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Stepwise Synthesis of Molybdenocene and Mixed-Ring Indenyl Analogues

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Summary: A simple stepwise preparation of [MoCp$_2$L$_2$]$^{n+}$ (L = CO, Cl, H) complexes from [MoCp(η^3-allyl)(CO)$_2$] is presented. The same type of procedure allows the preparation of mixed-ring [MoCp(Ind)L$_2$]$^{n+}$ analogues.

The replacement of the cyclopentadienyl (Cp = η^5-C$_5$H$_5$) ligand by other η^5 cyclic analogues (Cp′) has been a successful means of controlling the stability, reactivity, and several other physicochemical properties of many organometallic complexes. The widespread use of the permethylated cyclopentadienyl ligand (Cp*; η^5-C$_5$Me$_5$) represents the most successful aspect of this strategy, which has allowed the characterization of a host of complexes and reaction intermediates often inaccessible to chemical and/or spectroscopic studies in the case of the corresponding Cp species. Indenyl (Ind = η^5-C$_9$H$_7$) complexes have long been known to display increased reactivity when compared to their Cp analogues.[1a] Quite recently, indenyl (and fluorenyl) analogues of group 4 metallocenes were used to introduce stereochemical control in the polymerization of olefins by Ti and Zr complexes, e.g. M(Ind)$_2$X$_2$.[1b]

Reflecting the difficulties in the synthesis of the parent metallocene complexes of group 6 metals, Cp$_2$MX$_2$, for which a simple alternative to the original report only appeared very recently for Cp$_2$WCl$_2$,[2] very few ring-substituted metallocene derivatives of these metals are known and even the derivatives Cp*$_2$MX$_2$ (M = Mo, W) are difficult to prepare.[3]

The alternative synthetic approach described below uses (Mo(Cp′)(CO)$_2$(η^4-diene)]$^+$ complexes to provide a high-yield route to molybdenocene as well as differentially substituted chiral and prochiral molybdenocene analogues, namely the indenyl congeners [MoCp(Ind)L$_2$]$^{n+}$.

Treatment of MoCp(η^3-C$_3$H$_5$)(CO)$_2$ (**1**) with HBF$_4$·Et$_2$O in dichloromethane gives the labile complex [MoCp(CO)$_2$(η^2-C$_3$H$_6$)FBF$_3$] (**2**),[4] which rapidly reacts with dienes, forming [MoCp(η^4-diene)(CO)$_2$][BF$_4$] (diene = C$_5$H$_6$ (**3a**), C$_5$HMe$_5$ (**3b**), 1,3-C$_6$H$_8$ (**3c**)). Complex **3b** is fluxional, like its known analogues **3a** and **3c**.[5a,b] The two interconverting isomers observed by low-temperature ^{1}H NMR correspond to the *endo* and *exo* conformations of the diene relative to the CpMo(CO)$_2$ fragment.[5c]

Hydride abstraction from **3a** with [Ph$_3$C]BF$_4$ gives the new molybdenocene dication [Cp$_2$Mo(CO)$_2$][BF$_4$]$_2$ (**4**) in a fashion similar to the formation of [MoCp$_2$(dppe)][PF$_6$]$_2$ from [CpMo(η^4-C$_5$H$_6$)dppe]PF$_6$.[6] The ν(CO) stretching vibrations of **4** are found at 2139 and 2108 cm^{-1}, reflecting weak back-donation from the [MoCp$_2$]$^{2+}$ fragment as seen in the isoelectronic [Cp$_2$Mo(CNMe)$_2$]$^{2+}$.[7] Alternatively, the molybdenocene fragment may be generated from **3a** by daylight or 60-W tungsten bulb irradiation in CH$_2$Cl$_2$ solution to give [MoCp$_2$H(CO)]BF$_4$.[8a] When a CH$_2$Cl$_2$/CHCl$_3$ mixture is used as solvent, [MoCp$_2$Cl(CO)]BF$_4$ (**5**) is directly formed in high yield.[8b] Similar irradiation of **5** in refluxing NCMe forms [MoCp$_2$Cl(NCMe)]BF$_4$ (**6**),[8c] which gives MoCp$_2$H$_2$ on reaction with LiAlH$_4$ or NaBH$_4$. The overall yield of **6** from **2** is 80%, and the operations may be performed in successive steps without intermediate purifications other than filtrations and washings.[9] [MoCpCp*X(CO)]$^+$ is not formed from **3b** under similar conditions.

Protonation of [Mo(Ind)(η^3-C$_3$H$_5$)(CO)$_2$] (**7**)[10a] with HBF$_4$·Et$_2$O in CH$_3$Cl$_2^-$, followed by addition of NCMe, gives [Mo(Ind)(CO)$_2$(NCMe)$_2$]BF$_4$ (**8**) in very high yield.[10b]

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(9) A solution of **1** (0.65 g, 2.52 mmol) in CH$_2$Cl$_2$ (30 mL) was treated with 1 equiv of HBF$_4$·OEt$_2$. After 15 min with stirring at room temperature, the solution was concentrated to *ca.* 20 mL and C$_5$H$_6$ (3 mL) was added. After 2 h, the solution was concentrated to *ca.* 10 mL and THF (20 mL) was added. The yellow precipitate was filtered and washed with Et$_2$O to give **3a** (0.8 g, 85%). This was dissolved in 30 mL of a 2:1 v/v CH$_2$Cl$_2$/CHCl$_3$ mixture and irradiated (14 h) with a 60-W tungsten bulb, with stirring. The violet precpitate was filtered, washed with ether, and dried to give **5** in >98% yield. Refluxing and simultaneously irradiating (60-W lamp) a solution **5** (0.98 g, 2.60 mmol) in 35 mL of NCMe for 3 h give a green solution. After concentration and addition of Et$_2$O the green precipitate of **6** may be isolated in 96% yield (0.98 g). Treatment of **6** with NaBH$_4$ in THF or LiAlH$_4$ in Et$_2$O gives a yellow solution. After filtration, hydrolysis, and extraction of the residue with Et$_2$O or toluene, Cp$_2$MoH$_2$ is obtained in 72% yield relative to **1**.

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Reaction of **8** with cyclopentadiene gives [Mo(Ind)(η^4-C_5H_6)$(CO)_2$]BF_4 (**9**) as a temperature-sensitive yellow crystalline complex.[11] As expected, **9** has two interconverting isomers (variable-temperature ^{1}H NMR) and its chemistry also follows that of **3a**. Reaction with [Ph_3C]BF_4 gives a yellow precipitate of [MoCp(Ind)$(CO)_2$][BF_4]$_2$ (**10**) with ν(CO) vibrations (2129 and 2054 cm^{-1}) similar to those of **4**. Attempted recrystallization from NCMe/Et_2O gives well-developed crystals of the substitution product [MoCp(Ind)(NCMe)(CO)][BF_4]$_2$ (**11**), which has the crystal structure shown in Figure 1.[12] According to the observed bond angles and distances, which are similar to the ones typically found for the pseudotetrahedral bent molybdenocene complexes,[7] **11** is, to our knowledge, the first structurally characterized indenyl-substituted derivative of group 6 metallocene complexes, the only other known example being [Mn(η^5-$C_5H_4{}^iPr$)(η^3-C_9H_7)(N^tBu)].[3d] A detailed discussion of the structural features will be given together with the structure of the η^3 analogue **14**.[13]

Irradiation of **9** in CH_2Cl_2/$CHCl_3$ gives a pink precipitate of [MoCp(Ind)Cl(CO)]BF_4 (**12**), which upon treatment with LiCl gives [MoCp(Ind)Cl_2] (**13**) as a purple-gray poorly soluble microcrystalline complex.[14]

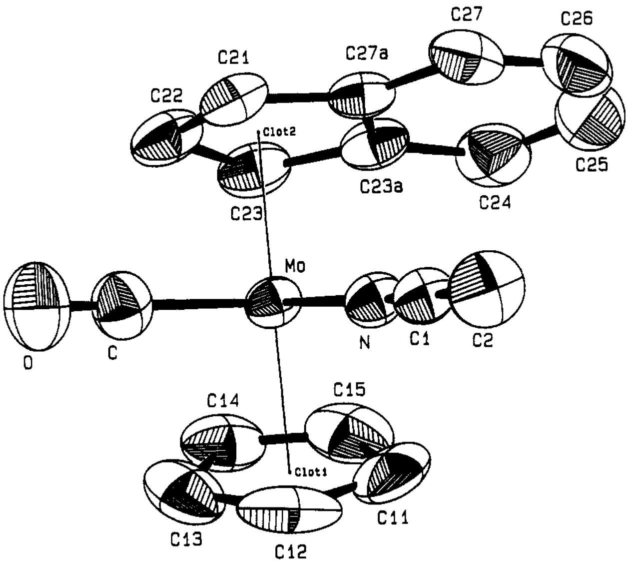
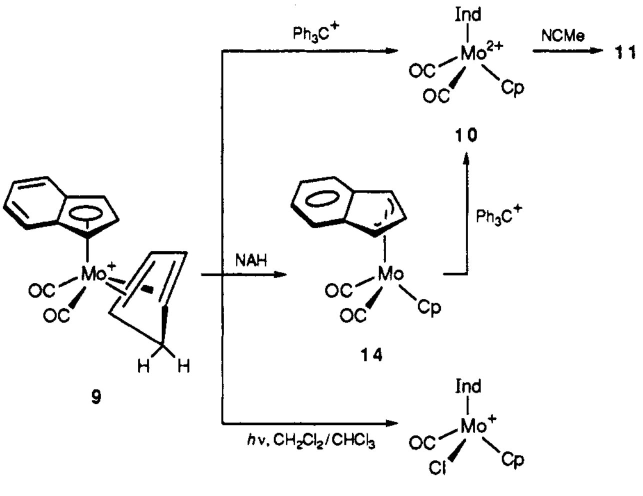


Figure 1. ORTEP diagram of **11**. Selected bond lengths (pm) and angles (deg): Mo–N = 211.9(2), Mo–C = 202.5(3), Mo–C11 = 228.4(3), Mo–C12 = 227.3(3), Mo–C13 = 231.8(3), Mo–C14 = 233.2(3), Mo–C15 = 232.0(3), Mo–C21 = 226.4(3), Mo–C22 = 226.2(3), Mo–C23 = 229.2(3), Mo–C23a = 240.3(3), Mo–C27a = 243.8(3), Mo–$C_{lot}1$ = 197.8, Mo–$C_{lot}2$ = 198.5; N–Mo–C = 85.5(1), N–Mo–$C_{lot}1$ = 106.0, N–Mo–$C_{lot}2$ = 109.8, C–Mo–$C_{lot}1$ = 105.7, C–Mo–$C_{lot}2$ = 99.2, $C_{lot}1$–Mo–$C_{lot}2$ = 137.6, Mo–N–C1 = 177.0(2), Mo–C–O = 178.4(3), N–Cl–C2 = 179.2(3). C_{lot} denotes the perpendicular projection of the heavy atom on the least-squares plane.

Scheme 1



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As depicted in Scheme 1, another entry into the chemistry of the mixed [MoCp(Ind)] fragment is provided by the treatment of **9** with NaH, in THF suspension, which gives [MoCp(η^3-C_9H_7)$(CO)_2$] (**14**). The η^3 coordination of the indenyl ligand is confirmed by both ^{1}H NMR and a crystal structure to be published separately.[13,16] The η^3 coordination of the indenyl ligand is expected in order to avoid a 20-electron EAN around the molybdenum, as observed in the related complexes [W(η^5-C_9H_7)(η^3-C_9H_7)$(CO)_2$][16] and [Mo(η^5-$C_5H_4{}^iPr$)(η^3-C_9H_7)(N^tBu)].[3d] **14** reacts neither with HCl/Et_2O nor with MeI but is readily oxidized to **10** by [Ph_3C]BF_4.

We are currently attempting to extend this procedure to the preparation of other substituted group 6 metallocenes [MCpCp′L_2] (M = Mo, W; Cp′ = η^5-fluorenyl, Cp*, RCp, and other formal analogues of Cp) as well as of their disubstituted congeners [M(Cp′)$_2L_2$]$^{n+}$, having in

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(11) A solution of **8** (1.6 g, 3.7 mmol) in CH_2Cl_2 (25 mL) was treated with C_5H_6 (5 mL) for 3 h. Upon concentration and addition of Et_2O a yellow precipitate of **9** was obtained, which was washed with THF and Et_2O and dried; yield 86%. Due to its thermal/photolytic sensitivity we could not obtain reproducible analytical data for **9**.

(12) The complex **11** was prepared by reaction of **9** (0.5 g, 1.2 mmol) in Ch_2Cl_2 (20 mL) with 1 equiv of [Ph_3C]BF_4. The yellow precipitate formed was filterd, washed with Et_2O, and dried under vacuum. Recrystallization from NCMe/Et_2O gave **11** as well-formed crystals in 91% overall yield. ^{1}H NMR (CD_3CN, 250 MHz): 7.94 (m, 2H, aromatic C_9H_7) 7.77 (m, 2H, aromatic C_9H_7), 6.93 (m, 1H, $H_{C9c(c')}$), 6.40 (t, 1H, H_d), 6.22 (m, 1H, $H_{c'(c)}$), 6.15 (s, 5H, Cp), 2.38 (s, 3H, CH_3CN). Crystallographic data for $C_{17}H_{15}MoNO(BF_4)_2$: M_r = 518.9, monoclinic, $P2_1/c$ (No. 14), a = 785.6(2) pm, b = 1803.9(2) pm, c = 1383.1(3) pm, β = 101.56(1)°, V = 1920 × 10^6 pm^3, Z = 4, ρ_{calcd} = 1.795 g cm^{-3}, F_{000} = 1024, μ = 7.5 cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromator: λ(Mo Kα) = 71.073 pm, ω scans, 2.0° < Θ < 25.0°. During data collection no decay was observed. No correction for absorption effects was applied, due to the small absorption coefficient and the isotropic crystal size (edge dimensions 0.5 × 0.5 × 0.3 mm), and no extinction effects were observed. From 3782 collected data 536 were rejected (systematic absences; negative intensities). After merging (R_{int} = 0.011) all 3027 unique data ($I > 0.0$) were used in the final refinement. The structure was solved with direct methods and refined by full-matrix least-squares calculations, with anisotropic thermal parameters for all non-hydrogen atoms except the two disordered BF_4^- anions. All hydrogen atoms were treated as idealized contributions. Refinement was concluded with R = 0.056 and R_w = 0.042; w = $1/\sigma^2(F_0)$. All software and the sources of the scattering factors are contained in the STRUX-IV system using the programs MULTAN 11/82, ORTEP II, PLATON 92″, PLUTON 92″, SCHAKAL, and SCP.

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(14) Due to its low solubility we could not get any reliable NMR spectrum on **13**, but its IR spectrum is remarkably similar to that of $MoCp_2Cl_2$.

(15) A suspension of **9** (1.6 g, 3.8 mmol) in THF (30 mL) was treated with excess NaH with vigorous stirring. After 2 h, the red-brown solution was filtered and evaporated to dryness. The product **14** was obtained after extraction of the residue with Et_2O followed by concentration and cooling; yield ca. 85%. ^{1}H NMR ($(CD_3)_2CO$, 250 MHz, −65 °C): δ 6.75 (t, 1H, *meso* allylic C_9H_7), 6.68 (m, 2H, aromatic) 6.46 (m, 2H, aromatic) 5.20 (d, 2H, *syn* allylic C_9H_7) 4.99 (s, 5H, Cp). Above this temperature the two lowest field signals overlap.

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mind the possibility of tuning the reactivity of the well-studied MCp_2 fragment.

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Supplementary Material Available: A table of analytical and spectroscopic data for the new compounds and listings of crystal data and structure solution and refinement details and positional and thermal parameters and a stereoview of the unit cell for compound 11 (12 pages). Ordering information is given on any current masthead page.

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