Organometallics **2004,** *23,* 3741−3744 3741

Notes

Synthesis of Substituted Arene Molybdenum Complexes by Arene Exchange

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Received March 23, 2004

*Summary: THF-mediated arene exchange in [Mo(benzene)(CO)$_3$] (**1**) at ambient temperature affords Mo(CO)$_3$ complexes of substituted arenes in good yields (13 examples).*

The synthetic opportunities offered by the complexation of an arene to the Cr(CO)$_3$ fragment has attracted much attention both in catalysis and in organic synthesis.[1] While other electrophilic and nucleophilic metal complex fragments have also seen development in organic synthesis,[1d,2] it is surprising that no analogous development has taken place for Mo(η^6-arene)(CO)$_3$ complexes.[3]

Thermochemical studies show that the arene−Mo bond (68 kcal·mol^{-1} in [Mo(η^6-C$_6$H$_6$)(CO)$_3$] (**1**)) is stronger than the arene−Cr bond (53 kcal·mol^{-1} in [Cr(η^6-C$_6$H$_6$)(CO)$_3$]).[4] M−H bonds are also stronger with the second-row transition metal as shown by the values of 62 and 54 kcal/mol in [MoCp(CO)$_3$(H)] and [CrCp(CO)$_3$(H)], respectively.[5] Kinetically, however, the situation is reversed. The metal−arene bond in [Mo(η^6-C$_6$H$_6$)(CO)$_3$] (**1**) is far more labile than that in [Cr(η^6-C$_6$H$_6$)(CO)$_3$]. This lability and the resulting difficulty in handling the Mo compounds have retarded their use in synthesis. In a preliminary communication we showed that there are different selectivities in the reactions of the Cr and Mo complexes and that the higher bond strength in the Mo−C and Mo−H bonds renders the isolation of intermediates possible that have eluded characterization in the Cr-mediated reaction sequence.[3]

In continuation of our research in arene transformations via temporary complexation to the Mo(CO)$_3$ fragment we examined the synthetic approaches to functionalized Mo(η^6-arene)(CO)$_3$ complexes, and this article reports our results on their synthesis.

A survey of the literature confirmed that the most direct synthesis of these complexes, thermolysis of the hexacarbonyl complex in the presence of an excess of the arene in a high-boiling solvent, is much more limited than for the analogous chromium complexes.[6] The long reaction times at elevated temperature (e.g., 10 days for the benzene complex **1**) and the high sensitivity to oxygen often result in low yields for substituted arenes.[7] While [Mo(η^6-C$_6$H$_6$)(CO)$_3$] (**1**) has been reportedly obtained in near quantitative yield, the yield was based on liberated CO rather than on the amount of isolated complex.[8] In our hands, an isolated yield of 50−60% of **1** is more realistic for this procedure. The reaction time can be shortened by reacting Mo(CO)$_6$ in benzene in the presence of pyridine in an autoclave.[7b] Toma and coworkers have described a different procedure that uses a double condenser system and decalin plus ethylformiate as solvent. With a bath temperature of 240 °C this cuts the preparation time of the *N*,*N*-dimethylaniline complex to 1 h (55% yield).[7a] Alternatively, Mo(CO)$_3$-

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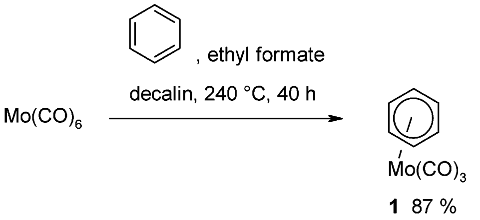
10.1021/om049792m CCC: $27.50
Publication on Web 06/17/2004

Scheme 1. Synthesis of $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (1)



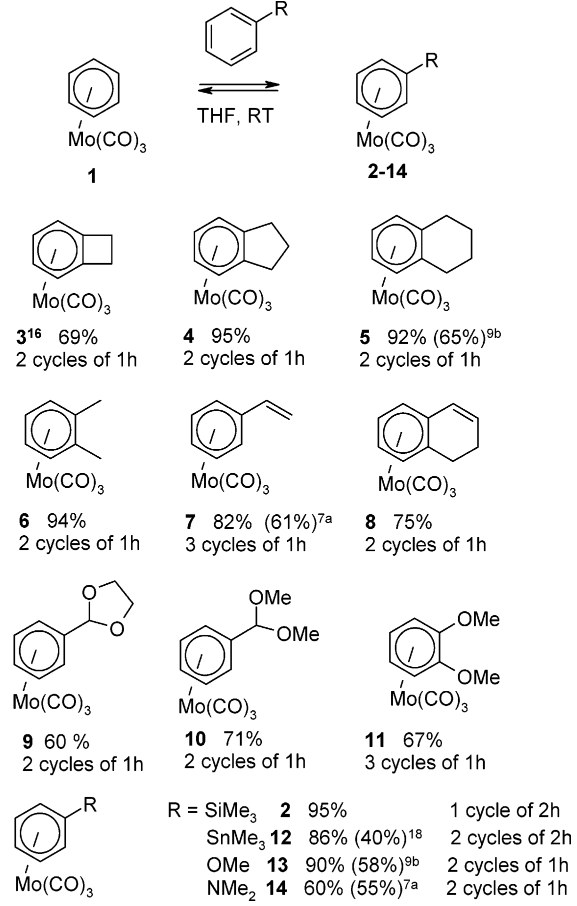
$(L)_3$ complexes (L = Py, DMF, $(L)_3$ = diglyme) can be used as more labile precursors, and with the pyridine and the DMF complexes ligand substitution for an arene or heteroarene can be performed at room temperature when BF_3-Et_2O is added.[9] Despite the diversity of methods reported for the synthesis of $Mo(\eta^6\text{-arene})(CO)_3$ complexes, reports on complexes involving arenes with functional groups other than alkyl are quite scarce and yields are often poor. It is apparent that there is a need for efficient alternative methods of access to these compounds.

The benzene ligand in $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) is susceptible to a rapid and complete displacement by THF at 25 °C to afford $[Mo(CO)_3(THF)_3]$.[10] Muetterties et al. studied arene exchange reactions of **1** and found that the addition of a catalytic amount of a Lewis basic solvent such as acetone or THF allows arene exchange to proceed under mild conditions.[11] In contrast, elevated temperatures (>140 °C in THF) are required for arene exchange in the Cr(arene)$(CO)_3$ complexes.[12] For this reason, arene exchange is a useful synthetic method only for labile complexes such as $[Cr(\eta^6\text{-naphthalene})(CO)_3]$,[13] $[Cr(\eta^6\text{-}C_6H_6)(\eta^2\text{-methyl acrylate})(CO)_2]$,[14] and $[Cr(\eta^5\text{-}N\text{-methylpyrrole})(CO)_3]$.[15]

Taking a cue from Muetterties pioneering work,[11] we chose $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) as $Mo(CO)_3$ transfer reagent. The starting complex **1** was in turn synthesized by applying the method used by Toma et al. for $[Mo(CO)_3(\eta^6\text{-}N,N\text{-dimethylaniline})]$[7a] mentioned above. After optimization, this afforded $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) in high yield (Scheme 1).

Stirring the benzene complex **1** in a mixture of trimethylphenylsilane and THF (3 molar equiv each) for 2 h at 25 °C resulted in quantitative arene exchange and the isolation of $[Mo(\eta^6\text{-}C_6H_5SiMe_3)(CO)_3]$ (**2**) in 95% yield. With all other arenes, exchange was not complete under these conditions and workup afforded mixtures of starting complex (minor) and arene exchange product (major). The equilibrium could be shifted by removal of volatiles (benzene, THF, and low molecular weight arenes) and renewed addition of THF or an arene/THF mixture in the case of volatile arenes. With most arenes listed in Scheme 2, this led to complete exchange except with styrene and veratrole, where an additional evaporation/arene addition proved advantageous. This simple procedure, carried out under strict exclusion of air, afforded the $Mo(\eta^6\text{-arene})(CO)_3$ complexes in satisfactory to excellent yields. The yields of the pale yellow functionalized arene complexes obtained by this procedure compare in all cases favorably with those reported using other precursors.[16]

Scheme 2. Synthesis of Substituted Tricarbonyl(η^6-arene)molybdenum Complexes (in parenthesis: previously reported yields using different methods of synthesis)



We have scaled up this arene exchange to 10 mmol scale for complexes **3** and **13** without loss of yield compared to the standard 1 mmol scale. Limitations of the method are with arenes bearing electron-withdrawing groups. Handling becomes very difficult due to the high lability of the metal–arene bond in these cases. Thus attempts to isolate pure samples of complexes such as $[Mo(\eta^6\text{-}C_6H_5\text{-}R)(CO)_3]$ (R = CHO, oxazoline, imine, esters) did not meet with success.

In conclusion, the advantages of the synthesis of $Mo(\eta^6\text{-arene})(CO)_3$ complexes via arene exchange reactions are higher yields, shorter reaction times, and easy workup. This efficient method provides a reliable access to $Mo(CO)_3$ complexes of substituted arenes and sets the stage for exploration into arene functionalization reactions using this class of compounds.

Experimental Section

All manipulations involving Mo complexes were carried out under an atmosphere of purified nitrogen (99.995%) using standard inert gas/vacuum double manifold and Schlenk techniques. All solutions were degassed via three freeze/pump/thaw cycles before addition of Mo(arene)$(CO)_3$ complexes. $[Mo(CO)_6]$ was obtained from Fluka and used as received. Tet-

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rahydrofuran was distilled from Na/benzophenone ketyl, benzene over Na, hexane, and methylene chloride over calcium hydride immediately before use. Arenes were dried over Na and distilled under reduced pressure. 1,2-Dihydrocyclobutabenzene was prepared according to a published procedure.[17]

Celite 545 (Fluka) was used as a filtering material for Mo compounds, and Polygram Sil G/UV_{254} precoated plastic sheets (Macherey-Nagel) were used for TLC. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using NaCl cells. NMR spectra were recorded on a Varian XL-200 or a Bruker AMX-400 spectrometer. The ^1H NMR spectra were referenced to the chemical shift of residual solvent resonances (D_5-benzene δ 7.16). $^{13}C\{^1H\}$ NMR spectra were referenced to D_6-benzene (δ 128.00). Electron ionization mass spectra (EIMS) were recorded on a Varian CH4 or SM1 spectrometer; relative intensities are given in parentheses. High-resolution mass spectra (HRMS) were recorded on a VG 7070E instrument. Melting points were measured on a Büchi 510 apparatus in sealed capillaries.

Preparation of Tricarbonyl(η^6-benzene)molybdenum (1).[7b,d,8,9a,b] A 500 mL round-bottomed flask charged with $[Mo(CO)_6]$ (10.00 g, 37.88 mmol) and equipped with a two-stage condenser[7a] was dried under vacuum during 30 min. The flask was then charged with degassed decalin (300 mL), benzene (13.40 mL, 151.51 mmol), and ethyl formate (16.80 mL, 208.38 mmol), and the mixture was stirred in the dark under N_2 at 240 °C for 40 h. [In the two-stage condenser, the lower stage was cooled by acetone (reflux).] $[Mo(CO)_6]$ sublimes to this level. The upper stage was cooled by water (solvents condensed here and then washed down the sublimed solids). The mixture was then cooled to room temperature (under N_2), resulting in the precipitation of a dark yellow residue, which was isolated by decantation, washed twice with 5 mL of hexane, and dried under vacuum. The crude product was dissolved in hot benzene and filtered over Celite under a N_2 atmosphere. Evaporation of all volatiles and sublimation of excess $[Mo(CO)_6]$ under vacuum gave **1** as a yellow solid (8.50 g, 87%). IR (hexane): ν(CO) 1987 (s), 1916 (m) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): 4.49 (s, 6H, C_6H_6). ^{13}C NMR (50 MHz, C_6D_6): 93.9 (CH), 221.2 (CO).

General Procedure for the Preparation of Substituted Tricarbonyl(η^6-arene)molybdenum Complexes. $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) was added to a degassed solution of a 3-fold excess of free arene and THF. After stirring at room temperature, all volatiles were removed under vacuum. Where necessary the same quantities of THF and arene (for volatile arenes only) were added and the above procedure was repeated.

Preparation of Tricarbonyl(trimethyl-η^6-phenylsilane)molybdenum (2).[18] A general procedure with $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) (0.50 g, 1.94 mmol), trimethylphenylsilane (1.00 mL, 5.81 mmol), and THF (0.47 mL, 5.81 mmol) with 2 h stirring was followed. The residue was dissolved in warm methylcyclohexane, filtered through Celite. Solvent removal under vacuum afforded yellow **2** (0.61 g, 95%). Mp: 86−88 °C (dec). IR (hexane): ν(CO) 1981 (s), 1947 (w), 1911 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): 0.02 (s, 9H, $Si(CH_3)_3$), 4.51 (t, J = 6.4 Hz, 2H, C_6H_5), 4.79 (t, J = 6.4 Hz, 1H, C_6H_5), 4.89 (d, J = 6.4 Hz, 2H, C_6H_5). ^{13}C NMR (100 MHz, C_6D_6): −1.2 (CH_3), 92.3 (CH), 95.8 (CH), 99.9 (CH), 102.6 ($C_{quaternary}$), 221.5 (CO). MS *m/z*: 332 (10, M^+, ^{98}Mo), 304 (2), 276 (11), 246 (47), 242 (35), 214 (7), 163 (3), 135 (100), 119 (3), 105 (9), 67 (3), 53 (9). HRMS: calcd for $C_{12}H_{14}{}^{98}MoO_3Si$ 331.9766; found 331.9736.

Preparation of Tricarbonyl(η^6-1,2-dihydrocyclobutabenzene)molybdenum (3). A general procedure with $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) (0.50 g, 1.94 mmol), 1,2-dihydrocyclobutabenzene (0.60 g, 5.81 mmol), and THF (0.47 mL, 5.81 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (new addition of arene and THF). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. Solvent removal under vacuum afforded yellow **3** (0.37 g, 69%). Mp: 95−100 °C (dec). IR (cyclohexane): ν(CO) 1978 (s), 1908 (s) cm^{-1}.^1H NMR (300 MHz, C_6D_6): 2.26−2.37 (m, 2H, CH_{exo}), 2.54−2.65 (m, 2H, CH_{endo}), 4.44−4.47 (m, 2H, C_6H_4), 4.86−4.88 (m, 2H, C_6H_4). ^{13}C NMR (75 MHz, C_6D_6): 29.9 (CH_2), 90.8 (CH), 92.3 (CH), 119.1 ($C_{quaternary}$), 222.1 (CO). MS *m/z*: 286 (9, M^+, ^{98}Mo), 258 (3), 200 (33), 141 (9), 104 (100), 78 (68), 51 (38). HRMS: calcd for $C_{11}H_8{}^{96}MoO_3$ 283.9520; found 283.9557.

Preparation of Tricarbonyl(η^6-indane)molybdenum (4). A general procedure with $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) (1.80 g, 6.97 mmol), indane (2.59 mL, 20.92 mmol), and THF (1.70 mL, 20.92 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (addition of THF only). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. Solvent removal under vacuum afforded yellow **4** (1.95 g, 94%). Mp: 89−92 °C (dec). IR (cyclohexane): 1976 (s), 1905 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): 1.45−1.54 (m, 1H, CH_2), 1.70−1.87 (m, 1H, CH_2, 2.06−2.24 (m, 4H, CH_2), 4.70−4.73 (m, 2H, C_6H_4), 4.97−5.00 (m, 2H, C_6H_4). ^{13}C NMR (75 MHz, C_6D_6): 24.3 (CH_2), 31.9 (CH_2), 91.6 (CH), 93.3 (CH), 117.9 ($C_{quaternary}$), 222.4 (CO). MS *m/z*: 182 (1), 117 (100), 91 (16), 58 (8), 51 (7). HRMS: calcd for $C_{12}H_{10}{}^{98}MoO_3$ 299.9684; found 299.9703.

Preparation of Tricarbonyl(η^6-tetralin)molybdenum (5).[9b] A general procedure with $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) (0.25 g, 0.97 mmol), tetralin (0.40 mL, 2.91 mmol), and THF (0.24 mL, 2.91 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (addition of THF only). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. Concentration to 1 mL caused precipitation of **5** as a yellow solid (0.28 g, 92%). Mp: 114−118 °C (dec). IR (methylcyclohexane): ν(CO) 1975 (s), 1902 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): 1.12−1.24 (m, 2H, CH_2), 1.38−1.49 (m, 2H, CH_2), 1.94−2.04 (m, 2H, CH_2), 2.24−2.34 (m, 2H, CH_2), 4.74−4.84 (m, 4H, C_6H_4). ^{13}C NMR (75 MHz, C_6D_6): 21.9 (CH_2), 27.9 (CH_2), 93.4 (CH), 95.1 (CH), 112.8 ($C_{quaternary}$), 222.4 (CO). MS *m/z*: 314 (10, M^+, ^{98}Mo), 286 (3), 254 (23), 226 (33), 198 (2), 170 (3), 141 (2), 132 (56), 104 (100), 77 (12), 51 (13). HRMS: calcd. for $C_{13}H_{12}{}^{96}MoO_3$ 311.9833; found 311.9822.

Preparation of Tricarbonyl(η^6-*o*-xylene)molybdenum (6). A general procedure with $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) (0.25 g, 0.97 mmol), *o*-xylene (0.35 mL, 2.91 mmol), and THF (0.24 mL, 2.91 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (addition of arene and THF). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. Solvent removal under vacuum afforded yellow **6** (0.26 g, 94%). Mp: 115−120 °C (dec). IR (methylcyclohexane): ν(CO) 1976 (s), 1905 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): 1.64 (s, 6H, CH_3), 4.73−4.77 (m, 2H, C_6H_4), 4.83−4.86 (m, 2H, C_6H_4). ^{13}C NMR (75 MHz, C_6D_6): 18.5 (CH_3), 93.3 (CH), 96.6 (CH), 110.7 ($C_{quaternary}$), 222.4 (CO). MS *m/z*: 288 (30, M^+, ^{98}Mo), 260 (9), 232 (18), 202 (100), 170 (18), 141 (11), 136 (6), 106 (46), 91 (84), 51 (14). HRMS: calcd for $C_{11}H_{10}{}^{98}MoO_3$ 287.9684; found 287.9658.

Preparation of Tricarbonyl(η^6-styrene)molybdenum (7).[9b] A general procedure with $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) (0.25 g, 0.97 mmol), styrene (0.34 mL, 2.91 mmol), and THF (0.24 mL, 2.91 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated twice (addition of THF and arene). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. Solvent removal under vacuum afforded yellow **7** (0.23 g, 82%). Mp: 74−78 °C (dec). IR (hexane): ν(CO) 1986 (s), 1918 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): 4.59 (t, J = 6.6 Hz, 1H, C_6H_5), 4.75 (t, J = 6.4 Hz, 2H, C_6H_5), 4.85−4.90 (m, 3H, C_6H_5, $CHCH_{2trans}$), 5.07 (d, J = 17.5 Hz, 1H, $CHCH_{2cis}$), 5.64 (dd, J = 17.5, 10.9 Hz, 1H, $CHCH_2$). ^{13}C NMR (75 MHz, C_6D_6): 91.2 (CH), 91.9 (CH), 93.8 (CH),

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(16) A number of substituted $Mo(CO)_3$(cyclobutabenzene) complexes were made using a similar procedure. See ref 1h.

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108.1 ($C_{quaternary}$), 115.6 (CH_2), 132.9 (CH), 221.0 (CO). MS *m/z*: 286 (7, M^+, ^{98}Mo), 258 (2), 230 (4), 202 (24), 174 (6), 148 (3), 123 (2), 104 (100), 78 (44), 51 (33). HRMS: calcd for $C_{11}H_8{}^{98}MoO_3$ 285.9527; found 285.9505.

Preparation of Tricarbonyl(η^6-1,2-dihydronaphthalene)molybdenum (8). A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (0.25 g, 0.97 mmol), 1,2-dihydronaphthalene (0.38 mL, 2.91 mmol), and THF (0.24 mL, 2.91 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (addition of THF only). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. Concentration and addition of hexane caused precipitation of **8** as a yellow solid (0.22 g, 75%). Mp: 118−123 °C (dec). IR (methylcyclohexane): ν(CO) 1976 (s), 1907 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): 1.71−1.98 (m, 2H, CH_2), 2.09−2.22 (m, 2H, CH_2), 4.60−4.81 (m, 4H, C_6H_4), 5.55−5.65 (m, 2H, CC*H*C*H*CH_2). ^{13}C NMR (75 MHz, C_6D_6): 23.6 (CH_2), 26.5 (CH_2), 93.0 (CH), 93.1 (CH), 94.3 (CH), 105.8 ($C_{quaternary}$), 111.6 ($C_{quaternary}$), 123.7 (CH), 132.2 (CH), 222.4 (CO). MS *m/z*: 312 (2, M^+, ^{98}Mo), 254 (2), 226 (5), 130 (100), 129 (79), 127 (22), 115 (44), 64 (15), 51 (18). HRMS: calcd for $C_{13}H_{10}{}^{98}MoO_3$ 311.96840; found 311.97146.

Preparation of Tricarbonyl[2-(η^6-phenyl)-[1,3]dioxolane]molybdenum (9). A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (0.50 g, 1.94 mmol), 2-phenyl-[1,3]dioxolane (0.87 g, 5.81 mmol), and THF (0.47 mL, 5.81 mmol) was followed. After removal of volatiles under vacuum, the residue was dissolved in 2 mL of a 1:1 degassed hexane−CH_2Cl_2 mixture and filtered through a silica gel pad (0.50 cm). The pad was rinsed with 4 × 2 mL of a 1:1 hexane−CH_2Cl_2 mixture. Concentration to 6 mL (a small quantity of residual CH_2Cl_2 is necessary for crystallization to occur) and cooling to −30 °C overnight afforded **9** as a yellow crystalline solid, which was washed with a single portion of cold (−30 °C) hexane. Yield of **9**: 0.38 g, 60%. Mp: 65−70 °C (dec). IR (hexane): ν(CO) 1986 (s), 1915 (s) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1973 (s), 1892 (s),1099 (w) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): 3.25−3.29 (m, 2H, OC*H*$_2$C*H*$_2$O), 3.46−3.51 (m, 2H, OC*H*$_2$C*H*$_2$O), 4.50−4.53 (m, 3H, C_6H_5), 5.10 (s, 1H, CC*H*($OCH_2)_2$), 5.17−5.21 (m, 2H, C_6H_5). ^{13}C NMR (50 MHz, C_6D_6): 65.6 (CH_2), 92.6 (CH), 92.8 (CH), 93.8 (CH), 101.1 (CH), 111.2 ($C_{quaternary}$), 221.0 (CO). MS *m/z*: 332 (2, M^+, ^{98}Mo), 260 (7), 220 (4), 214 (7), 176 (16), 149 (100), 130 (8), 105 (40), 78 (52), 52 (24). HRMS: calcd for $C_{12}H_{10}{}^{96}MoO_5$ 329.9575; found 329.9572.

Preparation of Tricarbonyl(dimethoxymethyl-η^6-benzene)molybdenum (10). A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (1.00 g, 3.87 mmol), benzaldehyde dimethyl acetal (1.74 mL, 11.62 mmol), and THF (0.94 mL, 11.62 mmol) was followed. After removal of volatiles under vacuum, the residue was dissolved in warm methylcyclohexane and filtered through Celite. The yellow solution was concentrated to 5 mL and cooled to −30 °C for one night. The yellow crystalline precipitate was separated and washed once with methylcyclohexane at −30 °C to give **10** (0.91 g, 71%). Mp: 45−48 °C (dec). IR (hexane): ν(CO) 1986 (s), 1916 (s) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): 2.98 (s, 6H, CH_3), 4.45 (t, *J* = 6.0 Hz, 1H, C_6H_5), 4.59 (t, *J* = 9.0 Hz, 2H, C_6H_5), 4.72 (s, 1H, CC*H*($OCH_3)_2$), 5.17 (d, *J* = 6 Hz, 2H, C_6H_5). ^{13}C NMR (75 MHz, C_6D_6): 52.9 (CH_3), 92.2 (CH), 92.8 (CH), 93.2 (CH), 101.2 (CH), 110.2 ($C_{quaternary}$), 220.8 (CO).

Preparation of Tricarbonyl(η^6-veratrole)molybdenum (11). A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (0.25 g, 0.97 mmol), veratrole (0.37 mL, 2.91 mmol), and THF (0.24 mL, 2.91 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated twice (addition of THF only). Following evaporation to dryness, the residue was dissolved in hexane−CH_2Cl_2 (2 mL of a 1:1 mixture) and filtered through a pad of silica gel (0.50 cm). The pad was rinsed with hexane−CH_2Cl_2 (1:1; 4 × 2 mL). Concentration to 6 mL (a small quantity of residual CH_2Cl_2 is necessary for crystallization to occur) and cooling to −30 °C for one night precipitated a yellow solid, which was washed with a hexane at −30 °C. Yield of **10**: 0.21 g, 67%. Mp: 85−90 °C (dec). IR (hexane): ν(CO) 1974 (s), 1897 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): 3.02 (s, 6H, CH_3), 4.49−4.52 (m, 2H, C_6H_4), 4.67−4.70 (m, 2H, C_6H_4). ^{13}C NMR (75 MHz, C_6D_6): 57.5 (CH_3), 81.5 (CH), 89.3 (CH), 136.4 ($C_{quaternary}$), 222.6 (CO). MS *m/z*: 320 (1, M^+, ^{98}Mo), 264 (2), 236 (3), 206 (1), 176 (1), 138 (100), 123 (44), 95 (41), 77 (35), 52 (14). HRMS: calcd for $C_{11}H_{10}{}^{96}MoO_5$ 317.9575; found 317.9596.

Preparation of Tricarbonyl(trimethyl-η^6-phenylstannane)molybdenum (12).[7c,18] A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (0.50 g, 1.94 mmol), trimethylphenyltin (1.06 mL, 5.81 mmol), and THF (0.47 mL, 5.81 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (addition of THF only). Following evaporation to dryness, the residue was dissolved in warm methylcyclohexane and filtered through Celite. The resulting yellow solution was concentrated to 1 mL and cooled to −30 °C overnigh. Separation of the yellow crystalline product and washing with methylcyclohexane at −30 °C afforded **12** (0.70 g, 86%). Mp: 95−95 °C (dec). IR (methylcyclohexane): 1979 (s), 1909 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): 0.12 (s, 9H, Sn-$(CH_3)_3$), 4.63 (t, *J* = 6.4 Hz, 2H, C_6H_5), 4.80−4.87 (m, 3H, C_6H_5). ^{13}C NMR (75 MHz, C_6D_6): −8.7 (CH_3), 94.2 (CH), 95.6 (CH), 101.8 (CH), 128.3 ($C_{quaternary}$), 221.8 (CO)). MS *m/z* : 422 (54, M^+, ^{98}Mo, ^{118}Sn), 394 (15), 366 (41), 336 (100), 306 (61), 243 (32), 227 (92), 197 (38), 145 (11), 120 (24), 78 (22), 51 (8). HRMS: calcd for $C_{11}H_{14}{}^{98}MoO_2{}^{118}Sn$ 393.90639; found 393.90731.

Preparation of Tricarbonyl(η^6-anisole)molybdenum (13).[9b] A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (2.60 g, 10.07 mmol), anisole (3.29 mL, 30.22 mmol), and THF (2.46 mL, 30.22 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated twice (addition of THF and arene). Following evaporation to dryness, the residue was dissolved in hexane−CH_2Cl_2 (20 mL of a 1:1 mixture). Filtration through a pad of silica gel (0.50 cm), rinsing with hexane−CH_2Cl_2 (1:1 mixture, 6 × 10 mL), concentration to 10 mL, and cooling overnight to −30 °C afforded **13** (2.60 g, 90%). Mp: 65−70 °C (dec). IR (hexane): ν(CO) 1987 (m), 1913 (m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): 2.83 (s, 3H, CH_3), 4.14 (t, *J* = 6.0 Hz, 1H, C_6H_5), 4.48 (d, *J* = 6.2 Hz, 2H, C_6H_5), 4.81 (t, *J* = 6.6 Hz, 2H, C_6H_5). ^{13}C NMR (100 MHz, C_6D_6): 55.4 (CH_3), 80.0 (CH), 87.1 (CH), 96.7 (CH), 222.0 (CO). MS *m/z*: 260 (1), 206 (1), 182 (2), 176 (3), 154 (2), 126 (2), 108 (88), 78 (100), 65 (54). HRMS: calcd for $C_{10}H_8{}^{98}MoO_4$ 289.9476; found 289.9469.

Preparation of Tricarbonyl(η^6-*N*,*N*-dimethylaniline)molybdenum (14).[7a] A general procedure with [Mo(η^6-C_6H_6)(CO)$_3$] (**1**) (0.50 g, 1.94 mmol), *N*,*N*-dimethylaniline (0.74 mL, 5.81 mmol), and THF (0.47 mL, 5.81 mmol) was followed. After stirring for 1 h and removal of volatiles, this procedure was repeated (addition of THF only). Following evaporation to dryness, a black oil was obtained, and addition of hexane caused precipitation of a solid, which was transferred on Celite. This solid was washed with hexane and then eluted into another Schlenk tube with benzene. The resulting yellow solution was evaporated under vacuum to give **14** (0.35 g, 60%). Mp: 139−142 °C (dec). IR (hexane): ν(CO) 1971 (s), 1897 (m), 1891 (m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): 1.99 (s, 6H, CH_3), 4.20 (d, *J* = 6.4 Hz, 2H, C_6H_5), 4.38 (t, *J* = 5.8 Hz, 1H, C_6H_5), 5.08 (t, *J* = 5.8 Hz, 2H, C_6H_5). ^{13}C NMR (125 MHz, C_6D_6): 39.3 (CH_3), 76.8 (CH), 84.8 (CH), 98.5 (CH), 137.6 ($C_{quaternary}$), 223.6 (3CO). MS *m/z*: 303 (1, M^+, ^{98}Mo), 217 (4), 215 (3), 120 (100), 105 (14), 77 (32), 51 (23). HRMS: calcd for $C_{11}H_{11}{}^{98}MoNO_3$ 302.9793; found 302.9800.

Acknowledgment. Support of this research by the Swiss National Foundation is gratefully acknowledged.

OM049792M

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