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Molybdenum Complexes with Sterically Demanding Cycloheptatrienyl Ligands

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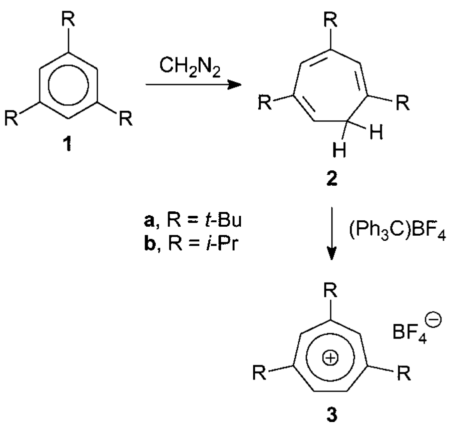
Sterically demanding tropylium salts of the type (1,3,5-$C_7H_4R_3$)BF_4 (**3a**, R = *tert*-butyl; **3b**, R = isopropyl) and (C_7H_6R)BF_4 (**3c**, R = *tert*-butyl; **3d**, R = $SiMe_3$) react with [(η^6-*p*-xylene)Mo(CO)$_3$] by arene exchange and Mo(CO)$_3$ group transfer leading to cationic η^7-cycloheptatrienyl complexes **4a**−**4d** in excellent yields. **4a** further reacts with alkali halides to give [(η^7-1,3,5-$C_7H_4R_3$)Mo(CO)$_2$X] (**5a**, R = *tert*-butyl, X = Cl; **6a**, R = *tert*-butyl, X = I). The X-ray crystal structures of 1,3,5-tri-*tert*-butyltropylium tetrafluoroborate (**3a**) and of [(η^7-1,3,5-$C_7H_4R_3$)Mo(CO)$_3$]BF_4 (**4a**, R = *tert*-butyl) are reported.

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 cyclopentadienes as organometallic ligands is due to the large number of ring-substituted derivatives that have been synthesized since the serendipitous synthesis and discovery of ferrocene. Successive replacement of hydrogen atoms by alkyl or aryl substituents alters the steric and electronic properties of the Cp ring and gives rise to increased steric bulk, solubility, and stability of the resulting complexes.[2] For instance, the introduction of persubstituted derivatives such as the pentamethylcyclopentadienyl ligand Cp* has resulted in the synthesis of a large number of novel complexes and in the discovery of new reactivity patterns.[1,2] This also holds true in the area of ring-substituted arene ligands,[1,3] whereas cycloheptatrienyl complexes, (η-C_7R_7)M, with sterically demanding peralkylated or perarylated ligands have been virtually unexplored[4] until we have recently been able to report on the X-ray crystal structure of a salt containing the heptamethylcycloheptatrienyl cation[5] and on the isolation of the first complexes containing the C_7Me_7 (CHT*) ligand.[6] The steric bulk caused by the seven methyl substituents, however, forces the seven-membered ring in (C_7Me_7)BF_4 to adopt a nonplanar boat conformation,[5] and hence, complexes of the type (η^7-C_7Me_7)M, in which the CHT* ligand is bound with all of its seven ring-carbon atoms, still remain elusive.

Scheme 1



In continuation of our work on transition metal complexes with novel cycloheptatrienyl ligands,[7] we also became interested in employing salts such as **3a** and **3b** containing the 1,3,5-tri-*tert*-butyltropylium or the 1,3,5-triisopropyltropylium ion, respectively, and in the use of these compounds as ligands in organotransition metal chemistry (Scheme 1). Taking into account that the unsubstituted η^7-cycloheptatrienyl ligand already subtends a cone angle closely similar to that of the η^5-pentamethylcyclopentadienyl ligand,[8] we anticipated that the introduction of the *tert*-butyl and isopropyl groups will create ligands with exceptionally large steric

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[†] X-ray crystal structure determinations.

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requirements, leading to complexes of enhanced stability and solubility. Nonetheless, the spatial separation of the three sterically demanding substituents should still be large enough to allow these ligands to coordinate in a planar η^7-fashion. Whereas the "organic" chemistry of the tropylium salts **3**, in particular that of **3a**, is well developed,[9] we wish to report herein on the preparation of the first complexes containing 1,3,5-tri-*tert*-butyl- and 1,3,5-triisopropylcycloheptatrienyl ligands. In addition, the use of $[(\eta^6\text{-}p\text{-xylene})\text{Mo(CO)}_3]$ as a Mo(CO)_3 group transfer reagent for the complexation of tropylium ions is introduced with this contribution, and in order to demonstrate the general applicability of this method, monosubstituted tropylium salts such as $(\text{C}_7\text{H}_6\text{R})\text{BF}_4$ (**3c**, R = *tert*-Bu; **3d**, R = SiMe_3) with decreased steric bulk have been employed, too.

The tropylium salts **3a** and **3b** can be prepared from the 1,3,5-substituted benzene derivatives **1a** and **1b** by CuBr-catalyzed ring-expansion with diazomethane[9b,10] followed by hydride abstraction from the resulting cycloheptatrienes **2a** and **2b** using triphenylcarbenium tetrafluoroborate, $(\text{Ph}_3\text{C})\text{BF}_4$. The conversion of **1** into **2** generally proceeds in only modest yield (approximately 30%). However, the ratio between the unreacted benzene derivative **2** and the corresponding cycloheptatriene **3** can be accurately determined by ^{1}H NMR spectroscopy, allowing the addition of an equimolar amount of $(\text{Ph}_3\text{C})\text{BF}_4$ based on **2**. Finally, the tropylium salt **3** is easily precipitated from the reaction mixture by addition of diethyl ether. The unreacted starting material **1** can be completely recovered and separated from triphenylmethane, Ph_3CH, by distillation under reduced pressure, giving a satisfactory yield based on reisolated **1**.

Only a limited number of high-quality X-ray crystal structures of tropylium salts can be found in the literature, as many of the previous X-ray crystallographic determinations have been of disordered crystals.[11] Hence, crystals of **3a** suitable for X-ray structure determination could be obtained from dichloromethane solution, and the molecular structure of **3a** is shown in Figure 1. The seven-membered ring is almost perfectly planar, and its plane also contains the quarternary carbon atoms C8, C12, and C16 to a good approximation.[12] The intra-ring bond distances in the cation show little but still significant variation (1.368(4)−1.417(4) Å), which may be due to the unsymmetric substitution pattern. The mean value of 1.39 Å, however, is similar to the average C−C distance found for other tropylium cations.[5,11] The bond angles in the seven-membered ring also exhibit some alternation, and all slightly deviate from 128.6° expected for a regular heptagon. Due to the steric demand of the *tert*-butyl groups, the angles about the three quarternary carbon atoms (123.3(3)−125.3(3)°) are significantly smaller than the angles about the four tertiary carbon atoms (131.0(3)−132.6(3)°).

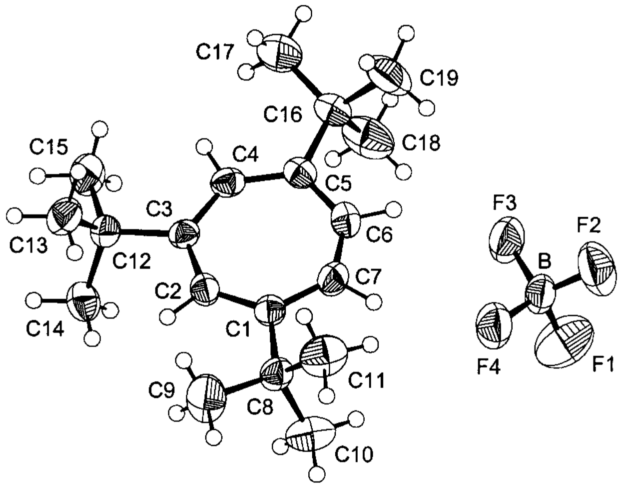

Figure 1. ORTEP drawing of **3a** with thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: C1−C2 1.385(4), C1−C7 1.399(4), C2−C3 1.417(4), C3−C4 1.385(4), C4−C5 1.389(4), C5−C6 1.393(4), C6−C7 1.368(4); C1−C2−C3 131.9(3), C2−C3−C4 125.3(3), C3−C4−C5 132.6(3), C4−C5−C6 123.3(3), C5−C6−C7 131.5(3), C6−C7−C1 131.0(3), C7−C1−C2 123.5(3).

Using the tropylium salts **3a** and **3b** for the preparation of the first transition metal complexes containing the sterically demanding 1,3,5-tri-*tert*-butyl- and 1,3,5-triisopropylcycloheptatrienyl ligands, respectively, we have aimed toward the synthesis of monocationic complexes of the type $[(\eta^7\text{-C}_7\text{H}_4\text{R}_3)\text{Mo(CO)}_3]^+$ since these could provide an extensive chemistry via $[(\eta^7\text{-C}_7\text{H}_4\text{R}_3)\text{Mo(CO)}_2\text{X}]$ (X = halide) or $[(\eta^7\text{-C}_7\text{H}_4\text{R}_3)\text{Mo}(\eta^6\text{-toluene})]^+$.[4,13−15] Usually, the preparation of such η^7-cycloheptatrienyl molybdenum complexes involves the reaction of cycloheptatrienes with a Mo(CO)_3 group transfer reagent, e.g., Mo(CO)_6 or *fac*-$[(\text{RCN})_3\text{Mo(CO)}_3]$ (R = Me, Et), to give η^6-cycloheptatriene complexes followed by hydride abstraction of the *exo*-hydrogen atom with a triphenylcarbenium salt. This approach is of limited use here, as it would require the isolation of the pure trisubstituted cycloheptatrienes **2a** and **2b**, which proved to be difficult under the reaction conditions outlined in Scheme 1 (vide supra). Alternatively, **3a** and **3b** could be reduced by reaction with a hydride source such as NaH or LiAlH_4, but it seems unlikely that this reaction would proceed in a regioselective manner to result in the exclusive formation of **2a** and **2b**, respectively.

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[12] The maximum deviations from the least-squares planes (C1−C7) and (C1−C7, C8, C12, C16) are −0.0615(21) and −0.1039(27) Å, respectively.

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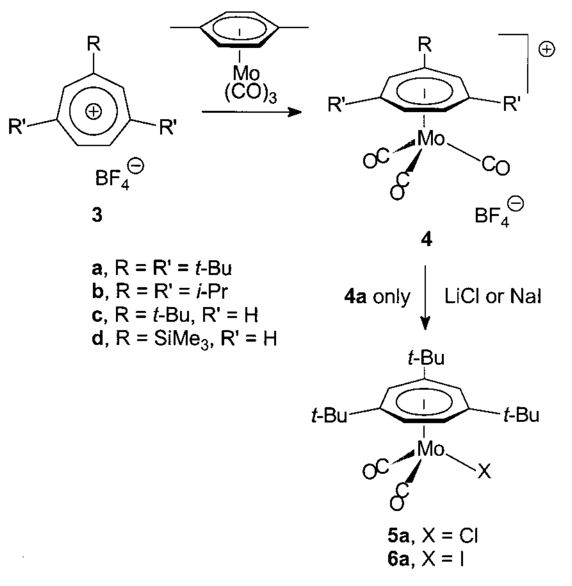
Scheme 2



Therefore, the development of a coordination chemistry based on the $C_7H_4R_3$ system (R = *tert*-butyl, isopropyl) required a high-yielding protocol for the direct complexation of the cations in **3a** and **3b**. Previously, Whiteley and co-workers have demonstrated that the direct reaction of monosubstituted cycloheptatrienyl cations with *fac*-$[(MeCN)_3Mo(CO)_3]$ in the presence of a catalytic amount of the ferricenium cation results in the formation of $[(\eta^7\text{-}C_7H_6R)Mo(CO)_3]^+$ (R = alkyl, alkynyl, aryl), albeit in only moderate yield.[13] Stimulated by reports[16,17] on the possibility of $Mo(CO)_3$ group transfer onto tropyne[16a] and 1,2,4,6-cycloheptatetraene[16b] complexes by using $[(\eta^6\text{-}p\text{-xylene})Mo(CO)_3]$,[18] we have studied the applicability of this method for the complexation of the trisubstituted tropylium cations in **3a** and **3b** as well as for the monosubstituted cations in **3c** and **3d** (Scheme 1). Accordingly, treatment of thf/CH_2Cl_2 solutions of the tropylium tetrafluoroborate salts **3** with a slight excess of $[(\eta^6\text{-}p\text{-xylene})Mo(CO)_3]$ leads to an instantaneous color change from yellow to brown-red and furnishes the cycloheptatrienyl complexes **4** in excellent yields (84–94%) after stirring for about 1 h. The air-stable complexes **4a**–**4d** are obtained as orange-brown, crystalline solids after precipitation with diethyl ether. Due to coordination of the seven-membered ring to the $Mo(CO)_3$ fragment, the NMR spectra of all complexes **4** 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 cations in **3a**–**3d**. The observation of arene exchange at the molybdenum center suggests that tropylium cations are generally bound more strongly than arenes, which is in agreement with the observation that for instance reaction of $[(\eta^7\text{-}C_7H_4R_3)Mo(\eta^6\text{-toluene})]^+$ with nucleophilic ligands leads to displacement of toluene, leaving the cycloheptatrienyl ligand intact.[15]

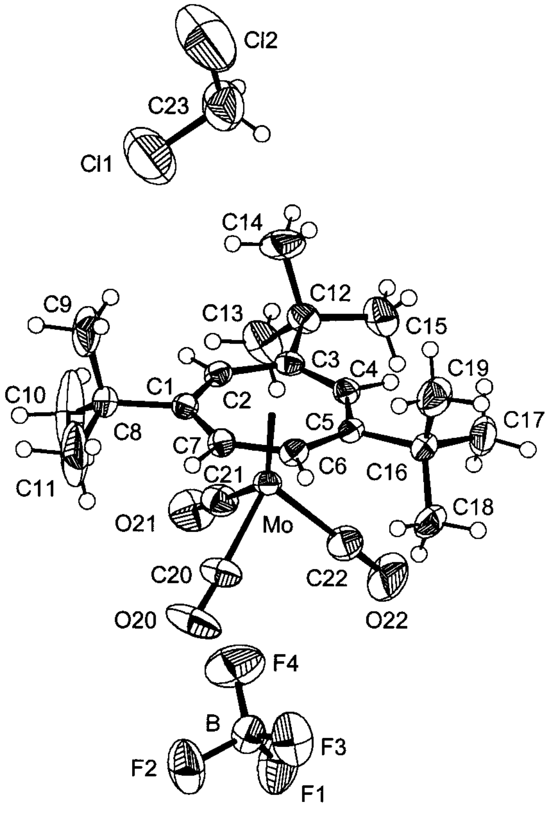


Figure 2. ORTEP drawing of **4a**·CH_2Cl_2 with thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: C1–C2 1.416(3), C1–C7 1.409(3), C2–C3 1.425(3), C3–C4 1.402(3), C4–C5 1.426(3), C5–C6 1.400(3), C6–C7 1.417(3), C20–O20 1.131(4), C21–O21 1.132(4), C22–O22 1.127(4), Mo–C1 2.376(2), Mo–C2 2.303(2), Mo–C3 2.386(2), Mo–C4 2.347(2), Mo–C5 2.396(2), Mo–C6 2.349(2), Mo–C7 2.309(2), Mo–C20 2.017(3), Mo–C21 2.021(3), Mo–C22 2.032(3); C1–C2–C3 132.9(2), C2–C3–C4 124.9(2), C3–C4–C5 132.4(2), C4–C5–C6 124.7(2), C5–C6–C7 130.0(2), C6–C7–C1 131.5(2), C7–C1–C2 123.3(2), Mo–C20–O20 178.2(3), Mo–C21–O21 178.7(3), Mo–C22–O22 179.4(4).

To evaluate structural changes upon coordination of the 1,3,5-tri-*tert*-butyltropylium cation to the $Mo(CO)_3$ fragment, the molecular structure of **4a** was determined by X-ray diffraction analysis of **4a**·CH_2Cl_2 (Figure 2). The seven-membered ring is coordinated in an almost perfectly planar fashion, with its plane also containing the quarternary carbon atoms C8, C12, and C16, which indicates that no bending of the *tert*-butyl groups toward or away from the metal center can be observed upon coordination of the seven-membered ring.[19] Within experimental error, all intra-ring C–C distances are almost identical, and a mean value of 1.41 Å is observed, which is slightly longer than the respective value found for the uncoordinated cation in **3a** (vide supra). This increase in the bond lengths, if significant at all, may be attributed to metal-to-ligand back-bonding, which leads to population of antibonding π^*-molecular orbitals and thus to a decreased C–C bond order. As described for **3a**, the bond angles differ from the expected 128.6°, with the angles being smaller at C1, C3, and C5 and larger at C2, C4, C6, and C7, respectively. The molybdenum atom is symmetrically η^7-coordinated, and all

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(19) The maximum deviations from the least-squares planes (C1–C7) and (C1–C7, C8, C12, C16) are 0.0214(17) and −0.0629(18) Å, respectively.

bond lengths and angles about the metal center fall in the expected ranges.[20]

As mentioned above, the molybdenum complexes **4a** and **4b** could potentially provide an extensive chemistry via complexes of the type $[(\eta^7\text{-C}_7\text{H}_4\text{R}_3)\text{Mo(CO)}_2\text{X}]$ (X = halide) or $[(\eta^7\text{-C}_7\text{H}_4\text{R}_3)\text{Mo}(\eta^6\text{-toluene})]^+$, which would allow to further exploit the chemistry of these sterically demanding cycloheptatrienyl molybdenum complexes.[4,13−15] Attempts to convert **4a** or **4b** into sandwich complexes of the latter type, however, have not yet been successful, and the reaction in refluxing toluene did not solely lead to displacement of the carbonyl groups but was predominantly accompanied by decomposition. Finally, the introduction of halide functional groups has been attempted, and treatment of **4a** with LiCl or NaI, respectively, results in the formation of neutraly charged $[(\eta^7\text{-1,3,5-tri-}\textit{tert}\text{-butylcycloheptatrienyl})\text{Mo(CO)}_2\text{X}]$ (X = Cl, **5a**; X = I, **6a**). Substitution of CO by chloride or iodide leaves the metal center in **5a** and **6a** more electron-rich, thus leading to an increase in backbonding 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 **4a**. These compounds will be particularly useful in view of the widespread use of isoelectronic cyclopentadienyl ruthenium derivatives of the type $[(\eta^5\text{-C}_5\text{R}_5)\text{RuL}_2\text{X}]$ (L = CO, phosphine) in organometallic synthesis and catalysis.[1,21]

In summary, we have presented methods for the high-yielding access to sterically demanding cycloheptatrienyl ligands and to molybdenum complexes thereof. These systems will be particularly useful in view of our general objectives to extend the chemistry of cycloheptatrienyl complexes and to raise their level of significance in comparison with that of cyclopentadienyl and benzene complexes.

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. Triphenylcarbenium tetrafluoroborate,[22] *N*-methyl-*N*-nitrosourea,[23] $[(\eta^6\text{-}p\text{-xylene})\text{Mo(CO)}_3]$,[18] $(\text{C}_7\text{H}_6\text{CMe}_3)\text{BF}_4$ (**3c**),[24] and $(\text{C}_7\text{H}_6\text{SiMe}_3)\text{BF}_4$ (**3d**)[25] were prepared according to published procedures. In principle, the preparation of salts containing the 1,3,5-tri-*tert*-butyltropylium and the 1,3,5-triisopropyltropylium ions had been reported,[9b,10] and the improved protocol for the syntheses of **3a** and **3b** described here is based on a recipe provided by T. Kitagawa (Kyoto University).

Preparation of 1,3,5-Tri-*tert*-butylcycloheptatrienylium Tetrafluoroborate (3a). A solution of diazomethane was prepared by the addition of solid *N*-methyl-*N*-nitrosourea (24.1 g, 234 mmol) to a mixture of KOH (23.25 g, 414 mmol), water (60 mL), and CH_2Cl_2 (180 mL) at −15 °C over 60 min. The organic phase was separated using a cooled separatory funnel and was dried over KOH pellets for 2 h at −78 °C. The diazomethane solution was added via a cooled (−78 °C) dropping funnel to a refluxing mixture of **1a** (23 g, 93 mmol), CuBr (10 g, 70 mmol), and CH_2Cl_2 (25 mL) over 3 h. CuBr was removed by filtration over Celite, and all volatiles were removed in vacuo. The ratio of **1a**:**2a** was determined by ^{1}H NMR spectroscopy and GC/MS to be approximately 65:35. The mixture was dissolved in CH_3CN (90 mL) and CH_2Cl_2 (10 mL) followed by the addition of $(\text{Ph}_3\text{C})\text{BF}_4$ (8.68 g, 26 mmol) and refluxing for 10 min. After evaporation of the solvents, the residue was extracted with petroleum ether (3 × 30 mL) to remove unreacted **1a** and Ph_3CH. The remaining solid was dissolved in the minimum amount of CH_2Cl_2, and this solution was added dropwise to rapidly stirred diethyl ether at 0 °C to precipitate **3a** as a white, crystalline solid, which was collected by filtration and dried in vacuo. The unreacted **1a** can be completely recovered and separated from Ph_3CH by distillation under reduced pressure. Yield: 7.36 g (23% based on converted **1a**, 81% based on reisolated **1a**). ^{1}H NMR (200 MHz, CD_3CN): δ 9.12 (s, 2H, C*H*), 9.06 (s, 2H, C*H*), 1.60 (s, 9H, CH_3), 1.57 (s, 18H, CH_3). ^{13}C NMR (50.3 MHz, CD_3CN): δ 178.6 (3-*C*-*t*-Bu), 178.3 (1,5-*C*-*t*-Bu), 149.9 (*C*H), 147.8 (*C*H), 42.7 (3-*C*CH$_3$), 41.4 (1,5-*C*CH$_3$), 31.1 (3-C*C*H$_3$), 30.7 (1,5-C*C*H$_3$). Anal. Calcd for $\text{C}_{19}\text{H}_{31}\text{BF}_4$ (M_r = 346.25): C, 65.91; H, 9.02. Found: C, 65.71; H, 9.09.

Preparation of 1,3,5-Triisopropylcycloheptatrienylium Tetrafluoroborate (3b). Following the procedure outlined for the synthesis of **3a**, a mixture of **1b** and **2b** was obtained from *N*-methyl-*N*-nitrosourea (24 g, 232 mmol), KOH (24 g, 428 mmol), CuBr (10 g, 70 mmol), and **1b** (25.8 g, 126 mmol). This mixture containing approximately 30% of **2b** was treated with $(\text{Ph}_3\text{C})\text{BF}_4$ (7.72 g, 23 mmol) as described above, and **3b** was isolated as an off-white solid. Yield: 5.53 g (14% based on converted **1b**, 78% based on reisolated **1b**). ^{1}H NMR (200 MHz, CD_3CN): δ 8.76 (s, 2H, C*H*), 8.72 (s, 2H, C*H*), 3.49 (m, 3H, C*H*CH$_3$), 1.45 (d, J = 6.8 Hz, 6H, 3-CHCH_3), 1.43 (d, J = 6.8 Hz, 12H, 1,5-CHCH_3). ^{13}C NMR (50.3 MHz, CD_3CN): δ 178.4 (3-*C*-*i*-Pr), 177.3 (1,5-*C*-*i*-Pr), 150.9 (*C*H), 150.7 (*C*H), 41.4 (3-*C*HCH$_3$), 40.5 (1,5-*C*HCH$_3$), 23.3 (3-CH*C*H$_3$) 23.1 (1,5-CH*C*H$_3$). Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{BF}_4$ (M_r = 304.18): C, 63.18; H, 8.28. Found: C, 62.75; H, 8.49.

Preparation of Tricarbonyl(1,3,5-tri-*tert*-butylcycloheptatrienyl)molybdenum Tetrafluoroborate (4a). **3a** (2.0 g, 5.8 mmol) was added to a solution of $[(\eta^6\text{-}p\text{-xylene})\text{Mo(CO)}_3]$ (1.8 g, 6.4 mmol) in thf (60 mL). After stirring the reaction mixture for 1 h under ambient conditions, the solution was reduced in volume to about 20 mL, and diethyl ether (100 mL) was added to precipitate **4a**, which was isolated as a yellow-brown solid after filtration. Yield: 2.8 g (92%). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.02 (s, 2H, C*H*), 6.94 (s, 2H, C*H*), 1.56 (s, 9H, CH_3), 1.54 (s, 18H, CH_3). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 210.7 (*C*O), 131.7 (1,5-*C*-*t*-Bu), 128.2 (3-*C*-*t*-Bu), 100.0 (*C*H), 98.6 (*C*H), 40.0 (3-*C*CH$_3$), 39.3 (1,5-*C*CH$_3$), 32.7 (3-C*C*H$_3$), 32.4 (1,5-C*C*H$_3$). IR (CH_2Cl_2): ν(CO) 2060, 2014, 1994 (sh) cm^{-1}. Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{BF}_4\text{MoO}_3$ (M_r = 526.22): C, 50.21; H, 5.94. Found: C, 50.26; H, 5.81.

Preparation of Tricarbonyl(1,3,5-triisopropylcycloheptatrienyl)molybdenum Tetrafluoroborate (4b). Following the procedure described for the synthesis of **4a**, **4b** was obtained as an orange solid from the reaction of **3b** (420 mg, 1.4 mmol) with $[(\eta^6\text{-}p\text{-xylene})\text{Mo(CO)}_3]$ (400 mg, 1.4 mmol) in thf (40 mL). Yield: 520 mg (84%). ^{1}H NMR (200 MHz, acetone-d_6): δ 6.54 (s, 2H, C*H*), 6.52 (s, 2H, C*H*), 3.18 (m, 3H, C*H*CH$_3$), 1.44 (m, 18H, 1,3,5-CHCH_3). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 210.1 (*C*O), 128.9 (1,5-*C*-*i*-Pr), 128.0 (3-*C*-*i*-Pr), 99.9 (*C*H), 99.4 (*C*H), 38.6 (3-*C*HCH$_3$), 38.0 (1,5-*C*HCH$_3$), 24.6 (1,5-CH*C*H$_3$) 24.5 (3-CH*C*H$_3$). IR (CH_2Cl_2): ν(CO) 2061, 2012 cm^{-1}. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{BF}_4\text{MoO}_3$ (M_r = 484.14): C, 47.14; H, 5.20. Found: C, 47.87; H, 5.26.

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Preparation of Tricarbonyl(*tert*-butylcycloheptatrienyl)molybdenum Tetrafluoroborate (4c). Following the procedure described for the synthesis of **4a**, **4c** was obtained as an orange solid from the reaction of **3c** (400 mg, 1.7 mmol) with [(η^6-*p*-xylene)Mo(CO)$_3$] (500 mg, 1.7 mmol) in thf (45 mL). Yield: 680 mg (94%). ^{1}H NMR (200 MHz, acetone-d_6): δ 6.97 (d, 2H, C*H*), 6.65 (dd, 2H, C*H*), 6.38 (m, 2H, C*H*) 1.53 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 208.8 (*C*O), 133.4 (*C*-*t*-Bu), 102.3, 100.8, 99.8 (*C*H), 38.6 (*C*CH$_3$), 32.3 (C*C*H$_3$). IR (CH$_2$Cl$_2$): ν(CO) 2074, 2017 cm^{-1}. Anal. Calcd for $C_{14}H_{15}BF_4MoO_3$ (M_r = 414.01): C, 40.62; H, 3.65. Found: C, 40.55; H, 3.67.

Preparation of Tricarbonyl(trimethylsilylcycloheptatrienyl)molybdenum Tetrafluoroborate (4d). Following the procedure described for the synthesis of **4a**, **4d** was obtained as orange-red solid from the reaction of **3d** (420 mg, 1.7 mmol) with [(η^6-*p*-xylene)Mo(CO)$_3$] (500 mg, 1.7 mmol) in thf (40 mL). Yield: 660 mg (88%). ^{1}H NMR (200 MHz, acetone-d_6): δ 6.81 (d, 2H, C*H*), 6.67 (dd, 2H, C*H*), 6.34 (m, 2H, C*H*) 0.47 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 208.6 (*C*O), 112.8 (*C*-SiCH$_3$), 106.4, 103.0, 102.8 (*C*H), −0.9 (Si*C*H$_3$). IR (CH$_2$Cl$_2$): ν(CO) 2076, 2021 cm^{-1}. Anal. Calcd for $C_{13}H_{15}BF_4MoO_3Si$ (M_r = 430.09): C, 36.30; H, 3.52. Found: C, 36.53; H, 3.29.

Preparation of Dicarbonyl(1,3,5-tri-*tert*-butylcycloheptatrienyl)molybdenum Chloride (5a). LiCl (51 mg, 2.1 mmol) was added to a solution of **4a** (1.0 g, 1.9 mmol) in acetone (20 mL), leading to an instantaneous color change from orange-red to green. After stirring for 1 h, the solvent was removed in vacuo, and the product was extracted with toluene (40 mL). After filtration over Celite, reducing the volume to 10 mL and addition of diethyl ether (30 mL), the mixture was cooled to −78 °C to afford **5a** as dark green crystals. Yield: 430 mg (51%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.89 (s, 2H, C*H*), 5.67 (s, 2H, C*H*), 1.48 (s, 18H, CH_3), 1.27 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 221.7 (*C*O), 127.8 (1,5-*C*-*t*-Bu), 117.6 (3-*C*-*t*-Bu), 100.3 (*C*H), 82.4 (*C*H), 37.5 (1,3,5-*C*CH$_3$), 32.4 (1,3,5-C*C*H$_3$). IR (CH$_2$Cl$_2$): ν(CO) 1989, 1936 cm^{-1}. Anal. Calcd for $C_{21}H_{31}ClMoO_2$ (M_r = 446.86): C, 56.44; H, 6.99. Found: C, 55.91; H, 6.76.

Preparation of Dicarbonyl(1,3,5-tri-*tert*-butylcycloheptatrienyl)molybdenum Iodide (6a). NaI (1.17 g, 7.8 mmol) was added to a solution of **4a** (0.82 g, 1.6 mmol) in acetone (40 mL), and the reaction mixture was stirred overnight. The solvent was removed in vacuo, and the product was extracted with CH$_2$Cl$_2$ (40 mL). After filtration over Celite, the residue was recrystallized from diethyl ether (15 mL) at −78 °C to afford **6a** as dark green crystals. Yield: 660 mg (79%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.96 (s, 2H, C*H*), 5.91 (s, 2H, C*H*), 1.47 (s, 18H, CH_3), 1.30 (s, 9H, CH_3). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 217.8 (*C*O), 125.9 (1,5-*C*-*t*-Bu), 98.9 (*C*H), 81.7 (*C*H), 37.2 (1,3,5-*C*CH$_3$), 32.5 (1,3,5-C*C*H$_3$), the resonance for 3-*C*-*t*-Bu could not be observed. IR (CH$_2$Cl$_2$): ν(CO) 1988, 1938 cm^{-1}. Anal. Calcd for $C_{21}H_{31}IMoO_2$ (M_r = 538.32): C, 46.86; H, 5.80. Found: C, 46.36; H, 5.78.

X-ray Crystallography. Data sets were collected with Enraf-Nonius CAD4 (**3a**) and Nonius KappaCCD diffractometers (**4a**·CH$_2$Cl$_2$), the latter one equipped with a rotating anode Nonius FR591 generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN[26] and Denzo-SMN,[27] absorption correction for CCD data SORTAV,[28] structure solution SHELXS-97,[29] structure refinement SHELXL-97,[30] graphics DIAMOND.[31] **3a**: formula $C_{19}H_{31}BF_4$, M = 346.25, colorless crystal 0.15 × 0.10 × 0.10 mm, $a = 10.223(5)$, $b = 10.936(3)$, $c = 18.195(6)$ Å, $\beta = 101.57(4)°$, $V = 1992.8(13)$ Å^3, $\rho_{calc} = 1.154$ g cm^{-3}, $\mu = 7.55$ cm^{-1}, empirical absorption correction via ψ scan data ($0.895 \leq T \leq 0.928$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3502 reflections collected ($\pm h$, $+k$, $+l$), [(sin θ)/λ] = 0.59 Å^{-1}, 3390 independent ($R_{int} = 0.085$) and 1701 observed reflections [$I \geq 2\sigma(I)$], 226 refined parameters, $R = 0.057$, $wR_2 = 0.141$, max. residual electron density 0.20 (−0.23) e Å^{-3}, hydrogens calculated and refined as riding atoms. **4a**·CH$_2$Cl$_2$: formula $C_{22}H_{31}O_3MoBF_4 \cdot CH_2Cl_2$, M = 611.14, orange crystal 0.40 × 0.25 × 0.20 mm, $a = 10.892(1)$, $b = 11.195(1)$, $c = 13.359(1)$ Å, $\alpha = 85.04(1)$, $\beta = 72.54(1)$, $\gamma = 64.09(1)°$, $V = 1395.8(2)$ Å^3, $\rho_{calc} = 1.454$ g cm^{-3}, $\mu = 7.09$ cm^{-1}, empirical absorption correction via SORTAV ($0.765 \leq T \leq 0.871$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 13 568 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 6317 independent ($R_{int} = 0.029$) and 5836 observed reflections [$I \geq 2\sigma(I)$], 316 refined parameters, $R = 0.038$, $wR_2 = 0.096$, max. residual electron density 0.68 (−0.83) e Å^{-3}, hydrogens calculated and refined as riding atoms.

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Supporting Information Available: Details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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