Synthesis and isomerism of methoxyallene derivatives of cymantrene

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All of the three isomeric complexes possible for monosubstituted allenes were obtained by the interaction of 1-methoxypropadiene with $CpMn(CO)_3$ under UV irradiation or with $CpMn(CO)_2(THF)$. The complexes were isolated as individual compounds and characterized by IR and ^1H and ^{13}C NMR spectroscopy.

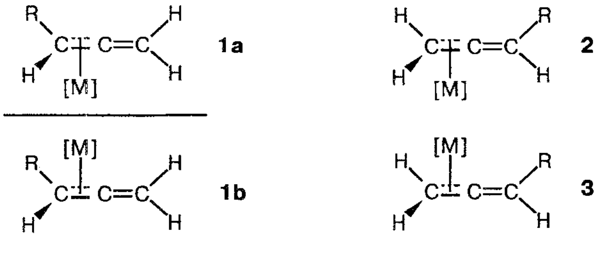
Key words: cyclopentadienylmanganesetricarbonyl, 1-methoxypropadiene, cyclopentadienylmanganesedicarbonyl(1-methoxypropadiene), isomerism; UV irradiation.

Complexes of transition metals with allenes have been investigated in numerous works.[1] Compounds of this type are interesting subjects for study due to their structure, reactivity, and stereochemical flexibility. The latter is caused by the ability of the organometallic fragment to migrate along the allenic ligand, as was observed[2] for the first time for the tetramethylallene complex of iron $(Me_2C{=}C{=}CMe_2)Fe(CO)_4$ (degenerate process). Non-symmetrically substituted allenes, *e.g.*, monosubstituted allenes, can exist in the form of isomers **1**—**3** (Scheme 1). In addition, compounds **1a** and **1b** are the enantiomers. The complex $[(MeCH{=}C{=}CH_2)Fe(CO)_2Cp]^+$ was observed to form type **2** and **3** isomers (Scheme 1), which mutually converted at the rate of the NMR time scale.[3]

It was not possible to identify a type **1** complex, though it was suggested that this complex may be formed as an intermediate product during the **2** $\rightleftharpoons$ **3** isomerization. Only a few type **1** complexes are known,[3,4] while the synthesis of all of three possible isomers has not been reported.

In the present work we have investigated the possible formation of type **1**—**3** isomeric complexes using the reaction of cyclopentadienylmanganesetricarbonyl (CMT) with methoxyallene (**4**). It was found that both the direct interaction of **4** with CMT under UV irradiation and the reaction of **4** with $CpMn(CO)_2(THF)$ without irradiation afford three compounds. On the basis of the spectral data, their isomeric structures were identified as those of complexes **5**—**7**. According to the ^1H NMR spectral data, when the mixture of CMT and **4** in benzene undergoes UV irradiation, complexes **5**, **6**, and **7** are formed in the ratio 42 : 30 : 28, while in the case of the interaction of $CpMn(CO)_2(THF)$ with **4** in THF, this ratio is 58 : 14 : 28.

Scheme 1



In both cases, the most intense signals of the ^1H NMR spectra are assigned to complex **5**. In fact, in the higher field, there is a triplet at 5.5 ppm, which is due to the proton of the CHOMe group at the coordinated double bond of methoxyallene (the shift of the signal for this proton is ~1.35 ppm from that of free methoxyallene). At the same time, the two doublets that correspond to the $=CH_2$ group lie in the ~5.5 to 6.5 ppm range characteristic of the protons at the non-coordinated double bond and are very close to the chemical shifts of these protons in non-coordinated methoxyallene. These data are also in good agreement with both proton-coupled and -decoupled ^{13}C NMR spectra. It should be pointed out that in compound **5** the carbon atoms of the two carbonyl groups are anisochronic, which attests to the absence of the plane of symmetry in this isomer, which is a mixture of the types **1a,b** enantiomers.

In the case of compounds **6** and **7**, the ^1H NMR spectra show two rather similar sets of signals. The coordination of the allenic ligand to the unsubstituted double bond is confirmed by the presence of two high field doublets (at 1.8 to 2.0 ppm). The triplets that correspond to the protons of the CHOMe group are in the low field at 7.35 and 6.60 ppm. The isomers that give rise to these signals are different with respect to the

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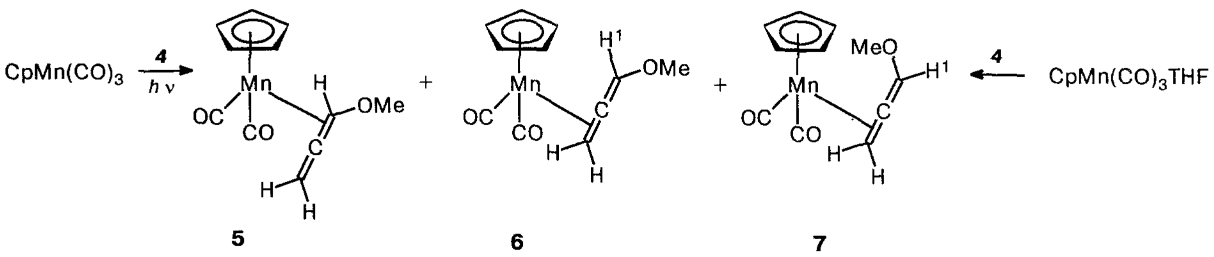
Scheme 2

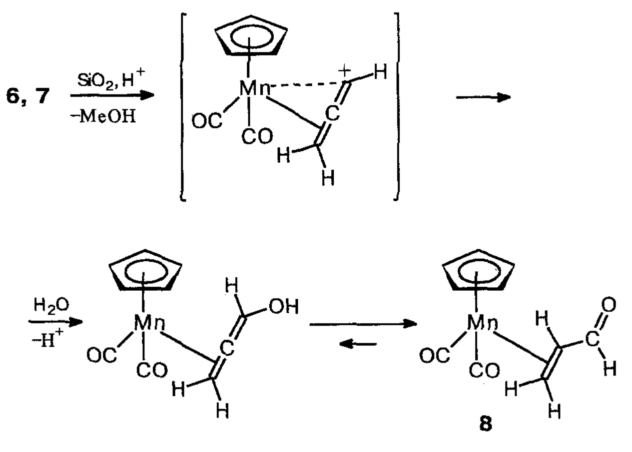


relative disposition of the OMe substituent and organometallic fragment. Both isomers have a symmetry plane, in which three carbon atoms of the allenic ligand, OMe, and H lie, and this accounts for the equivalence of the protons of the $=CH_2$ group.

An attempt to isolate complexes **5—7** as individual isomers using chromatography on silica gel at 0 °C resulted only in isolation of **5**, while under these conditions compounds **6** and **7** were completely hydrolyzed to form the acrolein complex **8**, which was characterized by the IR and ^1H NMR spectral data. The spectral characteristics are similar to those of the compound that was previously obtained from $CpMn(CO)_3$ and acrolein.[6,7] These results support the conclusion that the cleavage of the C—OMe bond in complexes **6** and **7** occurs so readily due to the intermediate formation of the allenylic cation stabilized by the transition metal atom (Scheme 3).

If complexes **5—7** are chromatographed at temperatures lower than −60 °C, all three of the isomers can be isolated in the individual state. These isomers are low-melting crystals that slowly decompose when stored in the air. All of them were characterized by IR and ^1H NMR spectra.

Scheme 3



It should be noted that complexes **5—7** are stereochemically rigid and do not transform into each other under normal conditions. However, we have shown that UV irradiation of a solution of **5** in benzene results in a mixture of all three of the isomers, and the ratio of them is the same as in the case of irradiating the mixture of **4** and CMT.

Isomers **6** and **7** cannot be unequivocally identified on the basis of the experimental data obtained. Nevertheless, we suggest that isomer **6** may be described by the structure in which the OMe group is directed opposite to the organometallic fragment. This proposal is based on our belief that proton 1 of isomer **6** is apparently deshielded by the Cp ring or by CO groups, and, therefore, this proton should resonate downfield relative to the corresponding proton in isomer **7**, as is reflected by the ^1H NMR spectra.

Thus, in the present work, for the first time all possible isomeric complexes of monosubstituted allene with cyclopentadienylmanganesetricarbonyl have been obtained and isolated in the individual state.

Experimental

All of the syntheses were carried out in an argon atmosphere using anhydrous solvents. UV irradiation was generated by a DRL immersion lamp. The course of the reaction was monitored by TLC on Silufol plates and by the IR spectra. Column chromatography was performed on L type silica gel (40—100 μm). IR spectra were recorded on a Specord IR-75 instrument. The ^1H and ^{13}C spectra were obtained on a Bruker WP-200 SY spectrometer with working frequencies 200.13 and 50.31 MHz, respectively (TMS was used as the internal standard).

The starting 1-methoxypropadiene (methoxyallene) was obtained by the procedure described in Ref. 8.

Synthesis of (η^2-1-methoxypropadiene)cyclopentadienyldicarbonylmanganese complexes from $CpMn(CO)_2(THF)$. A solution of 1 g (5 mmol) of CMT in 120 mL of THF was irradiated by UV with stirring for 2 h at 5 °C. Cooling and irradiation were stopped, and 0.5 mL (6 mmol) of methoxyallene was added. The reaction mixture was stirred for 3 h more at −20 °C. The formation of three products was observed by TLC. The contents of the reactor were evaporated, dissolved in a minimum amount of hexane, and filtered off. The solvent was removed *in vacuo*. The ^1H NMR spectrum of the reaction mixture (C_6D_6), δ: 5.47 (t, 1 H, =C$\underline{H}$OMe, *J* = 2.6 Hz), 5.95 (d, 1 H, =C$\underline{H}$(1)H(2), *J* = 2.5 Hz), 6.65 (d, 1 H, =CH(1)$\underline{H}$(2), *J* = 2.8 Hz), 3.16 (s, 3 H, OCH_3), 4.15 (s, 5 H, C_5H_5), 2.01 (d, 2 H, =CH_2, *J* = 2.9 Hz), 6.60 (t, 1 H, =C$\underline{H}$OMe, *J* = 2.9 Hz), 3.60 (s, 3 H, OMe), 4.04 (s, 5 H, C_5H_5), 1.89 (d, 2 H, =CH_2, *J* = 2.9 Hz), 2.01 (d, 2 H, =CH_2, *J* = 2.9 Hz), 7.35 (t, 1 H, =C$\underline{H}$OMe), 4.27 (s, 5 H, C_5H_5). The ratio of isomers **5**, **6**, and **7** was 58 : 28 : 14. The reaction mixture was chromatographed on a column with silica gel at 0 °C using hexane. CMT recovery was 0.24 g (18 %). By a hexane—toluene mixture (7 : 1, then 3 : 1) 0.32 g (24 %) of dark yellow complex **5** was eluted, m.p. 33—34 °C, R_f 0.49 (hexane—ether, 2 : 1). Found (%): C, 53.83; H, 4.58; Mn, 22.20. $C_{11}H_{11}MnO_3$. Calc (%): C, 53.68; H, 4.50; Mn, 22.32. IR (heptane), ν/cm^{-1}: 1924, 1980 (C≡O). ^{1}H NMR (C_6D_6), δ: 5.46 (t, 1 H, =C$\underline{H}$OMe, *J* = 2.6 Hz), 5.96 (d, 1 H, =C$\underline{H}$(1)H(2), *J* = 2.5 Hz), 6.67 (d, 1 H, =CH(1)$\underline{H}$(2), *J* = 2.7 Hz), 3.14 (s, 3 H, OMe), 4.11 (s, 5 H, C_5H_5). ^{13}C NMR (C_6H_6), δ: 56.63 (q, OMe, *J* = 143.5 Hz), 80.96 (d, =C$\underline{H}$OMe, *J* = 185.3 Hz), 86.03 (d.t., 5 C, C_5H_5, *J* = 178.02 Hz, *J* = 6.4 Hz), 114.10 (t, =CH_2, *J* = 163.2 Hz), 164.45 (s, =C=), 229.62 (s, CO), 234.38 (s, CO). 0.28 g (21 %) of compound **8** was eluted with ether. IR (CH_2Cl_2), ν/cm^{-1}: 1924, 1988 (C≡O), 1674 (>C=O). Chromatography on silica gel (at temperatures lower −60 °C) resulted in the sequential isolation of 0.11 g (8.3 %) of complex **6**, 0.42 g (31.5 %) of complex **5**, and 0.19 g (14.3 %) of complex **7** as individual compounds (eluents hexane, hexane—toluene, 7 : 1, 3 : 1). Compound **6** is a yellow-orange crystalline substance, m.p. 31—32 °C, R_f 0.56 (hexane—ether, 2 : 1). IR (heptane), ν/cm^{-1}: 1934, 1990 (C≡O). ^{1}H NMR (C_6D_6), δ: 1.90 (d, 2 H, =CH_2, *J* = 2.9 Hz), 7.35 (t, 1 H, =C$\underline{H}$OMe, *J* = 2.9 Hz), 3.50 (s, 3 H, OMe), 4.24 (s, 5 H, C_5H_5). Compound **7** is a bright yellow crystalline substance. M.p. 45—46 °C, R_f 0.43 (hexane—ether, 2:1). IR (heptane), ν/cm^{-1}: 1932, 1987 (C≡O). ^{1}H NMR (C_6D_6), δ: 2.00 (d, 2 H, =CH_2, *J* = 2.9 Hz), 6.64 (t, 1 H, =C$\underline{H}$OMe, *J* = 2.9 Hz), 3.61 (s, 3 H, OMe), 3.97 (s, 5 H, C_5H_5).

Synthesis of (η^2-1-methoxypropadiene)cyclopentadienyldicarbonylmanganese complexes by irradiating a mixture of cymantrene with 1-methoxypropadiene. A solution of 0.21 g (1 mmol) of CMT and 0.15 mL (1.8 mmol) of methoxyallene in 120 mL of benzene was irradiated by UV for 15 min with stirring and cooling. The TLC data indicated the formation of three products. The reaction mixture was evaporated, dissolved in a minimum amount of hexane, and filtered off. The solvent was removed *in vacuo*. The ^{1}H NMR spectrum of the reaction mixture in C_6D_6 is analogous to that obtained in the case of the reaction in darkness. The ratio of isomers **5**, **6**, and **7** is 42 : 28 : 30.

UV irradiation of complex (5). A solution of 0.1 g of complex **5** in 120 mL of benzene was irradiated by UV for 25 min with stirring and cooling by running water to +10 °C. The reaction mixture was evaporated, extracted with 10 mL of hexane until the extract became colorless, and filtered off. The solvent was removed *in vacuo*. A mixture (0.03 g, 30 %) of isomers **5**, **6**, and **7** was obtained in the ratio 38 : 28 : 34, respectively (^{1}H NMR).

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