Ring-Functionalized Molybdenocene Complexes

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The synthesis and characterization of new ring-functionalized molybdenocene derivatives $[CpCp'Mo(CO)_2]^{2+}$ and $[CpCp'Mo(CO)Br]^+$ (η^5-C_5H_4R; R = CH_2CH_2OMe, CH_2CH_2COOEt, CH_2CH_2OOCMe, COOMe) are reported. Three alternative routes were used to assemble the CpCp′Mo moiety. Following route I, the unsubstituted precursor $[CpMo(CO)_2(NCMe)_2]^+$ reacts with substituted cyclopentadienes (Cp′H) to give after oxidation dicationic compounds $[CpCp'Mo(CO)_2]^{2+}$. Alternatively, route II introduces the substituent in the first reaction step upon the synthesis of $[Cp'Mo(CO)_2(NCMe)_2]^+$. In this case, the bis-cyclopentadienyl compounds $[CpCp'Mo(CO)_2]^{2+}$ were obtained after reaction with cyclopentadiene (C_5H_6) and subsequent oxidation. The NMR spectroscopic measurements prove that the reaction pathways of routes I and II go through different intermediates. The bromo complexes $[CpCp'Mo(CO)Br]^+$ were synthesized using route III. Reaction of $[Cp'Mo(CO)_2(NCMe)_2]^+$ with $C_5H_5SiMe_3$ gives hydride complexes $[CpCp'Mo(CO)H]^+$. 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 $[CpMo(\eta^5\text{-}C_5H_4CH_2CH_2COOEt)(CO)_2][MoOBr_4(H_2O)][Br]$, $[(\eta^5\text{-}C_5H_4COOMe)Mo(\eta^3\text{-}C_3H_5)(CO)_2]$, $[(\eta^5\text{-}C_5H_4COOMe)Mo(CO)_2(NCMe)_2][BF_4]$, $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(NCMe)_2][BF_4]$, and $[CpMo(\eta^5\text{-}C_5H_4COOMe)(CO)H][BF_4]$ were determined with X-ray diffraction analysis.

Introduction

Bent metallocene compounds $[Cp'_2ML_2]^{n+}$ (Cp′ = substituted Cp; Cp = η^5-C_5H_5, M = group IV, V, VI metal) have raised great interest due to their pronounced biological[1] and catalytic activity.[2] The presence of substituents in the cyclopentadienyl rings strongly modulates their catalytic properties through steric and electronic effects. In contrast, unsubstituted metallocene species seemed for a long time to have much better antitumor properties than any of their ring-substituted analogues.[3] 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.[4,5] Furthermore, such modifications circumvent many problems related to low water solubility.[5]

Our focus on the modification of molybdenocene compounds through functionalization of cyclopentadienyl rings follows a recent comprehensive scrutiny of Cp_2MoCl_2 focused on its mechanism of action[6] 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,[7] nitrile hydration,[8] and hydrolysis of organophosphates.[9]

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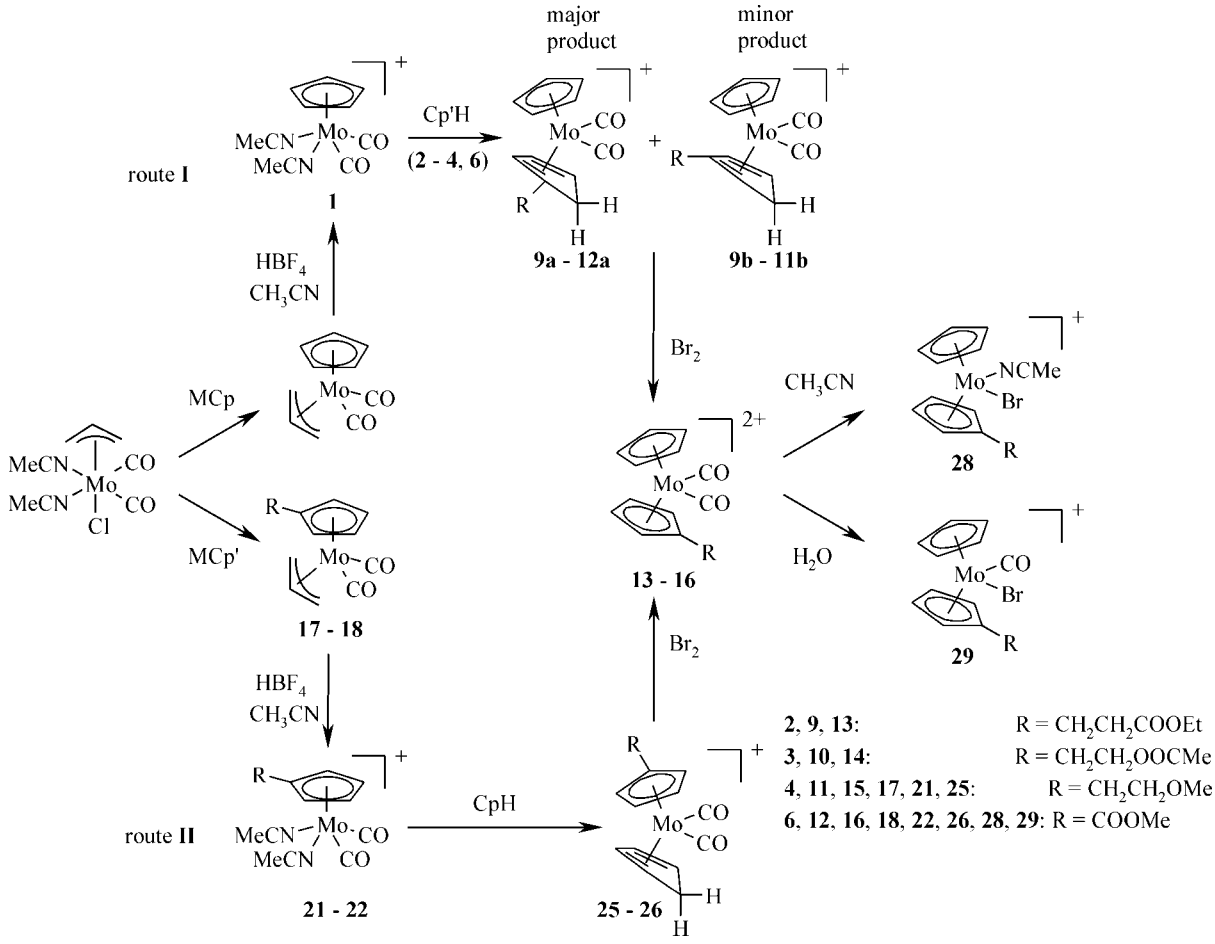
Scheme 1. Synthesis of Bis-cyclopentadienyl Molybdenum(IV) Compounds



Previous studies show that the original synthetic route for Cp_2MoCl_2[10] and its modifications[11] are suitable for alkyl-[12] and silyl-substituted[13] analogues. Some compounds with both Cp rings connected with an *ansa*-bridge[14] 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 η^5:η^1-cyclopentadiendiylethyl 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 $[(Cp')Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ Cp′ = Cp*, Ind) activated with HBF_4 or their stabilized analogues $[Cp'Mo(CO)_2(NCMe)_2][BF_4]$ coordinate monomeric cyclopentadiene, giving η^4-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 $[IndMo(\eta^5\text{-}C_5H_4CH_2\text{-}\eta^1\text{-}CH_2)(CO)][BF_4]$ when spiro[2.4]hepta-4,6-diene is used. This *ansa*-compound was found to be a suitable precursor for haloethyl-substituted complexes $[IndMo(\eta^5\text{-}C_5H_4(CH_2)_2X)(CO)X][BF_4]$ (X = Br, I).[20]

In this work we proved the ability of the above-mentioned method for the synthesis of methoxyalkyl- and ester-substituted molybdenocenes. In addition the new pathway giving complexes $[CpCp'Mo(CO)H][BF_4]$ will be described.

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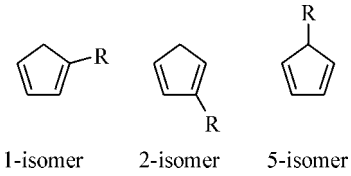
Scheme 2. Isomers of Monosubstituted Cyclopentadienes



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, $[CpMo(CO)_2(NCMe)_2][BF_4]$ (**1**), is reacted with substituted cyclopentadienes (Cp′H) to give appropriate η^4-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 $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$. In this case, the reaction pathway goes through $[Cp'Mo(\eta^4\text{-}C_5H_6)(CO)_2][BF_4]$, 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** = $C_5H_5CH_2CH_2COOEt$, **3** = $C_5H_5CH_2CH_2OOCMe$, **4** = $C_5H_5CH_2CH_2OMe$, **5** = $C_5H_5CH_2CH_2CN$, **6** = C_5H_5COOMe, **7** = $C_5H_5SiMe_3$, **8** = $C_5H_4(SiMe_3)_2$. 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 CH_2 protons of the alkyl group and CH_2 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 $[CpMo(CO)_2(NCMe)_2][BF_4]$ (**1**) to give the η^4-complexes **9**−**11**, respectively, as a mixture of isomers with coordinated 1- and 2-substituted cyclopentadienes, as was evidenced by ^{1}H NMR and COSY experiments. The molar ratio between isomers does not correspond to the composition of the mixture of free cyclopentadienes. 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 ^{1}H NMR spectroscopy. The diene system of the 1-isomers (**9a**−**11a**) shows two low-field multiplets at ∼6.4 and 6.3 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 ($^2J(^1H,^1H) \approx 15$ Hz) for the cyclopentadiene CH_2 protons. These doublets are very characteristic for η^4-cyclopentadienes without substituents in the 5-position. The coordinated 1-substituted cyclopentadienes in compounds **9a**−**11a** show cyclopentadiene CH_2 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 BF_4 anion at ca. −1 ppm was observed in the ^{11}B NMR spectra of compounds **9**−**11**.

The attempts to coordinate cyanoethyl-cyclopentadiene (**5**) failed due to its fast polymerization catalyzed by **1**. In this case, no evidence for the formation of a η^4-complex was observed.

Further examination of this pathway was done with C_5H_5COOMe (**6**). Free cyclopentadiene **6** forms the 1-isomer as was described previously[21] 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 (C_5H_6).[22] Nevertheless, the NMR samples of **6** measured after standing for 18 h at room temperature still contained sufficient amount of the monomer. $[CpMo(CO)_2(NCMe)_2][BF_4]$ (**1**) reacts with C_5H_5COOMe (**6**) to give the expected η^4-cyclopentadiene complex $[CpMo(\eta^4\text{-}C_5H_5COOMe)(CO)_2][BF_4]$ (**12**). NMR measurements prove the presence of only one isomer, **12a**, which has the carboxylic group in the 1-possition 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 CH_2 group were found at 3.99 and 3.46 ppm.

Trimethylsilyl-substituted cyclopentadienes $C_5H_5SiMe_3$ (**7**) and $C_5H_4(SiMe_3)_2$ (**8**) do not give any stable η^4-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 η^4-complexes **9**−**12** with Br_2. 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 CD_3CN or CD_3OD. However, these solvents are not fully inert: acetonitrile slowly replaces coordinated carbonyl ligands,[19] and methanol causes slow decomposition. ^{1}H NMR spectra of the compounds **13**−**16** are consistent with the expected molecular structures. The spectrum of compound **13** measured in CD_3CN shows significant signal broadening that is caused by the paramagnetic complex anion $[MoOBr_4(H_2O)]^-$ 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 $[MoOBr_4(H_2O)]^-$ 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 $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ (**17**, **18**) were prepared from the allyl complex $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ and the appropriate cyclopentadienides (**4-Li**, **6-Na**) in line with the method developed for the unsubstituted analogue (**1**).[24] This

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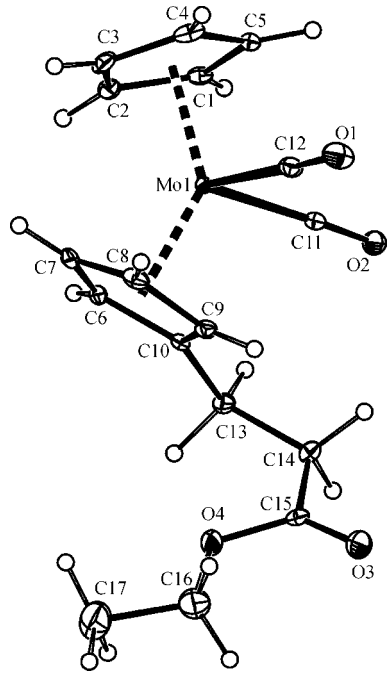


Figure 1. ORTEP drawing of the dicationic complex $[CpMo(\eta^5\text{-}C_5H_4CH_2CH_2COOEt)(CO)_2]^{2+}$ present in the crystal structure of **13** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and angles (deg): Mo1−C11 2.056(3), Mo1−C12 2.051(3), Mo1−C1 2.306(3), Mo1−C2 2.333(3), Mo1−C3 2.335(3), Mo1−C4 2.323(3), Mo1−C5 2.286(3), Mo1−C6 2.354(3), Mo1−C7 2.315(3), Mo1−C8 2.278(3), Mo1−C9 2.297(3), Mo1−C10 2.399(2), C11−O2 1.118(3), C12−O1 1.127(3), C15−O3 1.208(4), C15−O4 1.333(3), O4−C16 1.468(4), C12−Mo1−C11 87.19(11).

route is suitable also for trimethylsilyl-substituted compounds (**19**, **20**), as shown in Scheme 3. The new allyl complexes $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ (**17**, **18**, **20**) were isolated and characterized by spectroscopic methods. Two characteristic bands of CO stretching were found in the infrared spectra at ∼1950 and ∼1860 cm^{-1}. NMR spectra show a typical pattern of allyl complexes. Multiplets at 3.9 (1H), 2.7 (2H), and 0.9 ppm (2H) were observed in the ^1H NMR spectra and signals at ∼68 (1C) and ∼41 ppm (2C) in the $^{13}C\{^1H\}$ NMR spectra. The structure of compound **18** was determined by X-ray diffraction analysis; see Figure 2.

The cationic monocyclopentadienyl complexes $[Cp'Mo(CO)_2(NCMe)_2][BF_4]$ (**21**, **22**) were obtained through reaction of complexes $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ (**17**, **18**) with HBF_4 in the presence of MeCN. ^1H NMR spectra of **21** and **22** prove the coordination of the substituted η^5-cyclopentadienyl (two triplets: δ ∼6.1−5.5 ppm) and two coordinated acetonitrile ligands (singlet: $\delta = 2.5$ ppm). The presence of two carbonyls is evident from infrared (ν_a ∼1980 cm^{-1}, ν_s ∼1890 cm^{-1}) and $^{13}C\{^1H\}$ NMR spectra (δ ∼250 ppm). Infrared spectra also show absorption bands of the other characteristic vibrations such as ν(C−H, Cp) at ∼3100 cm^{-1}, ν_a(C≡N) at ∼2320 cm^{-1}, ν_s(C≡N) at ∼2290 cm^{-1}, and ν(B−F) at ∼1060 cm^{-1}. The ionic character of compounds **21** and **22** is evident from ^{11}B NMR spectra. The signal observed at ca. −1 ppm is typical for a BF_4 anion. The structure of the compound **22** was determined by X-ray structure analysis.

Protonation of the trimethylsilyl-substituted compounds (**19**, **20**) with HBF_4 does not give only the expected cationic complexes (**23**, **24**) but also products of desilylation, as shown in Scheme 3. The crude compound **23** was contaminated with ∼33% of unsubstututed analogue **1** according to ^1H NMR spectra. This impurity was removed using fractional crystallization. This method was applied also for purification of **24**. In this case the crude product contained ∼54% of **23** and ∼7% of **1**. The trimethylsilyl-substituted compounds **23** and **24** were characterized by spectroscopic methods and mass spectrometry. The structure of compound **23** was determined by X-ray diffraction analysis.

The cationic complexes **21**−**23** react with cyclopentadiene, forming η^4-complexes **25**−**27**. Coordinated cyclopentadiene shows two triplets (δ ∼6.5, 4.6 ppm; $^3J(^1H,^1H) = 2.7$ Hz) and two doublets (δ ∼3.8, 3.5 ppm; $^2J(^1H,^1H) = 15$ Hz) in the ^1H NMR spectra. Such a pattern is characteristic for compounds with η^4-coordinated cyclopentadiene. Reaction of cyclopentadiene with the methoxyethyl-substituted complex **21** was found to be considerably faster than with complexes **22** and **23**. This pendant arm effect shortens the reaction time to 2 h instead of the 18 h that is necessary for other cyclopentadienyl complexes.

Repeated crystallization of compound **26** gives a single crystal of appropriate hydride complex $[CpMo(\eta^5\text{-}C_5H_4COOMe)(CO)H][BF_4]$ (**26a**). This rearrangement was previously described for the unsubstituted analogues $[CpMo(\eta^4\text{-}C_5H_6)(CO)_2][BF_4]$.[19] The structure of compound **26a** was determined by X-ray analysis (see Figure 5).

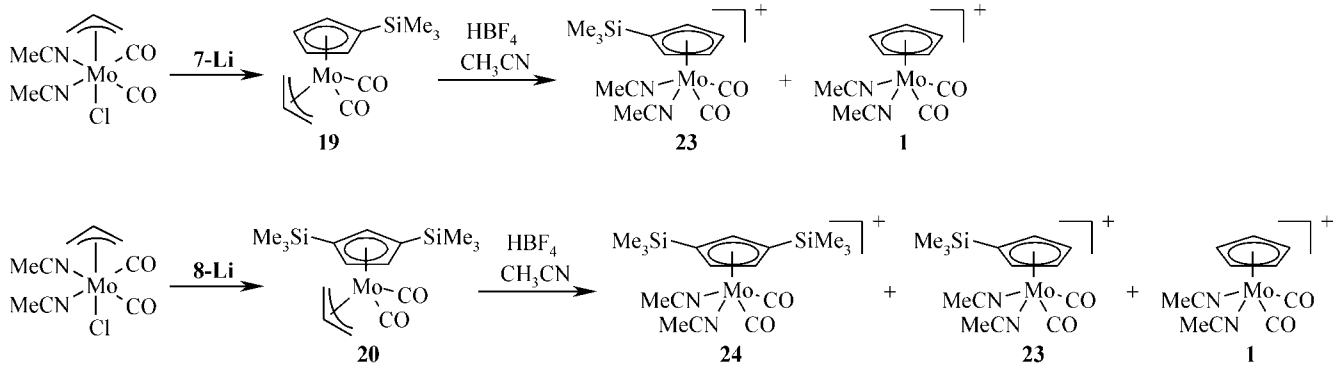
Oxidation of complexes **25** and **26** gives the dications $[CpCp'Mo(CO)_2]^{2+}$ (**15**, **16**). ^1H NMR and IR spectroscopic measurements prove that these compounds are identical to those prepared using route I. The reactivity of compound **16** was further investigated. It was found that both CO ligands are released in acetonitrile, forming the bromo complex $[CpMo(\eta^5\text{-}C_5H_4COOMe)(NCMe)Br][BF_4]$ (**28**). The IR spectrum of this compound does not show any band in the region of the CO stretching. The ^1H NMR spectrum is consistent with the substituted metallocene framework and the coordination of acetonitrile.

The monocarbonyl complex $[CpMo(\eta^5\text{-}C_5H_4COOMe)(CO)Br][BF_4]$ (**29**) 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 ^1H 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 η^4-cyclopentadiene complex. Instead, the hydride complex **30** was isolated from the reaction mixture (Scheme 4). Spectroscopic data collected for **30** are in agreement with those reported previously.[19] The low stability of the expected η^4-cyclopentadiene complexes is probably caused by the presence of the trimethylsilyl group in *exo*-5-position. Such an intermediate was not trapped, but its formation is in line with sterical hindrance of the bulky trimethylsilyl group and the fact that free cyclopentadiene **7** was observed as a mixture of the 5-isomer (90%), 1-isomer, and 2-isomer at room temperature.[25] Reaction with disubstituted cyclopentadiene **8** gives further experimental data showing that formation of the intermediates with the $SiMe_3$ group in *endo*-5-possition is not possible. Due to steric hindrance, $C_5H_4(SiMe_3)_2$ (**8**), which forms at room temperature the 5,5-isomer,[25] reacts with $[CpMo(CO)_2(NCMe)_2][BF_4]$ (**1**) very

(25) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983–996.

Scheme 3. Synthesis of Trimethylsilyl-Substituted Compounds 23 and 24



7-Li = $LiC_5H_4Si(Me)_3$; **8-Li** = $LiC_5H_3(Si(Me)_3)_2$.

sluggishly. It gives only a small amount of untractable products. Bulky substituents in both 5-positions disable the formation of the η^4-intermediate that could be necessary for desilylation reaction. So far only a few η^4-cyclopentadiene complexes with substituents in the *endo*-5-position have been described. All of them are less bulky than the trimethylsilyl group: [CpMo(η^4-$C_5H_4(CH_2)_n$)$(CO)_2$][BF_4] ($n = 2, 4$),[20] [CpMo(η^4-C_5Me_5H)$(CO)_2$]-[BF_4],[19] and [CpMo(η^4-C_5H_5Et)PR_3Cl] [26]

The use of desilylation reactions for preparation of ring-functionalized compounds was further examined. Reaction of ring-substituted complex [(η^5-$C_5H_4CH_2CH_2OMe$)$Mo(CO)_2$-$(NCMe)_2$][BF_4] (**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 ^1H NMR spectrum. The high-field signal at −8.2 ppm is typical for a Mo−H bond. The resonance of the CO carbon was found to be at ∼223 ppm.

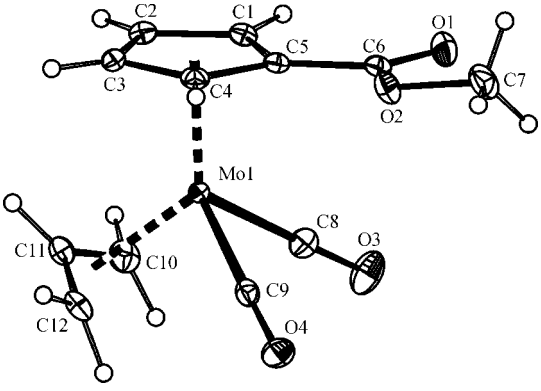


Figure 2. ORTEP drawing of the complex [(η^5-C_5H_4COOMe)Mo(η^3-C_3H_5)$(CO)_2$] (**18**) with atom numbering of non-hydrogen atoms (ellipsoids: 30% probability). Selected bond lengths (Å) and angles (deg): Mo1−C8 1.954(3), Mo1−C9 1.937(2), Mo1−C10 2.337(2), Mo1−C11 2.235(2), Mo1−C12 2.344(2), Mo1−C1 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).

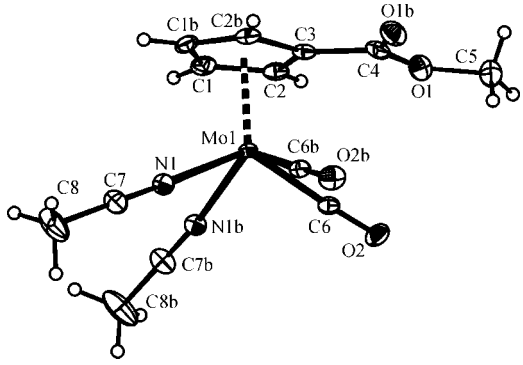


Figure 3. ORTEP drawing of the cationic complex [(η^5-C_5H_4COOMe)Mo$(CO)_2(NCMe)_2]^+$ present in the crystal structure of **22** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and angles (deg): Mo1−C6 1.9766(17), Mo1−N1 2.1564(15), Mo1−C1 2.3955(17), Mo1−C2 2.2858(17), Mo1−C3 2.233(2), C6−O2 1.146(2), C7−N1 1.128(2), C3−C4 1.478(4), C6−Mo1−C6b 74.56(10), N1−Mo1−N1b 76.00(8).

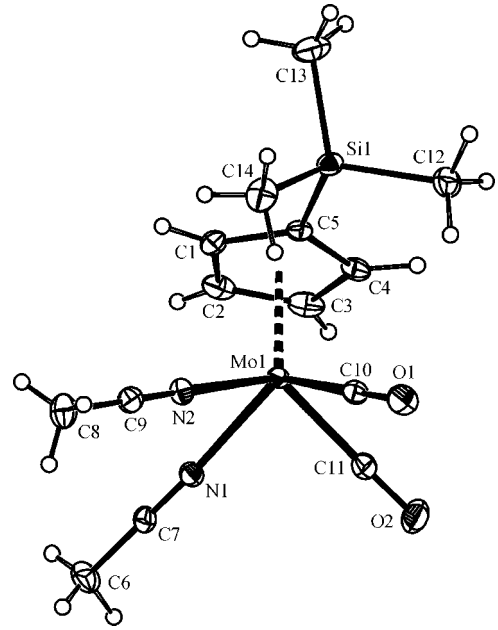


Figure 4. ORTEP drawing of the cationic complex [(η^5-$C_5H_4SiMe_3$)Mo$(CO)_2(NCMe)_2]^+$ present in the crystal structure of **23** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and angles (deg): Mo1−C10 1.972(4), Mo1 C11−1.978(4), Mo1−N1 2.166(3), 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−Mo1−C11 73.89(15), N1−Mo1−N2 76.89(11).

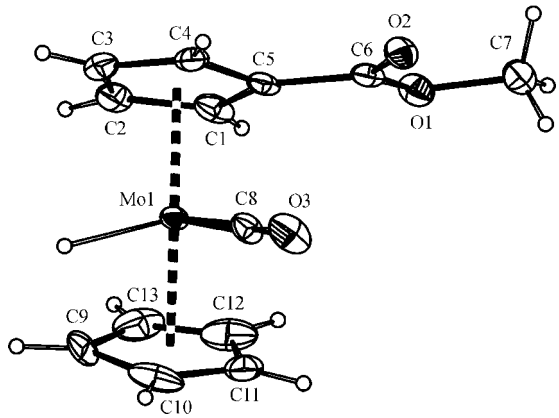
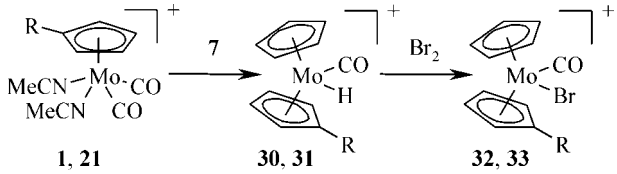


Figure 5. ORTEP drawing of the cationic complex $[CpMo(\eta^5\text{-}C_5H_4CH_2CH_2OMe)(CO)H]^+$ present in the crystal structure of **26a** (ellipsoids: 20% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and angles (deg): Mo1−C8 2.008(5), Mo1−C1 2.279(6), Mo1−C2 2.307(5), Mo1−C3 2.339(6), Mo1−C4 2.288(5), Mo1−C5 2.277(5), Mo1−C9 2.281(6), Mo1−C10 2.282(7), Mo1−C11 2.310(6), Mo1−C12 2.271(7), Mo1−C13 2.278(7), C8−O3 1.124(6), C6−O2 1.196(6), C6−O1 1.319(7), C7−O1 1.452(8), C5−C6 1.481(7).

Scheme 4. Synthesis of $[CpCp'Mo(CO)Br]^+$ Using Route III



7 = $C_5H_5Si(Me)_3$; **1**, **30**, **32**: R = H;
21, **31**, **33**: R = CH_2CH_2OMe.

Reaction of hydrides **30** and **31** with bromine gives bromides **32** and **33**, respectively. The ligand exchange is accompanied with shifting of the CO stretching to higher wavelengths (IR: ∼2050 cm^{-1}). ^1H and ^{13}C NMR spectra show signals of the cyclopentadienyl ring at lower field when compared with the parent hydride complexes. The resonance of the carbonyl carbon is shifted to higher field than in the parent hydrides (at ∼216 ppm).

Mass Spectrometry. Compounds **13**−**16**, **21**−**24**, **32**, and **33** were characterized by ESI mass spectrometry. Bis-cyclopentadienyl compounds **13**−**16**, **32**, and **33** give peaks of $[CpCp'MoBr]^+$ in positive-ion mode. The $[CpCp'Mo(CO)Br]^+$ ion was observed in the case of compound **33**. The absence of $[CpCp'Mo(CO)_2]^{2+}$ and in some cases also $[CpCp'Mo(CO)Br]^+$ for dicationic compounds **13**−**16** corresponds with the lability of the Mo−CO bond that was already mentioned in the previous section. The complex anion of compound **13** was detected in the negative mode as an ion without the coordinated water molecule $[MoOBr_4]^-$.

Compounds **21**−**24** give peaks assigned to $[Cp'Mo(CO)_2(MeCN)]^+$. In particular cases, peaks of $[Cp'Mo(CO)_3(MeCN)]^+$, $[Cp'Mo(CO)_3]^+$, $[Cp'Mo(CO)(MeCN)]^+$, and $[Cp'Mo(CO)_2]^+$ were observed.

Crystal Structures. The structures of three monocyclopentadienyl compounds (**18**, **22**, and **23**) and two bis-cyclopentadienyl compounds (**13**, **26a**) were determined by X-ray diffraction analysis. Their crystallographic data are summarized in Table 1.

The molecule of compound **18** has pseudotetrahedral coordination around the Mo(II) center with η^3-allyl, η^5-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 $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ ($\eta^5\text{-}C_5H_4COCH_3$, $\eta^5\text{-}C_5H_4CO\text{-Phe-OMe}$).[27]

The cations of the compounds **22** and **23** show the distorted pseudosquare pyramid, in which two *cis*-coordinated carbonyl groups and two acetonitrile ligands forms the basal plane. The apical position is occupied by the η^5-coordinated substituted-cyclopentadienyl ligand (Figures 2 and 3). The Mo−Cg(Cp′) 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).[28] The differences in other parameters defining the geometry around the molybdenum center are negligable (Mo−C(CO) ∼1.97 Å, Mo−N(MeCN) ∼2.16 Å, C(CO)−Mo−C(CO) ∼74°, 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 η^5-cyclopentadienyl, one η^5-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(CO)−Mo−C(CO) 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 $[MoOBr_4(H_2O)]^-$ and Br^-. Two $[MoOBr_4(H_2O)]^-$ units and two bromides are linked via hydrogen bonds, as shown in Figure 6. A similar supramolecular structure containing three $[MoOBr_4(H_2O)]^-$ units linked through two bromides was described previously.[29] The cation of compound **26a** has one carbonyl and one hydride bonded on the molybdenum(IV) center. The bond length Mo−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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(27) (a) Vanarsdale, W. E.; Kochi, J. K. *J. Organomet. Chem.* **1986**, *317*, 215–232. (b) van Staveren, D. R.; Weyhermüller, T.; Metzler-Nolte, N. *Organometallics* **2000**, *19*, 3730–3735.
(28) Pereira, C. C. L.; Braga, S. S.; Paz, F. A. A.; Pillinger, M.; Klinowski, J.; Gonçalves, I. S. *Eur. J. Inorg. Chem.* **2006**, 4278–4288.
(29) Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 2710–2713.

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

	13	18	22	23	26a
formula	$C_{17}H_{20}Br_5Mo_2O_6$	$C_{12}H_{12}MoO_4$	$C_{13}H_{13}BF_4MoN_2O_4$	$C_{14}H_{19}BF_4MoN_2O_2Si$	$C_{13}H_{13}BF_4MoO_3$
fw	911.76	316.16	444.00	458.15	399.98
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/m$	$P2_1/c$	$C2/c$
a (Å)	8.3871(5)	17.015(3)	6.4180(13)	6.8769(2)	15.658(3)
b (Å)	9.8162(5)	12.215(2)	11.568(2)	16.9608(4)	14.019(3)
c (Å)	16.1219(9)	13.816(3)	11.538(2)	16.8468(4)	15.379(3)
α (deg)	102.907(2)				
β (deg)	102.697(2)	123.32(3)	97.91(3)	100.4070(10)	119.87(3)
γ (deg)	97.302(3)				
V (Å^3)	1240.28(12)	2399.4(8)	848.5(3)	1932.65(9)	2927.1(10)
Z	2	8	2	4	8
D_c (g cm^{-3})	2.441	1.750	1.738	1.575	1.815
μ (mm^{-1})	9.095	1.092	0.834	0.786	0.948
F(000)	858	1264	440	920	1584
cryst size (mm)	0.30 × 0.10 × 0.02	0.30 × 0.20 × 0.10	0.22 × 0.06 × 0.04	0.50 × 0.20 × 0.10	0.40 × 0.20 × 0.05
θ range	1.34 to 33.16	2.20 to 25.00	2.51 to 30.53	2.40 to 29.59	2.91 to 28.12
index ranges	$-12 \le h \le 10$	$-19 \le h \le 20$	$-9 \le h \le 7$	$-9 \le h \le 9$	$-21 \le h \le 21$
	$-14 \le k \le 15$	$-14 \le k \le 14$	$-15 \le k \le 16$	$-20 \le k \le 23$	$-17 \le k \le 19$
	$-24 \le l \le 24$	$-16 \le l \le 16$	$-16 \le l \le 15$	$-22 \le l \le 23$	$-21 \le l \le 21$
reflns collected	31 026	26 612	12 579	24 454	15 910
indep reflns	8835 (R_{int} = 0.0473)	2117 (R_{int} = 0.0227)	2416 (R_{int} = 0.0234)	5278 (R_{int} = 0.0416)	3873 (R_{int} = 0.0308)
parameters	351	202	148	320	213
final R indices	$R1$ = 0.0291	$R1$ = 0.0209	$R1$ = 0.0221	$R1$ = 0.0430	$R1$ = 0.0548
$[I > 2\sigma(I)]^{a,b}$	$wR2$ = 0.0665	$wR2$ = 0.0558	$wR2$ = 0.0547	$wR2$ = 0.1068	$wR2$ = 0.1396
final R indices	$R1$ = 0.0434	$R1$ = 0.0220	$R1$ = 0.0255	$R1$ = 0.0673	$R1$ = 0.0760
(all data)^{a,b}	$wR2$ = 0.0792	$wR2$ = 0.0571	$wR2$ = 0.0564	$wR2$ = 0.1189	$wR2$ = 0.1531
largest diff peak and hole (e Å^{-3})	0.952, −1.052	1.708, −0.284	0.393, −0.387	1.187, −0.960	1.366, −0.774

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

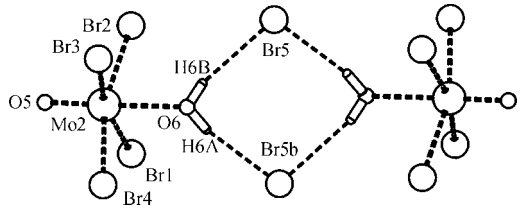

Figure 6. Hydrogen bonds in **13**: two $[MoOBr_4(H_2O)]^-$ units are linked via a pair of bromides. Selected bond lengths (Å) and angles (deg): Mo2−O5 1.656(2), Mo2−O6 2.317(2), Mo2−Br1 2.5527(3), Mo2−Br2 2.5330(4), Mo2−Br3 2.5337(4), Mo2−Br4 2.5239(4), O5−Mo2−O6 179.24(9), Br1−Mo2−Br3 166.361(14), Br2−Mo2−Br4 163.761(14), O6−H6A 0.86(5), H6A···Br5b 2.49(5), O6···Br5b 3.247(2), O6−H6A···Br5b 148(4), O6−H6B 0.77(4), H6B···Br5 2.62(4), O6···Br5 3.354(2), O6−H6B···Br5 161(4) [symmetry code 1 − x, 1 − y, −z corresponds to Br5b].

= 1.959(4) Å). The bond angle Cg(Cp)−Mo−Cg(Cp′) was found to be 143.54(17)°.

Discussion

Molybdenocenes with one of the rings substituted with ether −CH_2CH_2OMe or carboxylic acid ester −CH_2CH_2COOEt, −CH_2CH_2OOCMe, or −COOMe 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, [Cp′Mo(η^3-C_3H_5)$(CO)_2$], [Cp′Mo$(CO)_2(NCMe)_2$][BF_4], and [Cp′Mo(η^4-C_5H_6)$(CO)_2$][BF_4], that have to be isolated. However, this does not usually bring any additional complication due to the similarity between the synthesis of [CpMo$(CO)_2(NCMe)_2$][BF_4] (**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 [Cp′Mo$(CO)_2(NCMe)_2$][BF_4] and the diene $C_5H_5SiMe_3$ (**7**). This reaction produces hydride complexes of formula [CpCp′Mo(CO)H][BF_4], from which the corresponding bromo complex [CpCp′Mo(CO)Br][BF_4] is readily obtained through reaction with bromine. Hydride complexes of the type [CpCp′Mo(CO)H][BF_4] (Cp′ = Cp, Ind) were previously prepared through a photochemical rearrangement of [Cp′Mo(η^4-C_5H_6)$(CO)_2$][BF_4].[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 HBF_4 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 [$(C_5H_4CH_2CH_2I)_2MoI_2$] using the nucleophilic substitution of iodine from the −CH_2CH_2I pendant

(30) Yeh, P.-H.; Pang, Z.; Johnston, R. F. *J. Organomet. Chem.* **1996**, *509*, 123–129.

groups.[16] 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, $[Cp'Mo(CO)_2(NCMe)_2][BF_4]$.

These methodologies elicit access to a wider variety of molybdenocene 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.[31] Starting materials were available commercially or prepared according to literature procedures: $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$,[24] $[CpMo(CO)_2(NCCH_3)_2][BF_4]$ (**1**),[28] C_5H_5COOMe (**6**),[32] NaC_5H_4COOMe (**6-Na**),[33] $C_5H_5SiMe_3$ (**7**),[34] $C_5H_4(SiMe_3)_2$ (**8**),[34] and $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ (**21**).[35] Monomeric cyclopentadiene was prepared by thermal retro-Diels−Alder reaction from dimer (Fluka) and used immediately after distillation.

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 ^{92}Mo 14.84%, ^{94}Mo 9.25%, ^{95}Mo 15.92%, ^{96}Mo 16.68%, ^{97}Mo 9.55%, ^{98}Mo 24.13%, ^{100}Mo 9.63%.[36] Spectra obtained were computer simulated (WSearch32 2005). Mass peaks listed refer to fragments with the isotopes ^{1}H, ^{11}B, ^{12}C, ^{14}N, ^{16}O, ^{19}F, ^{28}Si, ^{79}Br, and ^{98}Mo. ^{1}H, ^{11}B, and ^{13}C{^{1}H} NMR spectra were measured in solutions on a Bruker Avance 400 spectrometer at room temperature. $CDCl_3$, CD_3CN, CD_3OD, and acetone-d_6 were used as obtained (Cambridge Isotope Laboratories) without further purification. Chemical shifts are given in ppm relative to TMS. IR spectra were recorded in the 4000−440 cm^{-1} region (step 2 cm^{-1}) on a Mattson 7000 FT-IR spectrometer using KBr pellets.

X-ray Structure Determination. The measurements were carried out on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from an X-ray tube. Details of crystallographic data and refinement parameters are given in Table 1. Programs used: data collection, Smart (Bruker 2003); data reduction, Saint (Bruker version 6); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement was done using SHELXTL (Bruker 2003). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. The non-hydrogen atoms were refined anisotropically.

Synthesis of $C_5H_5CH_2CH_2COOEt$ (2). Cyclopentadiene (8.4 mL; 0.1 mol) was added dropwise to the suspension of NaH (0.12 mol) in 100 mL of THF. When addition was completed, the reaction mixture was stirred for 10 min at room temperature. The pink solution was then cooled at −78 °C, and ethyl 3-chloropropionate (13.6 g, 0.1 mol) was added in one portion. The reaction mixture was stirred for 10 min at room temperature. The obtained suspension was diluted with a water/pentane mixture. The organic layer was separated, 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%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1:2.3 mixture of isomers **2a** and **2b**, 6.42−6.37 (m, 2H of **a** and 1H of **b**, C_5H_5), 6.24 (m, 1H of **b**, C_5H_5) 6.16 (m, 1H of **b**, C_5H_5), 6.02 (m, 1H of **a**, C_5H_5), 4.12 (q, $^3J(^1H,^1H) = 7.1$ Hz, 2H of **a** and 2H of **b**, CH_2CH_3), 2.92 (m, 1H of **a**, C_5H_5), 2.87 (m, 1H of **b**, C_5H_5), 2.73 (m, 2H of **b**, $C_5H_5CH_2CH_2$), 2.68 (m, 2H of **a**, $C_5H_5CH_2CH_2$), 2.53 (m, 2H of **a** and 2H of **b**, $C_5H_5CH_2CH_2$), 1.23 (t, $^3J(^1H,^1H) = 7.1$ Hz, 3H of **a** and 3H of **b**, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ ppm): 172.9 (1C of **a** and 1C of **b**, *C*OO), 147.5 (1C of **b**, C_{ipso}), 145.4 (1C of **a**, C_{ipso}), 134.2, 133.9 (2C of **a**, C_5H_5), 132.2, 130.8, 126.9 (3C of **b**, C_5H_5), 126.2 (1C of **a**, C_5H_5), 60.2 (1C of **a** and 1C of **b**, CH_2CH_3), 43.2 (1C of **b**, C_5H_5), 41.2 (1C of **a**, C_5H_5), 34.2 (1C of **b**, $C_5H_5CH_2CH_2$), 33.6 (1C of **a**, $C_5H_5CH_2CH_2$), 25.9 (1C of **b**, $C_5H_5CH_2CH_2$), 25.1 (1C of **a**, $C_5H_5CH_2CH_2$), 14.1 (1C of **a** and 1C of **b**, CH_2CH_3).

Synthesis of $[CpMo(\eta^4\text{-}C_5H_5CH_2CH_2COOEt)(CO)_2][BF_4]$ (9). The solution of compound **1** (0.56 g, 1.45 mmol) in CH_2Cl_2 was treated with an excess of cyclopentadiene **2** (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 CH_2Cl_2/ether. The obtained yellow powder was vacuum-dried. Yield: 0.61 g (1.3 mmol, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 4:1 mixture of isomers **9a** and **9b**, 6.61 (m, 1H of **b**, C_5H_5R), 6.39 (m, 1H of **a**, C_5H_5R), 6.20 (m, 1H of **a**, C_5H_5R), 5.80 (s, 5H of **a**, C_5H_5), 5.79 (s, 5H of **b**, C_5H_5), 4.71 (m, 1H of **a**, C_5H_5R), 4.51 (m, 1H of **b**, C_5H_4R), 4.47 (m, 1H of **b**, C_5H_4R), 4.13 (q, $^3J(^1H,^1H) = 7.2$ Hz, 2H of **a** and **b**, CH_2CH_3), 3.92 (d, $^2J(^1H,^1H) = 15.0$ Hz, 1H of **a**, C_5H_5R), 3.82 (d, $^2J(^1H,^1H) = 14.0$ Hz, 1H of **b**, C_5H_5R), 3.38 (d, $^2J(^1H,^1H) = 15.0$ Hz, 1H of **a**, C_5H_5R), 3.34 (d, 1H of **b**, C_5H_5R), 2.60−2.28 (m, 4H of **a** and **b**, CH_2CH_2), 1.24 (t, $^3J(^1H,^1H) = 7.2$ Hz, 2H of **a** and **b**, CH_2CH_3). ^{11}B NMR ($CDCl_3$, 149 MHz, δ ppm): −0.97.

Synthesis of $[CpMo(\eta^5\text{-}C_5H_4CH_2CH_2COOEt)(CO)_2][MoOBr_4(H_2O)][Br]$ (13). The solution of compound **9** (0.47 g, 1 mmol) in CH_2Cl_2 was cooled to −80 °C and treated with an excess of Br_2. The solution was slowly warmed to room temperature. During that time a yellow precipitate was formed. Solvents with an excess of Br_2 were vacuum evaporated. The product was washed three times with CH_2Cl_2 and twice with ether, recrystallized from MeCN/Et_2O, and vacuum-dried. Yield: 0.31 g (0.34 mmol, 34%). Anal. Calcd for $C_{17}H_{20}Br_5Mo_2O_6$: C, 23.40; H, 2.21. Found: C, 23.22; H, 2.14. Positive-ion MS: $m/z = 407$ (100%) $[M - 2(CO) + Br]^+$. Negative-ion MS: $m/z = 430$ (100%) $[MoOBr_4]^-$. ^{1}H NMR (CD_3CN, 400 MHz, δ ppm): 6.52 (s, 2H, C_5H_4), 6.50 (s, 5H, C_5H_5), 6.41 (s, 2H, C_5H_4), 4.13 (q, $^3J(^1H,^1H) = 6.9$ Hz, 2H, CH_2CH_3), 2.84 (br, 2H, $C_5H_4CH_2$), 2.74 (br, 2H, CH_2COO), 1.23 (t, $^3J(^1H,^1H) = 6.7$ Hz, 3H, CH_2CH_3). ^{1}H NMR (CD_3OD, 400 MHz, δ ppm): 6.22 (s, 5H, C_5H_5), 6.22 (m, 1H, C_5H_4), 6.14 (m, 1H, C_5H_4), 6.04 (m, 1H, C_5H_4), 5.99 (m, 1H, C_5H_4), 4.16 (q, $^3J(^1H,^1H) = 7.1$ Hz, 2H, CH_2CH_3), 2.90−2.84 (m, 2H, $C_5H_4CH_2$), 2.74−2.68 (m, 2H, CH_2COO), 1.26 (t, $^3J(^1H,^1H) = 7.1$ Hz, 3H, CH_2CH_3). FTIR (KBr, cm^{-1}): 3102 m [$\nu(CH_{Cp})$], 3060 m [$\nu(CH_{Cp})$], 2120 vs [$\nu_a(CO)$], 2088 vs [$\nu_s(CO)$], 1714 s [$\nu_a(CO_{COO})$]. Crystals suitable for X-ray structure analysis were prepared by careful overlayering of the acetonitrile solution with ether.

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Synthesis of [(η^5-$C_5H_4CH_2CH_2OMe$)Mo(η^3-C_3H_5)$(CO)_2$] (17). $C_5H_5CH_2CH_2OMe$ (**4**) (0.62 g, 5 mmol) was diluted with 50 mL of Et_2O, 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 [(η^3-C_3H_5)Mo$(CO)_2(NCMe)_2$Cl] (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 (2.8 mmol, 56%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 5.19 (s br, 2H, C_5H_4), 5.14 (s br, 2H, C_5H_4), 3.87 (m, 1H, C_3H_5), 3.46 (t, $^3J(^1H,^1H) = 6.4$ Hz, 2H, CH_2), 3.32 (s, 3H, OCH_3), 2.71 (d, $^3J(^1H,^1H) = 6.8$ Hz, 2H, C_3H_5), 2.44 (t, $^3J(^1H,^1H) = 6.4$ Hz, 2H, CH_2), 0.93 (d, $^3J(^1H,^1H) = 10.6$ Hz, 2H, C_3H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ ppm): 92.6 (C_5H_4), 89.7 (C_5H_4), 73.3 (CH_2OCH_3), 69.0 (C_3H_5), 58.9 (OCH_3), 41.1 (C_3H_5), 29.2 ($C_5H_4CH_2$). FTIR (KBr, cm^{-1}): 3062 m [ν(CHCp)], 1941 vs [νa(CO)], 1857 vs [ν_s(CO)].

Synthesis of [(η^5-$C_5H_4CH_2CH_2OMe$)Mo$(CO)_2(NCMe)_2$][BF_4] (21). [(η^5-$C_5H_4CH_2CH_2OMe$)Mo(η^3-C_3H_5)$(CO)_2$] (**17**) (1.65 g, 5.2 mmol) was dissolved in CH_2Cl_2 and treated with 1 equiv of $HBF_4 \cdot Et_2O$ at 0 °C. The solution immediately changed color from yellow to dark red. After 10 min an excess of acetonitrile was added and the reaction was warmed to room temperature and stirred for one more hour. The reaction mixture was concentrated *in vacuo* to ~3 mL, and Et_2O was added to precipitate the red solid. The crude product was washed with Et_2O, hexane, and toluene and dried *in vacuo*, giving a red oily solid. Recrystallization from MeCN/Et_2O at −40 °C gave an orange powder. Yield: 1.6 g (3.6 mmol, 69%). Anal. Calcd for $C_{14}H_{17}BF_4MoN_2O_3$: C, 37.87; H, 3.86; N, 6.31. Found: C, 37.99; H, 4.03; N, 6.25. Positive-ion MS: $m/z = 346$ $[M - MeCN + CO]^+$, 318 (100%) $[M - MeCN]^+$, 305 $[M - 2(MeCN) + CO]^+$, 290 $[M - MeCN - CO]^+$, 277 $[M - 2(MeCN)]^+$. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 5.66 (t, $^3J(^1H,^1H) = 2.1$ Hz, 2H, C_5H_4), 5.46 (t, $^3J(^1H,^1H) = 2.1$ Hz, 2H, C_5H_4), 3.50 (t, $^3J(^1H,^1H) = 6.0$ Hz, 2H, $CH_2CH_2OCH_3$), 3.29 (s, 3H, OCH_3), 2.50 (s, 6H, CH_3CN), 2.47 (t, $^3J(^1H,^1H) = 6.0$ Hz, 2H, $CH_2CH_2OCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ ppm): 250.3 (2C, *C*O), 142.4 (2C, *C*N), 119.8 (C_{ipso}, C_5H_4), 96.3 (2C, C_5H_4), 92.3 (2C, C_5H_4), 71.5 (1C, $CH_2CH_2OCH_3$), 58.3 (1C, OCH_3), 28.3 (1C, $CH_2CH_2OCH_3$), 4.0 (2C, CH_3CN). ^{11}B NMR ($CDCl_3$, 149 MHz, δ ppm): −1.24. FTIR (KBr, cm^{-1}): 3095 m [$\nu(CH_{Cp})$], 2317 m [ν_a(CN)], 2288 m [ν_s(CN)], 1961 vs [ν_a(CO)], 1863 vs [ν_s(CO)], 1059 vs br [ν_s(BF)].

Synthesis of [CpMo(η^5-$C_5H_4CH_2CH_2OMe$)(CO)H][BF_4] (31). A solution of compound **21** (0.45 g, 1 mmol) in CH_2Cl_2 was treated with an excess of $C_5H_5SiMe_3$ (**7**; 0.41 g, 3 mmol). After stirring the reaction mixture for 2.5 h, the volatiles were vacuum evaporated. The crude product was washed with ether and recrystallized from CH_2Cl_2/ether. Yield: 0.28 g (0.7 mmol, 69%). Anal. Calcd for $C_{14}H_{17}BF_4MoO_2$: C, 42.03; H, 4.28. Found: C, 42.41; H, 4.59. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 5.65 (m, 1H, C_5H_4), 5.59 (s, 5H, C_5H_5), 5.54 (m, 3H, C_5H_4), 3.49 (t, $^3J(^1H,^1H) = 5.7$ Hz, 2H, $C_5H_4CH_2CH_2$), 3.30 (s, 3H, OCH_3), 2.63 (t, $^3J(^1H,^1H) = 5.7$ Hz, 2H, $C_5H_4CH_2CH_2$), −8.21 (s, 1H, Mo-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ ppm): 223.0 (1C, *C*O), 111.5 (C_{ipso}, C_5H_4), 89.6 (1C, C_5H_4), 88.9 (1C, C_5H_4), 88.5 (5C, C_5H_5), 88.1 (1C, C_5H_4), 85.9 (1C, C_5H_4), 72.5 (1C, $C_5H_4CH_2CH_2$), 58.9 (1C, OCH_3), 29.6 (1C, $C_5H_4CH_2CH_2$). ^{11}B NMR ($CDCl_3$, 149 MHz, δ ppm): −1.04. FTIR (KBr, cm^{-1}): 3110 m [$\nu(CH_{Cp})$], 2014 vs [ν(CO)], 1054 vs br [ν_s(BF)].

Synthesis of [CpMo(η^5-$C_5H_4CH_2CH_2OMe$)(CO)Br][BF_4] (33). A solution of compound **31** (0.28 g, 0.7 mmol) in CH_2Cl_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 $C_{14}H_{16}BBrF_4MoO_2$: C, 35.11; H, 3.37. Found: C, 35.04; H, 3.30. Positive-ion MS: $m/z = 365$ (100%) $[M - CO]^+$. ^{1}H NMR (CD_3OD, 400 MHz, δ ppm): 6.21 (s, 5H, C_5H_5), 6.19 (m, 1H, C_5H_4), 6.16 (m, 1H, C_5H_4), 6.03 (t, $J(^1H,^1H) = 2.75$ Hz, 2H, C_5H_4), 3.62 (t, $^3J(^1H,^1H) = 5.7$ Hz, 2H, $C_5H_4CH_2CH_2$), 3.36 (s, 3H, CH_3), 2.81 (m, 2H, $C_5H_4CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_3OD, 101 MHz, δ ppm): 216.6 (1C, *C*O), 102.3 (1C, C_5H_4), 101.9 (1C, C_5H_4), 100.8 (5C, C_5H_5), 99.6 (1C, C_5H_4), 94.1 (1C, C_5H_4), 72.5 (1C, $C_5H_4CH_2CH_2$), 59.1 (1C, OCH_3), 31.0 (1C, $C_5H_4CH_2CH_2$). FTIR (KBr, cm^{-1}): 3090 s [$\nu(CH_{Cp})$], 2049 vs [ν(CO)], 1085 vs br [ν_s(BF)].

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Supporting Information Available: Crystallographic data for **13**, **18**, **22**, **23**, and **26a**, experimental procedures, spectroscopic and analytical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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