Ring-Functionalized Molybdenocene Complexes

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Received February 11, 2009

The synthesis and characterization of new ring-functionalized molybdenocene derivatives \([\text{CpCp'Mo(CO)}]^{2+}\) and \([\text{CpCp'Mo(CO)Br}]^{+}\) (\(\eta^5\)-\(\text{C}_5\text{H}_4\text{R}; \text{R} = \text{CH}_2\text{CH}_2\text{OMe}, \text{CH}_2\text{CH}_2\text{COOEt}, \text{CH}_2\text{CH}_2\text{OCOMe}, \text{COOMe}\)) are reported. Three alternative routes were used to assemble the \(\text{CpCp'Mo}\) moiety. Following route I, the unsubstituted precursor \([\text{CpMo(CO)}]^{2+}\) reacts with substituted cyclopentadienyls (CpH) to give after oxidation dicationic compounds \([\text{CpCp'Mo(CO)}]^{2+}\). Alternatively, route II introduces the substituent in the first reaction step upon the synthesis of \([\text{CpCp'Mo(CO)}]^{2+}\). In this case, the bis-cyclopentadienyl compounds \([\text{CpCp'Mo(CO)}]^{2+}\) were obtained after reaction with cyclopentadiene (C\(\text{H}_2\)) and subsequent oxidation. The NMR spectroscopic measurements prove that the reaction pathways of routes I and II go through different intermediates. The bromo complexes \([\text{CpCp'Mo(CO)Br}]^{+}\) were synthesized using route III. Reaction of \([\text{CpCp'Mo(CO)}]^{2+}\) with \(\text{C}_2\text{H}_5\text{SiMe}_3\) gives hydride complexes \([\text{CpCp'Mo(CO)H}]^{+}\). Appropriate bromo complexes were obtained upon reaction with bromine. The ring-functionalized bis-cyclopentadienyl molybdenum(IV) compounds and their monocyclopentadienyl precursors were characterized by spectroscopic methods. Structures of \([\text{CpMo(\eta^5-C}_5\text{H}_4\text{COOEOE})\text{CO}]^{2+}[\text{MoOBr}_2\text{H}_3\text{O}]^{+}[\text{Br}], [\eta^5\text{C}_2\text{H}_5\text{COOMeMo(\eta^5-C}_5\text{H}_4\text{CO})]^+, [\eta^5\text{C}_2\text{H}_5\text{SiMe}_3\text{Mo(CO)}^2\text{NCEM}_{2}]^{2+}[\text{BF}_4]^{-}, [\eta^5\text{C}_2\text{H}_5\text{COOMe(CO)}^2\text{NCEM}_{2}]^{2+}[\text{BF}_4]^{-}\) and \([\text{CpMo(\eta^5-C}_5\text{H}_4\text{MOOEOE})\text{CO}]^{2+}[\text{BF}_4]^{-}\) were determined with X-ray diffraction analysis.

Introduction

Bent metalloocene compounds [\(\text{Cp}_{2}\text{ML}_2]\) (Cp = substituted Cp; \(\text{Cp} = \eta^5\text{-C}_5\text{H}_4\text{M}; \text{M} = \text{group IV, V, VI metal}) have raised great interest due to their pronounced biological and catalytic activity. The presence of substituents in the cyclopentadienyl rings strongly modulates their catalytic properties through steric and electronic effects. In contrast, unsubstituted metalloccenes species seemed for a long time to have much better antioxidant properties than any of their ring-substituted analogues. Nevertheless, the recent studies made with a broader range of ring-substituted titanocene compounds have shown that substitution with polar functional groups can improve their activity even toward cisplatin-resistant tumor cells. Furthermore, such modifications circumvent many problems related to low water solubility.

Our focus on the modification of molybdenocene compounds through functionalization of cyclopentadienyl rings follows a recent comprehensive scrutiny of \(\text{Cp}_{2}\text{MoCl}_2\) focused on its mechanism of action and corresponds to our long-standing interest in the chemistry of molybdenum compounds. The functionalized compounds should be also suitable for developing new molybdenocene catalysts capable of H/D exchange, nitrile hydration, and hydrolysis of organophosphates.
Previous studies show that the original synthetic route for Cp₂MoCl₂ and its modifications¹¹ are suitable for alkyl-¹² and silyl-substituted¹³ analogues. Some compounds with both Cp rings connected with an ansa-bridge¹⁴ are also available in this way. However, due to its harsh conditions, this route cannot be used for the synthesis of ring-functionalized compounds. For this purpose, compounds with η⁵:η¹-cyclopentadienylethyl ligands seem to be more efficient because their reaction with iodine gives compounds with iodoethyl-substituted cyclopentadienyl rings.¹⁵ A variety of functionalized compounds is then available through the nucleophilic substitution of iodide.¹⁶

Another synthetic problem arises when attempting to introduce substituents in only one of the rings. The first method reported used nucleophilic attack at the Cp ring.¹⁷ Another method uses the dienophilic properties of cationic molybdenum(II) compounds. Allyl complexes [(Cp′Mo(η₃-C₃H₅)(CO)₂]Cp′)Cp*, Ind) activated with HBF₄ or their stabilized analogues [Cp′Mo(CO)₂(NCMe)₂][BF₄] coordinate monomeric cyclopentadiene, giving η₄-cyclopentadiene complexes. Compounds with the CpCp′Mo moiety are then available through the oxidative, reductive, or photochemical pathways.¹⁸,¹⁹ Recently we have shown that this approach could be used for the synthesis of [IndMo(η₅-C₅H₄CH₂-η¹-CH₂)(CO)][BF₄] when spiro[2.4]hepta-4,6-diene is used. This ansa-compound was found to be a suitable precursor for haloethyl-substituted complexes [IndMo(η₅-C₅H₄(CH₂)₂X)(CO)X][BF₄](X = Br, I).²⁰

In this work we proved the ability of the above-mentioned method for the synthesis of methoxylalkyl- and ester-substituted molybdenocenes. In addition the new pathway giving complexes [CpCp′Mo(CO)H][BF₄] will be described.

Results

The synthesis of the complexes [CpCp′Mo(CO)2]2+ was done using the two alternative reaction routes shown in Scheme 1. Following route I, the precursor with the unsubstituted Cp ring, [CpMo(CO)2(NCMe)2][BF4] (1), is reacted with substituted cyclopentadienes (C5H5) to give appropriate η4-complexes. The desired bis-cyclopentadienyl compounds are obtained after oxidation of the Mo(II) diene complexes. Alternatively, route II introduces the substituent R in the first reaction step, the synthesis of [CpMo(η4-C5H4)(CO)2][BF4]. In this case, the reaction pathway goes through [Cp′Mo(η4-C5H4)(CO)2][BF4], the oxidation of which, for a given R, gives the bis-cyclopentadienyl compound of the same molecular formula as route I.

Synthesis of Dicationic Complexes [CpCp′Mo(CO)2]2+

Using Route I. The examination of this pathway was done using the substituted cyclopentadienes 2–8. 2 = C2H2CH2CH2COOEt, 3 = C2H2CH2CH2OOCMe, 4 = C2H2CH2CHOOMe, 5 = C2H2CH2CH2CN, 6 = C2H2COOMe, 7 = C2H2SiMe3, 8 = C2H2(SiMe3)2. Compounds 2–5 have the functional groups separated from the cyclopentadiene system by an ethylene spacer. NMR spectra of these starting compounds prove formation of 1- and 2-isomers (Scheme 2).

The 5-isomer was not observed at room temperature. Isomers of compounds 2–5 were distinguished using COSY experiment. The 1-isomer shows the interaction over four bonds between CH2 protons of the alkyl group and CH2 protons of the cyclopentadiene. For the 2-isomer such interaction was not detected because these groups interact over five bonds. At room temperature, the molar ratios between 1- and 2-isomers were found to be 1:2.3 for 2, 1:1.3 for 3, 1.17:1 for 4, and 1.14:1 for 5.

Cyclopentadienes 2–4 react with [CpMo(CO)2(NCMe)2][BF4] (1) to give the η4-complexes 9–11, respectively, as a mixture of isomers with coordinated 1- and 2-substituted cyclopentadienes, as evidenced by 1H NMR and COSY experiments. The molar ratio between isomers does not correspond to the composition of the mixture of free cyclopentadienyl compounds. Coordination of the 1-isomer is preferred for cyclopentadienes 2–4 since 9a–11a are the major products. This fact probably results from the lower sterical hindrance of the 1-isomer.

The complexes of 1- and 2-substituted cyclopentadienes were distinguished by 1H NMR spectroscopy. The diene system of the 1-isomers (9a–11a) shows two low-field multiplets at ∼6.4 ppm and one high-field multiplet at ∼4.7 ppm, while the 2-isomers (9b–11b) give one multiplet at low field, ∼6.6 ppm, and two at high field, ∼4.6 and 4.5 ppm. Both isomers give two doublets (JH(1H,1H) ≈ 15 Hz) for the cyclopentadiene CH2 protons. These doublets are very characteristic for η4-cyclopentadienyl without substituents in the 5-position. The coordinated 1-substituted cyclopentadienes in compounds 9a–11a show cyclopentadiene CH2 protons at lower field than their corresponding 2-isomers 9b–11b. This effect is more significant for the higher fielded proton (a: 3.92–3.97 ppm; b: 3.82–3.85 ppm). The connectivity between protons of coordinated cyclopentadiene was proven by COSY spectra. In keeping with their ionic character the singlet of the BF4 anion at ca. −1 ppm was observed in the 11B NMR spectra of compounds 9–11.

The attempts to coordinate cyanoethyl-cyclopentadiene (5) failed due to its fast polymerization catalyzed by I. In this case, no evidence for the formation of a η4-complex was observed.

Further examination of this pathway was done with C2H2COOMe (6). Free cyclopentadiene 6 forms the 1-isomer as was described previously21 and further proved by NMR spectroscopy. The samples used for our reactions were contaminated with 10–30% of the dimer of 6 because Diels–Alder dimerization of compound 6 is about 200 times faster than that of cyclopentadiene (C5H4).22 Nevertheless, the NMR samples of 6 measured after standing for 18 h at room temperature still contained sufficient amount of the monomer. [CpMo(CO)2(NCMe)2][BF4] (1) reacts with C2H2COOMe (6) to give the expected η4-cyclopentadiene complex [CpMo(η4-C5H4-COOMe)(CO)2][BF4] (12). NMR measurements prove the presence of only one isomer, 12a, which has the carboxyl group in the 1-position of the cyclopentadiene ring. The coordinated cyclopentadiene shows two multiplets of the allylic protons at low field (at 6.97 and 6.74 ppm) and one at high field (5.01 ppm). The doublets of the CH2 group were found at 3.99 and 3.46 ppm.

Trimethylsilyl-substituted cyclopentadienes C2H2SiMe3 (7) and C2H2(SiMe3)2 (8) do not give any stable η4-complex. Their reactivity will be discussed in a separate section.

The bis-cyclopentadienyl compounds [CpCp′Mo(CO)2]2+ (13–16) were obtained through the reaction of η4-complexes 9–12 with Br2. These products were characterized with IR, NMR, and mass spectra. The structure of compound 13 was determined by X-ray diffraction analysis (Figure 1). Infrared spectra of compounds 13–16 show two C=O stretching bands at ∼2130 cm−1 (vs) and ∼2100 cm−1 (vs), in keeping with two carbonyl ligands in the molecule. Compounds containing carboxylic groups (13, 14, 16) show C=O stretching bands at ∼1730 cm−1 (vs). The broad bands at ∼1060 cm−1 (vs) found in spectra of compounds 14–16 were assigned to B–F stretching. Due to insolubility in less polar solvents, the NMR spectra of the compounds 13–16 were measured in CD3CN or CD3OD. However, these solvents are not fully inert: acetonitrile slowly replaces coordinated carbonyl ligands,19 and methanol causes slow decomposition. 1H NMR spectra of the compounds 13–16 are consistent with the expected molecular structures. The spectrum of compound 13 measured in CD3CN shows significant signal broadening that is caused by the paramagnetic complex anion [MoOBr4(H2O)]− that appeared as a side product during the oxidation of compound 9 with bromine. The broadening was not observed in methanolic solution due to formation of diamagnetic oligomeric anions.23 The appearance of [MoOBr4(H2O)]− was proven with mass spectrometry and X-ray diffraction analysis.

Synthesis of Dicationic Complexes [CpCp′Mo(CO)2]2+

Using Route II. Route II was successfully exemplified by the assembly of the methoxyethyl- and methoxycarbonyl-substituted molybdenocene framework (Scheme 1). Monocyclopentadienyl compounds [Cp′Mo(η4-C5H4-CO)2] (17, 18) were prepared from the allyl complex [η4-C5H4-Mo(CO)2(NCMe)2] and the appropriate cyclopentadienides (4-Li, 6-Na) in line with the method developed for the unsubstituted analogue (1).24 This

The signal observed at ca. 3100 cm$^{-1}$ is typical for a BF$_4$ anion. Due to steric hindrance, formation of the intermediate with the SiMe$_3$ group in 5-position is not possible. Due to steric hindrance, formation of the intermediates with the SiMe$_3$ group in 5-position is not possible. Due to steric hindrance, formation of the intermediates with the SiMe$_3$ group in 5-position is not possible. 

The monocarbonyl complex [CpMo(CO)(NCMe)$_2$][BF$_4$] (22) was obtained immediately after dissolution of compound 16 in water. The complex crystallizes upon cooling of the saturated aqueous solution. Bonding of one CO ligand is evident from the infrared spectrum: CO stretching at 2089 cm$^{-1}$ (vs). The $^1$H NMR spectrum is in agreement with the proposed structure. Oxidation of the trimethylsilyl-substituted compound 27 does not give the expected dication. Only a mixture of untractable products was obtained.

Desilylation Reactions (Route III). The reaction between [CpMo(CO)$_2$(NCMe)$_2$][BF$_4$] (1) and trimethylsilyl-substituted cyclopentadiene 7 does not give a stable $\eta^2$-cyclopentadiene complex. Instead, the hydride complex [CpMo(CO)$_2$(NCMe)$_2$][BF$_4$] is formed immediately after dissolution of compound 16.

The IR spectrum of this compound does not show any band in the region of the CO stretching. The $^1$H NMR spectrum is consistent with the substituted metallocene framework and the coordination of acetonitrile.
sluggishly. It gives only a small amount of untractable products. Bulky substituents in both 5-positions disable the formation of the \( \eta^4 \)-intermediate that could be necessary for desilylation reaction. So far only a few \( \eta^4 \)-cyclopentadiene complexes with substituents in the \textit{endo}-5-position have been described. All of them are less bulky than the trimethylsilyl group: \([\text{CpMo}(\eta^4-\text{C}_5\text{H}_4(\text{CH}_2)_n(\text{CO})_2)]\text{[BF}_4\text{]}_2, 20\), \([\text{CpMo}(\eta^4-\text{C}_5\text{Me}_5\text{H})(\text{CO})_2]\text{[BF}_4\text{]}, 19\) and \([\text{CpMo}(\eta^4-\text{C}_5\text{H}_5\text{Et})\text{PR}_3\text{Cl}]\ 26\).

The use of desilylation reactions for preparation of ring-functionalized compounds was further examined. Reaction of ring-substituted complex \([\eta^5-\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})\text{Mo}(\text{CO})_2-(\text{NCMe})_2]\text{[BF}_4\text{]}_2, 21\) with cyclopentadiene 7 gives hydride 31, as shown in Scheme 4. As expected, the pendant arm effect accelerates the reaction. The reaction time was particularly shortened, as observed for reaction of 21 with cyclopentadiene. Compound 31 shows only one CO stretching band in the infrared spectrum (at 1831 cm\(^{-1}\)). The formation of the hydride complex is evident from the \( ^1\text{H} \) NMR spectrum. The high-field signal at \(-8.5\ ppm\) is typical for a Mo–H bond. The resonance of the CO carbon was found to be at \( \sim 223\ ppm\).

### Figure 2.
ORTEP drawing of the complex \([\eta^5-\text{C}_5\text{H}_4\text{COOMe})\text{Mo}(\eta^3-\text{C}_3\text{H}_5)(\text{CO})_2]\text{[BF}_4\text{]}_2\) (18) with atom numbering of non-hydrogen atoms (ellipsoids: 30% probability). Selected bond lengths (Å) and angles (deg): Mo1–C8 1.954(3), Mo1–C9 1.937(2), Mo1–C10 2.337(2), Mo1–C11 2.235(2), Mo1–C12 2.344(2), Mo1–C1 2.337(2), Mo1–C2 2.402(2), Mo1–C3 2.395(2), Mo1–C4 2.335(2), Mo1–C5 2.288(2), C8–O3 1.150(3), C9–O4 1.161(3), C5–C6 1.474(3), C6–O1 1.205(3), C6–O2 1.339(3), C9–Mo1–C8 78.51(9).

### Figure 3.
ORTEP drawing of the cationic complex \([\eta^5-\text{C}_5\text{H}_4\text{COOMe})\text{Mo}(\text{CO})_2(\text{NCMe})_2]^+\) present in the crystal structure of 22 (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and angles (deg): Mo1–C6 1.9766(17), Mo1–C9 1.937(2), Mo1–C10 2.337(2), Mo1–C11 2.235(2), Mo1–C12 2.344(2), Mo1–C1 2.337(2), Mo1–C2 2.402(2), Mo1–C3 2.395(2), Mo1–C4 2.335(2), Mo1–C5 2.288(2), C8–O3 1.150(3), C9–O4 1.161(3), C5–C6 1.474(3), C6–O1 1.205(3), C6–O2 1.339(3), C9–Mo1–C8 78.51(9).

### Figure 4.
ORTEP drawing of the cationic complex \([\eta^5-\text{C}_5\text{H}_4\text{SiMe}_3)\text{Mo}(\text{CO})_2(\text{NCMe})_2]^+\) present in the crystal structure of 23 (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and angles (deg): Mo1–C10 1.972(4), Mo1–C11 1.978(4), Mo1–N1 2.166(3), Mo1–N2 2.165(3), Mo1–C1 2.366(3), Mo1–C2 2.379(4), Mo1–C3 2.296(4), Mo1–C4 2.258(3), Mo1–C5 2.307(3), C10–O1 1.150(4), C11–O2 1.142(5), Si1–C5 1.875(3), C7–N1 1.134(5), C9–N2 1.133(5), Si1–C12 1.866(4), Si1–C13 1.865(4), Si1–C14 1.854(5), C10–Mo–C11 73.89(15), N1–Mo–N2 76.89(11).
The molecule of compound 18 has pseudotetrahedral coordination around the Mo(II) center with $\eta^2$-allyl, $\eta^2$-bonded substituted cyclopentadienyl and two carbonyl ligands (Figure 1). The allyl ligand is in exo orientation. Bond lengths Mo–C(allyl) are 2.338(3), 2.236(3), and 2.345(3) Å. The distance between molybdenum and the centroid of the cyclopentadienyl ring is 2.0198(13) Å. The cyclopentadienyl ligand takes the conformation with methoxycarbonyl substituent above the OC–Mo–CO moiety. The COOMe group is in the same plane with the cyclopentadienyl ring, as was previously observed for analogous compounds with other carbonyl substituents in the cyclopentadienyl ring [Cp′Mo($\eta^5$-C$_5$H$_4$CO)(CO)]$_2$ ($\eta^2$-C$_5$H$_4$COCH$_3$, $\eta^2$-C$_5$H$_4$CO-Phe-OMe). 27

The cations of the compounds 22 and 23 show the distorted pseudosquare pyramid, in which two cis-coordinated carbonyl groups and two acetonirole ligands forms the basal plane. The apical position is occupied by the $\eta^1$-coordinated substituted-cyclopentadienyl ligand (Figures 2 and 3). The Mo–Cg(α) bond distances in compounds 22 (1.9825(10) Å) and 23 (1.9848(16) Å) are comparable with that previously observed for unsubstituted analogue 1 (1.977(1) Å). The differences in other parameters defining the geometry around the molybdenum center are negligible (Mo–C(CO) ~ 1.97 Å, Mo–N(MeCN) ~ 2.16 Å, C(CO)–Mo–C(CO) ~ 174°, N(MeCN)–Mo–N(MeCN) ~ 76°). Compounds 22 and 23 have different conformations of the cyclopentadienyl ring. The methoxycarbonyl substituent of compound 22 is oriented above the OC–Mo–CO moiety, while the trimethylsilyl group in compound 23 was found above the OC–Mo–NCMe moiety. In compound 22, half a molecule is present in the asymmetric unit, and, due to the symmetry-generated positional disorder, the methyl group of the acetate moiety was refined with 50% occupancy.

Cations of the compounds 13 and 26a have the typical bent metallocene structure, in which one $\eta^1$-cyclopentadienyl, one $\eta^1$-bonded substituted-cyclopentadienyl, and two other ligands make a distorted tetrahedron around the Mo(IV) center (Figures 4 and 5). These compounds show very similar conformations of the cyclopentadienyl rings with the substituent on the side of the molecule. The dication of compound 13 contains two carbonyl ligands. Bond lengths Mo–C(CO) were found to be ~2.05 Å, and the bond angle C(O)–Mo–C(O) is 87.19(11)°. The bond distance between molybdenum and the substituted cyclopentadienyl ring (Mo–Cg(Cp) = 1.9919(14) Å) is only slightly longer than in the case of the unsubstituted ring (Mo–Cg(Cp) = 1.9789(12) Å). The angle between centroids of the cyclopentadienyl rings and molybdenum is 136.39(6)°. The anionic part of compound 13 contains [MoOBr$_4$(H$_2$O)$_2$]$^-$ and Br$^-$. Two [MoOBr$_4$(H$_2$O)$_2$]$^-$ units and two bromides are linked via hydrogen bonds, as shown in Figure 6. A similar supramolecular structure containing three [MoOBr$_4$(H$_2$O)$_2$]$^-$ units linked through two bromides was described previously. 28 The cation of compound 26a has one carbonyl and one hydride bonded on the molybdenum(IV) center. The bond length Mo–C(CO) is 2.009(7) Å. The distances between molybdenum and the substituted cyclopentadienyl ring (Cg(Cp) = 1.958(3) Å) is the same as in the case of the unsubstituted ring (Cg(Cp)

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Table 1. Crystallographic Data for Compounds 13, 18, 22, 23, and 26a

| Compound | Formula | fw | Symmetry | space group | a (Å) | b (Å) | c (Å) | α (deg) | β (deg) | γ (deg) | V (Å³) | Z | D, (g cm⁻³) | μ (mm⁻¹) | F(000) | Refinement

| 13 | C₇H₄Br₂Mo₂O₆ | 911.76 | P1 | C2/c | 8.387(5) | 17.015(3) | 6.4180(13) | 102.907(2) | 123.32(3) | 179.24(9) | 13 | 2 | 2.441 | 9.095 | 858 | 351 202 148 320 213

| 18 | C₇H₆Br₂Mo₂ | 316.16 | P1 | C2/c | 8.387(5) | 17.015(3) | 6.4180(13) | 102.907(2) | 123.32(3) | 179.24(9) | 13 | 2 | 2.441 | 9.095 | 858 | 351 202 148 320 213

| 22 | C₇H₆Br₂Mo₂O₄ | 444.00 | P2₁/m | C2/c | 16.1219(9) | 11.538(2) | 16.8468(4) | 102.907(2) | 123.32(3) | 179.24(9) | 13 | 2 | 2.441 | 9.095 | 858 | 351 202 148 320 213

| 23 | C₇H₆Br₂Mo₂N₄O₄Si | 458.15 | P2₁/c | C2/c | 16.1219(9) | 11.538(2) | 16.8468(4) | 102.907(2) | 123.32(3) | 179.24(9) | 13 | 2 | 2.441 | 9.095 | 858 | 351 202 148 320 213

| 26a | C₇H₆Br₂Mo₂N₂O₂Si | 399.98 | P2₁/c | C2/c | 16.1219(9) | 11.538(2) | 16.8468(4) | 102.907(2) | 123.32(3) | 179.24(9) | 13 | 2 | 2.441 | 9.095 | 858 | 351 202 148 320 213

Discussion

Molybdenocenes with one of the rings substituted with either \(-\text{CH}_2\text{CH}_2\text{OOCMe}\) or carboxylic acid ester \(-\text{CH}_2\text{CH}_2\text{OCOEt}\), \(-\text{CH}_2\text{CH}_2\text{OOCMe}\), or \(-\text{COO}Me\) functions were prepared using three procedures. The main advantage of route I (Scheme 1) is that it does not use any reactive Cp'M derivatives such as alkali metal or thallium cyclopentadienides. The substituted cyclopentadiene (Cp'H) is activated by coordination, and its aromatization is achieved through oxidation. The synthesis of ester-substituted molybdenocenes (13, 14) has been chosen to exemplify the suitable application of route I. In this case, it avoids working with toxic thallium cyclopentadienides,\(^{30}\) which are apparently necessary for the preparation of these compounds using the other two pathways.

The application of route II (Scheme I) for the synthesis of ring-substituted molybdenocenes seems to be more difficult due to the presence of three new reaction intermediates, \([\text{Cp'Mo(\eta^5-C_5H_5)}\text{CO}_2]_2\), \([\text{Cp'Mo(\eta^5-Me_5C_5)}\text{CO}_2]\)\(_2\)[BF₄], and \([\text{Cp'Mo(\eta^5-C_5H_5)}\text{CO}_2]\)\(_2\)[BF₄], that have to be isolated. However, this does not usually bring any additional complication due to the similarity between the synthesis of \([\text{Cp'Mo(\eta^5-Me_5C_5)}\text{CO}_2]\)\(_2\)[BF₄] (1) and its ring-substituted analogues. However, the use of route II is clearly advantageous whenever the required cyclopentadienes undergo fast Diels–Alder dimerization at room temperature. Due to this fact, route II was more efficient for the synthesis of the methoxycarbonyl-substituted molybdenocene complex (16).

The novel method established for the synthesis of ring-substituted molybdenocenes (route III; Scheme 4) is based on the reaction between \([\text{Cp'Mo(\eta^5-Me_5C_5)}\text{CO}_2]\)\(_2\)[BF₄] and the diene \(\text{C}_8\text{H}_8\text{SiMe}_3\) (7). This reaction produces hydride complexes of formula \([\text{Cp'Mo(\text{CO})H)]\text{BF}_4}\)\(_2\) from which the corresponding bromo complex \([\text{Cp'Mo(\text{CO})Br)]\text{BF}_4}\)\(_2\) is readily obtained through reaction with bromine. Hydride complexes of the type \([\text{Cp'Mo(\text{CO})H)]\text{BF}_4}\)\(_2\) (\(\text{Cp'} = \text{Cp}, \text{Ind}) were previously prepared through a photochemical rearrangement of \([\text{Cp'Mo(\eta^5-C_5H_5)}\text{CO}_2]\)\(_2\)[BF₄].\(^{19}\) As used, route III saves one reaction step and does not require photochemical conditions. It also avoids unwanted cationic cyclopentadiene polymerization catalyzed by acid impurities that often plague routes I and II after the step where HBF₄ is used.

Conclusions

So far only a few ring-substituted molybdenocenes containing substituents other than alkyl or silyl have been described. All of them were prepared from \([\text{C}_6\text{H}_6\text{CH}_2\text{CH}_3\text{MoI}_3]\) using the nucleophilic substitution of iodine from the \(-\text{CH}_2\text{CH}_2\text{I}\) pendant.
groups. In this work, we have used other synthetic procedures to extend the group of ring-functionalized compounds to those containing ether and carboxylic acid ester groups in the side chain. Three reaction pathways were examined. The choice of one particular method depends mainly on the properties of the actual cyclopentadiene (Cp'H), cyclopentadienide (Cp'M), or cyclopentadienyl-molybdenum precursor, [Cp'Mo(CO)2(NCMe)2][BF4].

These methodologies elicit access to a wider variety of molybdenene derivatives designed for improved biocompatibility and/or bioactivity.

Experimental Section

Methods and Materials. All operations were performed under nitrogen using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods. Starting materials were available commercially or prepared according to literature methods.

Molybdenocene derivatives designed for improved biocompatibility and/or bioactivity.

Syntheses of compounds 2, 9, 13, 17, 21, 31, and 33 are outlined in detail as an example of the general methodology for the synthesis of the compounds reported here. Synthetic details of all new compounds and spectroscopic and analytic data are available in the Supporting Information.

Measurements. Positive- and negative-ion electrospray ionization (ESI) mass spectra were recorded on an API Ion Trap (PO 03 MS). Samples were measured in MeCN solution. The molybdenum-containing ions had a clearly visible metal isotope pattern, arising from the distribution Mo 14.84%, Mo 9.25%, Mo 15.92%, Mo 16.68%, Mo 9.55%, Mo 24.13%, and Mo 96.63%. Spectra obtained were computer simulated (WSearch32 2005). Mass peaks listed refer to fragments with the isotopes 1H, 11B, 12C, 14N, 16O, and 19F. A colorless oil. Yield: 4.1 g (25 mmol, 25%). 1H NMR (CDCl3, 400 MHz, δ ppm): 1.23 mixture of isomers 2a and 2b, 6.42–6.37 (m, 2H of a and 1H of b), 6.24 (m, 1H of b, C4H5), 5.61 (m, 1H of b, C4H5), 5.62 (m, 1H of a, C4H5), 4.12 (q, J(1H,1H) = 7.1 Hz, 2H of a and 2H of b, CH2CH2), 2.92 (m, 1H of a, C4H5), 2.87 (m, 1H of b, C4H5), 2.73 (m, 2H of b, CH2CH2), 2.68 (m, 2H of a, C4H5CH2CH2), 2.53 (m, 2H of a and 2H of b, CH2CH2), 1.23 (t, J(1H,1H) = 7.1 Hz, 3H of a and 3H of b, CH3CH2). 13C NMR (CDCl3, 101 MHz, δ ppm): 172.9 (1C of a and 1C of b, COO), 147.5 (1C of a, C3H5), 145.4 (1C of a, C3H5), 134.2, 133.9 (2C of a, C3H5), 132.2, 130.8, 126.9 (3C of b, CH2), 126.2 (1C of a, CH3), 60.2 (1C of a and 1C of b, CH3CH2), 43.1 (1C of a, CH3), 41.2 (1C of a, CH3), 34.2 (1C of a, CH3CH2CH2), 33.6 (1C of a, CH3CH2CH2), 25.9 (1C of b, CH3CH2CH2), 25.1 (1C of a, CH3CH2CH2), 14.1 (1C of a and 1C of b, CH3CH2).

Synthesis of [CpMo(CO)2(C2H5CH2COOET)(CO)2][BF4] (9). The solution of compound 1 (0.56 g, 1.45 mmol) in CH2Cl2 was treated with an excess of cyclopentadiene (0.7 g, 4.2 mmol). After stirring the reaction mixture for 16 h, the volatiles were evaporated in vacuo. The crude product was washed with ether and recrystallized from CH2Cl2/ether. The obtained yellow powder was vacuum-dried. Yield: 0.61 g (1.3 mmol, 89%). 1H NMR (CDCl3, 400 MHz, δ ppm): 0.14 mixture of isomers 9a and 9b, 6.61 (1H of b, C4H5), 6.39 (m, 1H of a, C4H5), 6.20 (1H of a, C4H5), 5.80 (5H of a, C4H5), 5.79 (5H of b, C4H5), 4.71 (1H of a, C4H5), 4.51 (1H of b, C4H5), 4.47 (1H of b, C4H5), 4.13 (q, J(1H,1H) = 7.2 Hz, 2H of a and b, CH2CH2), 3.92 (d, J(1H,1H) = 15.0 Hz, 1H of a, CH2CH2), 3.82 (d, J(1H,1H) = 14.0 Hz, 1H of b, CH2CH2), 3.38 (d, J(1H,1H) = 15.0 Hz, 1H of a, CH2CH2), 3.34 (1H of b, CH2CH2), 2.60–2.28 (4H of a and b, CH2CH2). 13B NMR (CDCl3, 149 MHz, δ ppm): 0.97. Synthesis of [CpMo(CO)2(C2H5CH2COOET)(CO)2][BF4] (13). The solution of compound 9 (0.47 g, 1 mmol) in CH2Cl2 was cooled to −80 °C and treated with an excess of Br2. The solution was slowly warmed to room temperature. During this time a yellow precipitate was formed. Solvents with an excess of Br2 were evaporated using a water/pentane mixture. The obtained precipitate was washed with water until neutral pH and dried with sodium sulfate. Solvents were evaporated at the normal pressure, and the residue was vacuum distilled at 50 °C (150 Pa) to obtain a colorless oil. Yield: 4.1 g (25 mmol, 25%). 1H NMR (CDCl3, 400 MHz, δ ppm): 1.23 mixture of isomers 2a and 2b, 6.42–6.37 (m, 2H of a and 1H of b, C4H5), 6.24 (m, 1H of b, C4H5), 6.16 (m, 1H of b, C4H5), 6.02 (m, 1H of a, C4H5), 4.12 (q, J(1H,1H) = 7.1 Hz, 2H of a and 2H of b, CH2CH2), 2.92 (m, 1H of a, C4H5), 2.87 (m, 1H of b, C4H5), 2.73 (m, 2H of b, CH2CH2), 2.68 (m, 2H of a, C4H5CH2CH2), 2.53 (m, 2H of a and 2H of b, CH2CH2), 1.23 (t, J(1H,1H) = 7.1 Hz, 3H of a and 3H of b, CH3CH2). 13C NMR (CDCl3, 101 MHz, δ ppm): 172.9 (1C of a and 1C of b, COO), 147.5 (1C of a, C3H5), 145.4 (1C of a, C3H5), 134.2, 133.9 (2C of a, C3H5), 132.2, 130.8, 126.9 (3C of b, CH2), 126.2 (1C of a, CH3), 60.2 (1C of a and 1C of b, CH3CH2), 43.1 (1C of a, CH3), 41.2 (1C of a, CH3), 34.2 (1C of a, CH3CH2CH2), 33.6 (1C of a, CH3CH2CH2), 25.9 (1C of b, CH3CH2CH2), 25.1 (1C of a, CH3CH2CH2), 14.1 (1C of a and 1C of b, CH3CH2).
Synthesis of \([q^2\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{OMe}Mo(q^2\text{C}_5\text{H}_5)(\text{CO})_2]\) (17). \(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OMe} (4) (0.62 \text{ g, 5 mmol})\) was diluted with 50 mL of Et,O cooled to \(0\) °C, and treated dropwise with 3.1 mL of \(n\)-BuLi (1.6 mol L\(^{-1}\)). The reaction mixture was stirred overnight and then vacuum evaporated. The residue was dissolved in THF (15 mL) and added dropwise to a THF solution of \([q^2\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{NCMe})_2]\) (1.55 g, 5 mmol) precooled to \(-80\) °C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The solid residue was extracted with hexane at \(50\) °C. The yellow extract was evaporated to dryness in vacuo. Yield: 0.89 g (25.6 mmol). \(^1\)H NMR (CDCl\(_3\), 400 MHz, \(\delta\) ppm): 5.19 (s, 2H, \(\text{C}_5\text{H}_5\)), 5.14 (s, 2H, \(\text{C}_5\text{H}_5\)), 3.87 (m, 1H, \(\text{C}_5\text{H}_5\)), 3.46 (t, \(\delta(H,1H) = 6.4\) Hz, 2H, \(\text{CH}_3\)), 3.32 (s, 3H, \(\text{OCH}_3\)), 2.71 (d, \(\delta(H,1H) = 6.8\) Hz, 2H, \(\text{CH}_3\)), 2.44 (t, \(\delta(H,1H) = 10.6\) Hz, 2H, \(\text{CH}_2\)). \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\), 101 MHz, \(\delta\) ppm): 92.6 (t, \(\delta(H,1H) = 3062\) m \(\nu(\text{CO})\)), 89.7 (C\(_5\text{H}_4\)), 73.3 (CH\(_2\text{OCH}_3\)), 69.0 (C\(_3\text{H}_5\)), 58.9 (OCH\(_3\)), 41.1 (C\(_5\)), 29.2 (C\(_2\text{H}_4\text{CH}_2\)). FTIR (KBr, cm\(^{-1}\)): 3062 m \(\nu(\text{CO})\), 2230 m \(\nu(\text{CN})\), 1961 vs \(\nu(\text{CN})\), 1863 vs \(\nu(\text{CO})\), 1800 s \(\nu(\text{CN})\), 1760 vs \(\nu(\text{CN})\), 1660 vs \(\nu(\text{CN})\), 1540 s \(\nu(\text{CO})\), 1423 s \(\nu(\text{CN})\), 1270 m \(\delta(\text{C}-\text{O})\), 1140 s \(\nu(\text{CN})\), 1050 s \(\nu(\text{CN})\), 1014 vs \(\nu(\text{CN})\), 997 s \(\nu(\text{CN})\), 938 m \(\delta(\text{C}-\text{N})\), 863 vs \(\nu(\text{CN})\), 798 vs \(\nu(\text{CN})\), 644 m \(\nu(\text{CN})\), 416 m \(\nu(\text{CN})\), 316 s \(\nu(\text{CN})\), 159 s \(\nu(\text{CN})\), 125 m \(\nu(\text{CN})\), 94 s \(\nu(\text{CN})\), 84 m \(\nu(\text{CN})\), 42 s \(\nu(\text{CN})\), 30 s \(\nu(\text{CN})\), 20 s \(\nu(\text{CN})\), 10 s \(\nu(\text{CN})\), 5 s \(\nu(\text{CN})\), 1 s \(\nu(\text{CN})\).}

**Synthesis of [CpMo(q^2-C_5H_5CH_2CH_2OMe)Me(CO)][BF_4] (31).** A solution of compound 21 (0.28 g, 0.7 mmol) in CH\(_2\)Cl\(_2\) was cooled to \(-80\) °C and treated with an excess of Br\(_2\). The solution was slowly warmed to room temperature. After stirring for 15 min at room temperature solvents with an excess of Br\(_2\) were vacuum evaporated. The product was washed twice with ether and cold MeCN and vacuum-dried. Yield: 0.28 g (0.58 mmol, 84%). Anal. Calcd for C\(_{14}\)H\(_{17}\)BF\(_4\)MoN\(_2\)O\(_3\): C, 37.87; H, 3.86; N, 6.31. Positive-ion MS: \(m/z = 365 (100\%) [\text{M} + \text{CO}]^+\). \(^{1}\)H NMR (CD\(_2\)OD, 400 MHz, \(\delta\) ppm): 6.21 (s, 5H, C\(_5\)), 6.19 (m, 1H, C\(_5\)), 6.16 (m, 1H, C\(_5\)), 6.03 (t, \(\delta(H,1H) = 2.75\) Hz, 2H, C\(_3\)), 3.62 (t, \(\delta(H,1H) = 5.7\) Hz, 2H, C\(_5\)), 3.36 (3H, C\(_3\)), 2.81 (2H, C\(_5\)), 2.22 (C\(_5\)). \(^{13}\)C\{\(^1\)H\} NMR (CD\(_2\)OD, 101 MHz, \(\delta\) ppm): 216.6 (1C, CO), 102.3 (1C, C\(_5\)), 101.9 (1C, C\(_5\)), 100.8 (5C, C\(_5\)), 99.6 (1C, C\(_5\)), 94.1 (1C, C\(_5\)), 72.5 (1C, C\(_5\)), 59.1 (1C, C\(_5\)), 31.0 (1C, C\(_5\)). FTIR (KBr, cm\(^{-1}\)): 3090 s \(\nu(\text{CH}_3)\), 2049 vs \(\nu(\text{CH}_3)\), 1085 vs br \(\nu(\text{BF})\).