the solvent, the green residue, which contained the intermediate complexes [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)I(PR$_3$)] (**8**), was dissolved in THF (60 mL). The resulting solution was cooled to −78 °C and treated with solid NaH (0.36 g, 15 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo, and the residue was extracted with diethyl ether. Filtration over Celite and purification by chromatography on alumina (4% H_2O) with petroleum ether/dichloromethane (1:1) afforded complexes **9** as brown-red solids, which could be recrystallized from diethyl ether.

Characterization of [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)(PPh$_3$)] (9a). Yield: 2.39 g (40%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (m, 5H, PC$_6$*H*$_5$), 7.35 (m, 10H, PC$_6$*H*$_5$), 7.17 (s, 1H, C$_6$ ring: C*H*), 6.80 (s, 1H, C$_6$ ring: C*H*), 5.08 (td, 1H, C$_7$ ring: *C*H), 5.04 (d, 1H, C$_7$ ring: *C*H), 4.69 (d, 1H, C$_7$ ring: *C*H), 4.61 (t, 1H, C$_7$ ring: *C*H), 4.57 (dd, 1H, C$_7$ ring: *C*H), 4.06 (td, 1H, C$_7$ ring: *C*H), 2.31 (s, 3H, C*H*$_3$), 1.80 (s, 3H, C*H*$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 239.4 (d, $^2J_{P,C}$ = 17 Hz, Mo*C*O), 173.6 (MoO*C*), 134.9 (d, $^1J_{P,C}$ = 35 Hz, P*C*), 133.5 (d, $^2J_{P,C}$ = 11 Hz, PC*C*), 130.8 (C$_6$ ring: *C*-1), 129.8 (PCCC*C*), 129.6 (C$_6$ ring: *C*H), 128.2 (d, $^3J_{P,C}$ = 10 Hz, PCC*C*), 126.1 (C$_6$ ring: *C*CH$_3$), 122.6 (C$_6$ ring: *C*H), 122.0 (C$_6$ ring: *C*CH$_3$), 120.4 (C$_7$ ring: *C*-1), 96.6, 88.3, 86.1, 84.0, 83.9, 83.4 (C$_7$ ring: *C*H), 20.4, 17.0 (*C*H$_3$). ^{31}P NMR (81 MHz, $CDCl_3$): δ 38.6. IR (CH_2Cl_2): ν(CO) 1932 cm^{-1}. Anal. Calcd for $C_{34}H_{29}MoO_2P$ (M_r = 596.52): C, 68.46; H, 4.90. Found: C, 68.86; H, 5.35.

Characterization of [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)(P(C$_6$H$_{11}$)$_3$)] (9b). Yield: 2.27 g (37%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (s, 1H, C$_6$ ring: C*H*), 6.79 (s, 1H, C$_6$ ring: C*H*), 5.39 (td, 1H, C$_7$ ring: C*H*), 5.02 (d, 1H, C$_7$ ring: C*H*), 4.91 (td, 1H, C$_7$ ring: C*H*), 4.78 (m, 2H, C$_7$ ring: C*H*), 4.61 (t, 1H, C$_7$ ring: C*H*), 2.29 (s, 3H, C*H*$_3$), 2.05 (m, 3H, PC*H*), 2.00 (s, 3H, C*H*$_3$), 2.00−1.14 (m, 30H, C*H*$_2$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 245.3 (d, $^2J_{C,P}$ = 18 Hz, Mo*C*O), 173.7 (MoO*C*), 131.0 (C$_6$ ring: *C*-1), 129.4 (C$_6$ ring: *C*H), 125.3 (C$_6$ ring: *C*CH$_3$), 122.7 (C$_6$ ring: *C*H), 121.4 (C$_6$ ring: *C*CH$_3$), 116.6 (C$_7$ ring: *C*-1), 95.9, 89.0, 86.0, 84.8, 84.6, 80.7 (C$_7$ ring: *C*H), 35.8 (d, $^1J_{C,P}$ = 14 Hz, P*C*H), 27.6 (d, $^2J_{C,P}$ = 10.6 Hz, PC*C*), 29.5, 26.5 (*C*H$_2$), 20.3, 17.3 (*C*H$_3$). ^{31}P NMR (81 MHz, $CDCl_3$): δ 34.9. IR (CH_2Cl_2): ν(CO) 1919 cm^{-1}. Anal. Calcd for $C_{34}H_{47}MoO_2P$ (M_r = 614.66): C, 66.44; H, 7.71. Found: C, 66.22; H, 7.80.

Characterization of [(OC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)(P(*i*-Pr)$_3$)] (9c). Yield: 1.48 g (30%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18 (s, 1H, C$_6$ ring: C*H*), 6.80 (s, 1H, C$_6$ ring: C*H*), 5.43 (m, 1H, C$_7$ ring: C*H*), 5.03−4.59 (m, 5H, C$_7$ ring: C*H*), 2.35 (sept, 3H, PC*H*), 2.30 (s, 3H, C$_6$ ring: CH_3), 1.98 (s, 3H, C$_6$ ring: CH_3), 1.25−1.11 (m, 18H, PCCH_3). ^{31}P NMR (81 MHz, $CDCl_3$): δ 40.6. IR (CH_2Cl_2): ν(CO) 1920 cm^{-1}. Anal. Calcd for $C_{25}H_{35}MoO_2P$ (M_r = 494.46): C, 60.73; H, 7.13. Found: C, 61.66; H, 7.11.

Preparation of [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)(PPh$_3$)]BF$_4$ (10). 9a (100 mg, 0.2 mmol) was dissolved in a mixture of diethyl ether (8 mL) and dichloromethane (3 mL). The resulting solution was cooled to −78 °C and treated with a solution of HBF_4 in diethyl ether (28 μL of a 54% solution, 0.2 mmol). The reaction mixture was allowed to slowly warm to room temperature, whereupon a light green precipitate formed, which was isolated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 112 mg (98%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.51 (tm, 3H, PC$_6$*H*$_5$), 7.45 (td, 6H, PC$_6$*H*$_5$), 7.30 (s br, 1H, C$_6$ ring: C*H*), 7.20 (tm, 6H, PC$_6$*H*$_5$), 6.93 (s, 1H, C$_6$ ring: C*H*), 5.99 (m br, 1H, C$_7$ ring: C*H*), 5.34 (m br, 1H, C$_7$ ring: C*H*), 5.07 (t, 1H, C$_7$ ring: C*H*), 5.00 (m br, 1H, C$_7$ ring: C*H*), 4.81 (dd br, 1H, C$_7$ ring: C*H*), 4.60 (dd br, 1H, C$_7$ ring: C*H*), 2.37 (s, 3H, C*H*$_3$), 1.67 (s br, 3H, C*H*$_3$). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 47.7. IR (CH_2Cl_2): ν(CO) 1936 cm^{-1}. Anal. Calcd for $C_{34}H_{30}MoBF_4O_2P$ (M_r = 684.33): C, 59.68; H, 4.42. Found: C, 59.21; H, 4.66.

Preparation of [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)(PPh$_3$)(CNC$_6$-H$_3$Me$_2$)] (11). A solution of **10** (120 mg, 0.2 mmol) in dichloromethane (5 mL) was treated with solid 2,6-dimethylphenyl isocyanide (25 mg, 0.2 mmol) causing an immediate color change from green to red. After being stirred for 15 min, the reaction mixture was added to rapidly stirred diethyl ether (40 mL) to precipitate **11** as a dark red crystalline solid, which was isolated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 135 mg (95%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.42−7.00 (m, 18H, PC$_6$*H*$_5$), 7.03 (s, 1H, C$_6$ ring: C*H*), 6.90 (s, 1H, C$_6$ ring: C*H*), 6.12 (d, 1H, C$_7$ ring: C*H*), 5.96 (s, 1H, O*H*), 5.84 (d, 1H, C$_7$ ring: C*H*), 5.56 (t, 1H, C$_7$ ring: C*H*), 5.32 (m, 2H, C$_7$ ring: C*H*), 5.01 (m, 1H, C$_7$ ring: C*H*), 2.23 (s, 3H, C*H*$_3$), 1.98 (s br, 9H, 3 × C*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 222.4 (d, $^2J_{C,P}$ = 18 Hz, Mo*C*O), 171.2 (s br, *C*≡N), 150.5 (*C*OH), 134.6 (d, $^1J_{C,P}$ = 45 Hz), 133.4 (d, $^2J_{C,P}$ = 10 Hz, PC*C*), 129.2 (d, $^3J_{C,P}$ = 11 Hz, PCC*C*), 133.4−125.5 (C$_6$ rings: *C*H + *C*CH$_3$), 110.5 (C$_7$ ring: *C*-1), 98.4, 97.8, 95.8, 95.7, 94.9, 92.7 (C$_7$ ring: *C*H), 20.2, 18.4, 16.2, 15.5 (*C*H$_3$). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 44.8. IR (CH_2Cl_2): ν 2111(CN), 1966 (CO) cm^{-1}. Anal. Calcd for $C_{43}H_{39}BF_4MoNO_2P$ (M_r = 815.50): C, 63.33; H, 4.82; N, 1.72. Found: C, 62.11; H, 4.66; N, 1.55.

Preparation of [(HOC$_6$H$_2$Me$_2$-η^7-C$_7$H$_6$)Mo(CO)$_2$(PPh$_3$)] (12). A solution of **10** (350 mg, 0.5 mmol) in dichloromethane (10 mL) was treated with phenylacetylene (57 mg, 0.6 mmol). After being heated to reflux for 30 min, the reaction mixture was reduced in volume to about 5 mL and added to rapidly stirred diethyl ether (40 mL) to precipitate **12** as a red-brown crystalline solid, which was isolated by filtration and dried in vacuo. Yield: 230 mg (63%).

Table 2. Crystallographic Data for **5**, **9a**, **10**·$2CH_2Cl_2$, **12**, **13**, and **15**

	5	**9a**	**10**·$2CH_2Cl_2$	**12**	**13**	**15**
formula	$C_{15}H_{13}BF_4O$	$C_{34}H_{29}MoO_2P$	$C_{36}H_{34}BCl_4F_4MoO_2P$	$C_{35}H_{30}BF_4MoO_3P$	$C_{43}H_{38}BrO_2P_3$	$C_{41}H_{38}F_6MoOP_3$
fw	296.06	596.48	854.15	712.31	760.61	849.56
λ, Å; T, K	1.541 78; 223	0.710 73; 198	0.710 73; 198	0.710 73; 198	0.710 73; 198	0.710 73; 198
(sin θ)/λ, Å^{-1}	0.53	0.65	0.62	0.65	0.65	0.59
a, Å	7.012(4)	9.915(1)	17.849(2)	12.453(1)	10.202(1)	12.283(1)
b, Å	26.498(3)	24.601(1)	20.516(2)	18.386(1)	10.211(1)	19.816(1)
c, Å	12.121(2)	11.707(1)	11.566(1)	15.388(1)	19.783(1)	15.790(1)
α, deg	90.00	90.00	90.00	90.00	92.62(1)	90.00
β, deg	98.59(3)	107.95(1)	119.96(1)	113.71(1)	98.02(1)	101.86(1)
γ, deg	90.00	90.00	90.00	90.00	119.01(1)	90.00
V, Å^3	1386.5(9)	2716.6(4)	3669.4(6)	3225.9(4)	1769.3(3)	3761.2(4)
d_{calc}, g cm^{-1}	1.418	1.458	1.546	1.467	1.428	1.500
cryst size, mm	0.03 × 0.05 × 0.05	0.20 × 0.10 × 0.05	0.45 × 0.30 × 0.15	0.40 × 0.30 × 0.10	0.60 × 0.30 × 0.08	0.25 × 0.25 × 0.10
Cryst color	yellow	yellow-orange	green	red	red	brown
Cryst system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)	Cc (9)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)
Z; μ, cm^{-1}	4; 10.66	4; 5.72	4; 7.45	4; 5.14	2; 5.01	4; 5.39
collcd data	1910	10 810	11 117	22 994	11 933	11 613
unique data (R_{int})	1744 (0.055)	6204 (0.023)	5752 (0.043)	7144 (0.063)	7988 (0.024)	6591 (0.067)
obsd data [$I > 2\sigma(I)$]	621	5134	5045	6004	6794	3746
R1; wR2 (obsd data)	0.077; 0.167	0.035; 0.076	0.061; 0.158	0.035; 0.073	0.035; 0.074	0.070; 0.138
transm min/max	0.740/0.949	0.894/0.972	0.730/0.896	0.821/0.950	0.753/0.961	0.877/0.948
no. of variables/flack	192	345	444/0.05(6)	457	444	471
resid electr dens, e/Å^3	0.39/−0.27	0.39/−0.48	0.70/−1.01	0.66/−0.68	0.52/−0.50	0.86/−0.35

^{1}H NMR (200 MHz, acetone-d_6): δ 8.05 (s, 1H, O*H*), 7.46 (m, 15H, PC_6H_5), 7.10 (s, 1H, C_6 ring: C*H*), 7.07 (s, 1H, C_6 ring: C*H*), 6.34 (d, 2H, C_7 ring: C*H*), 5.96 (m, 4H, C_7 ring: C*H*), 2.32 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 216.9 (d, $^2J_{C,P}$ = 17 Hz, Mo*C*O), 151.1 (*C*OH), 134.0 (d, $^2J_{C,P}$ = 13 Hz, PC*C*), 132.1 (PCCC*C*), 130.6 (C_6 ring: *C*H), 130.5 (C_6 ring: *C*H), 129.9 (d, $^3J_{C,P}$ = 10 Hz, PCC*C*), 126.6, 125.5 (C_6 ring: *C*CH$_3$), 115.0 (C_7 ring: *C*-1), 100.6, 100.2, 97.5 (C_7 ring: *C*H), 20.4, 16.8 (*C*H$_3$). The P*C* resonance and one of the *C*H (C_6 ring) resonances were partially concealed by other signals. ^{31}P NMR (81 MHz, acetone-d_6): δ 46.1. IR (CH_2Cl_2): ν(CO) 2019, 1976 cm^{-1}.

Preparation of [($OC_6H_2Me_2$-η^3-C_7H_6)Mo(CO)$_2$(dppe)] (13). A solution of **7** (500 mg, 1.0 mmol) in toluene (20 mL) was treated with the dppe (430 mg, 1.1 mmol), and the reaction mixture was heated to 90 °C for 5 h. After evaporation of the solvent, the product was purified by chromatography on alumina (4% H_2O) with petroleum ether/dichloromethane (1:1) to afford **13** as a red crystalline solid. Yield: 350 mg (45%). ^{1}H NMR (600 MHz, $CDCl_3$, T = 298 K): δ 7.68 (m, 4H, PC_6H_5), 7.48 (m, 10H, PC_6H_5), 7.35 (m, 2H, PC_6H_5), 7.27 (m, 4H, PC_6H_5), 6.92 (s, 1H, C_6 ring: C*H*), 6.65 (s, 1H, C_6 ring: C*H*), 6.21 (m br, 2H, C_7 ring: C*H*), 5.49 (m br, 2H, C_7 ring: C*H*), 5.31 (s br, 2H, C_7 ring: C*H*), 2.96 (m, 2H, PCH_2), 2.33 (m, 2H, PCH_2), 2.18 (s, 3H, CH_3), 1.60 (s, 3H, CH_3). ^{1}H NMR (600 MHz, $CDCl_3$, T = 193 K): δ 7.94 (t, 2H, PC_6H_5), 7.62 (t, 1H, PC_6H_5), 7.57 (t, 2H, PC_6H_5), 7.54 (t, 2H, PC_6H_5), 7.39 (t, 1H, C_7 ring: 2-C*H*), 7.33 (m, 8H, PC_6H_5), 7.26 (dd, 1H, PC_6H_5), 7.18 (m, 4H, PC_6H_5), 6.88 (s, 1H, C_6 ring: C*H*), 6.68 (t, 1H, C_7 ring: 5-C*H*), 6.59 (s, 1H, C_6 ring: C*H*), 5.92 (dd, 1H, C_7 ring: 3-C*H*), 5.75 (dd, 1H, C_7 ring: 4-C*H*), 4.98 (dd, 1H, C_7 ring: 6-C*H*), 2.95 (dm, 1H, PCH_2), 2.81 (m, 1H, PCH_2), 2.63 (dm, 1H, PCH_2), 2.12 (s, 3H, CH_3), 1.81 (m, 1H, PCH_2), 1.44 (s, 3H, CH_3), 1.06 (m br, 1H, C_7 ring: 7-C*H*). ^{13}C NMR (50.3 MHz, $CDCl_3$ T = 298 K): δ 225.5 (t, $^2J_{P,C}$ = 12 Hz, Mo*C*O), 166.2 (MoO*C*), 133.2−128.3 (PC_6H_5 + C_6 ring: *C*H + 4 × C_7 ring: *C*H), 126.2 (C_7 ring: *C*-1), 125.1, 119.7 (C_7 ring: *C*H), 25.3 (dd, $^2J_{C,P}$ = 18 Hz, P*C*H$_2$), 20.4, 16.4 (*C*H$_3$). ^{31}P NMR (81 MHz, $CDCl_3$, T = 298 K): δ 43.9. ^{31}P NMR (81 MHz, $CDCl_3$, T = 243 K): δ 45.3, 43.2. IR (CH_2Cl_2): ν(CO) 1922, 1848 cm^{-1}. Anal. Calcd for $C_{43}H_{38}MoO_3P_2$ (M_r = 760.66): C, 67.90; H, 5.04. Found: C, 67.50; H, 5.37.

Preparation of [($OC_6H_2Me_2$-η^7-C_7H_6)Mo(dppe)] (14). A solution of **13** (1.5 g, 2.0 mmol) in THF (200 mL) was irradiated in a photoreactor until the evolution of CO had ceased (approximately for 48 h). Evaporation of the solvent in vacuo afforded **14** as a dark green solid, which must be handled with great care due to its air sensitivity. Yield: 1.33 g (96%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61−7.00 (m, 21H, PC_6H_5 + C_6 ring: C*H*), 6.81 (s, 1H, C_6 ring: C*H*), 5.02 (m, 2H, C_7 ring: C*H*), 4.12 (m, 2H, C_7 ring: C*H*), 3.73 (m, 2H, C_7 ring: C*H*), 2.48−2.02 (m br, 4H, PCH_2), 2.33 (s, 3H, CH_3), 1.73 (s, 3H, CH_3). ^{31}P NMR (81 MHz, $CDCl_3$): δ 57.8. MS (EI): m/z (%) 706 (100) [M$^+$], 398 (12) [$(C_{26}H_{24}P_2)^+$], 308 (3) [(M − $C_{26}H_{24}P_2$)$^+$]. Anal. Calcd for $C_{41}H_{38}MoOP_2$ (M_r = 704.64): C, 69.89; H, 5.44. Found: C, 69.93; H, 5.48.

Preparation of [($OC_6H_2Me_2$-η^7-C_7H_6)Mo(dppe)]PF6 (15). A solution of **14** (200 mg, 0.3 mmol) in dichloromethane (10 mL) was treated with ferricenium hexafluorophosphate (94 mg, 0.3 mmol). After being stirred for 2 h, the reaction mixture was reduced in volume to about 5 mL and added to rapidly stirred diethyl ether (80 mL) to precipitate **15** as a dark green crystalline solid. Yield: 130 mg (54%). Anal. Calcd for $C_{41}H_{38}F_6MoOP_3$ (M_r = 849.60): C, 57.96; H, 4.51. Found: C, 57.78; H, 4.56.

Physical Measurements. Elemental analyses (C, H, N) were performed on a Haraeus CHNO rapid elemental analyzer. EI and ESI mass spectra were recorded on a Varian MAT 212 or on a Micromass Quattro LCZ mass spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were measured on Bruker AC 200, Bruker AMX 400, or Varian U 600 spectrometers using the solvent as internal standard, whereas ^{31}P NMR measurements were run on a Bruker AC 200 spectrometer using aqueous H_3PO_4 (85%) as an external reference. IR spectra were recorded on a Bruker Vector 22 instrument, and the X-band EPR spectrum was measured on a Bruker ESP 300 spectrometer. The cyclic voltammogram was obtained by use of a Eco-Chemie/Metrohm potentiostat/galvanostat (model PGSTAT 30) on a CH_3CN solution containing 0.1 M TBA-(BF_4) as supporting electrolyte. Platinum and graphite were used as working and counter electrode, respectively, and the potentials were measured against a Ag/AgCl reference electrode (3 M KCl).

The Fc^+/Fc couple displays a reversible cyclic voltammetric trace with a redox potential $E° = +480$ mV under these conditions.

X-ray Crystallography. Data sets were collected with an Enraf Nonius CAD4 and a Nonius KappaCCD diffractometer, the latter one equipped with a rotating anode generator Nonius FR591. Programs used: data collection, EXPRESS (Nonius BV, 1994) and COLLECT (Nonius BV, 1998); data reduction, MolEN (K. Fair, Enraf-Nonius BV, 1990) and Denzo-SMN;[45] absorption correction for CCD data, SORTAV;[46] structure solution, SHELXS-97;[47] structure refinement, SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997); graphics DIAMOND (K. Brandenburg, Universität Bonn, 1997). Crystallographic data for **5**, **9a**, **10**·$2CH_2Cl_2$, **12**, **13**, and **15** are summarized in Table 2. The position of all hydrogens were calculated and refined at riding atoms. In **12**, O1 is disordered at C13 and C9 (ratio 0.87:0.13(1)). In addition, the disordered BF_4 anion was refined with split positions.

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Supporting Information Available: Tables giving details of the X-ray crystal structure analyses and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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