Bicymantrenyl chemistry
5.* Substitution reactions in Cp rings of $(CO)_3MnC_5H_4C_5H_4Mn(CO)_2PPh_3$ complex

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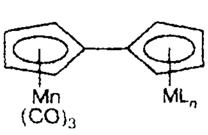
The complex $(CO)_3MnC_5H_4C_5H_4Mn(CO)_2PPh_3$ (**2**) can be involved in electrophilic reactions such as hydrogen-deuterium exchange with CF_3COOD in CH_2Cl_2 and acetylation with a $MeCOCl-AlCl_3$ mixture. In both cases, the substituent (D or MeCO) only enters the $C_5H_4Mn(CO)_2PPh_3$ ring. Metallation of **2** with BuLi (THF, −60 °C) occurs exclusively in the $C_5H_4Mn(CO)_3$ ring. Quenching of Li-containing derivatives with DMF results in a mixture of two isomeric aldehydes with the substituent in position 2 or 3. Reduction of 3-aldehyde with $NaBH_4$ gives the corresponding carbinol (**6b**). Metallation of the latter followed by quenching with DMF gives hydroxyaldehyde $(CO)_2PPh_3MnC_5H_4C_5H_2(CH_2OH)(CHO)Mn(CO)_3$.

Key words: manganese, cyclopentadienyl, carbonyl, complexes; acylation, hydrogen-deuterium exchange, metallation; aldehydes, ketones, synthesis.

Synthetic chemistry of cymantrene (cyclopentadienyltricarbonylmanganese, CTM) has been developed in detail.[2,3] It is known that substitution of one CO group in the CTM molecule by donor ligands (tertiary phosphines) substantially changes the reactivity of the complexes. For example the replacement of CO by different PR_3 groups results in a strong (by 3—4 orders of magnitude) increase in the reaction rate of electrophilic H/D exchange with acids.[4,5] The replacement of CO by PPh_3 changes the direction of attack of such a strong electrophilic reagent as $Hg(OCOCF_3)_2$. In the case of unsubstituted CTM, exhaustive mercuration of the Cp ring occurs, while the $CpMn(CO)_2PPh_3$ complex gives an adduct to the Mn atom, which has been structurally characterized.[6] The chemistry of bicymantrenyl (**1**) began to develop only recently.[1,7—9] Unlike $CpMn(CO)_2PPh_3$,[10] chemical transformations of monophosphine $(CO)_3MnC_5H_4C_5H_4Mn(CO)_2PPh_3$ complex (**2**) described in Ref. 11 have not yet been studied. In this work, some reactions of hydrogen substitution in the Cp rings of complex **2** are studied.



ML_n = $Mn(CO)_3$ (**1**), $Mn(CO)_2PPh_3$ (**2**), FeCp (**3**)

Three substitution reactions typical of CTM and its derivatives were chosen as model reactions: electrophilic isotopic H/D exchange with CF_3COOD, acetylation by a $MeCOCl-AlCl_3$ mixture (Scheme 1), and metallation by butyllithium.

Complex **2** enters the reaction of isotopic exchange of hydrogen with CF_3COOD in CH_2Cl_2 under the same conditions as $CpMn(CO)_2PPh_3$,[4,5] and it follows from the ^1H NMR spectra that only the H atoms in the $C_5H_4Mn(CO)_2PPh_3$ ring are substituted by deuterium. The ^1H NMR spectrum of complex **2** contains four signals with equal intensities (in the ratio of 1 : 1 : 1 : 1), which can easily be assigned on the basis of the differences in their multiplicities. Four protons of the $C_5H_4Mn(CO)_3$ fragment give two signals in a downfield region (4.882 and 4.720 ppm) in the form of triplets with a slightly broadened central line (doublets of doublets, where the two central lines are not resolved) with spin-spin coupling constants of $J_{H,H}$ = 2.0 and 2.2 Hz. The two signals, each of which consists of four lines, in the upper field (4.571 and 4.136 ppm) correspond to four protons of $C_5H_4Mn(CO)_2PPh_3$. Splitting into a pseudo-quadruplet is associated with the fact that these protons equivalent in pairs interact with each other and with the ^{31}P nucleus, and the $J_{H,H}$ and J_{H-Mn-P} constants are close or coincide and are equal to 2.1—2.2 Hz.

After isotopic exchange with CF_3COOD in CH_2Cl_2, in the ^1H NMR spectrum of complex **2**, the intensities of only two signals from $C_5H_4Mn(CO)_2PPh_3$ rings decrease, and the ratio of the intensities of all signals is equal to 1.00 : 1.00 : 0.85 : 0.75. It follows from this that only the H atoms in the C_5H_4 ring coordinated with

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* For Part 4, see Ref. 1.

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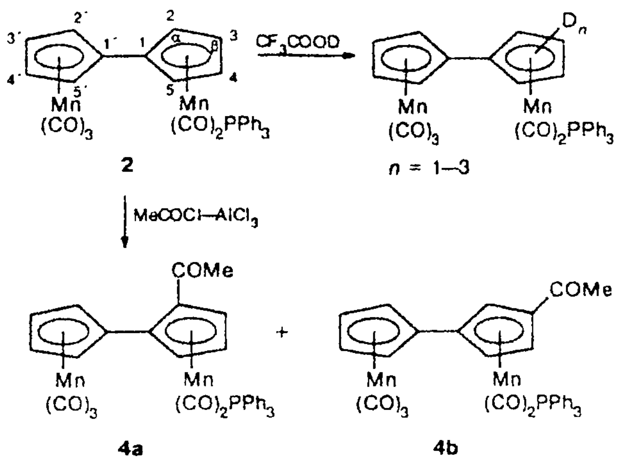
Scheme 1



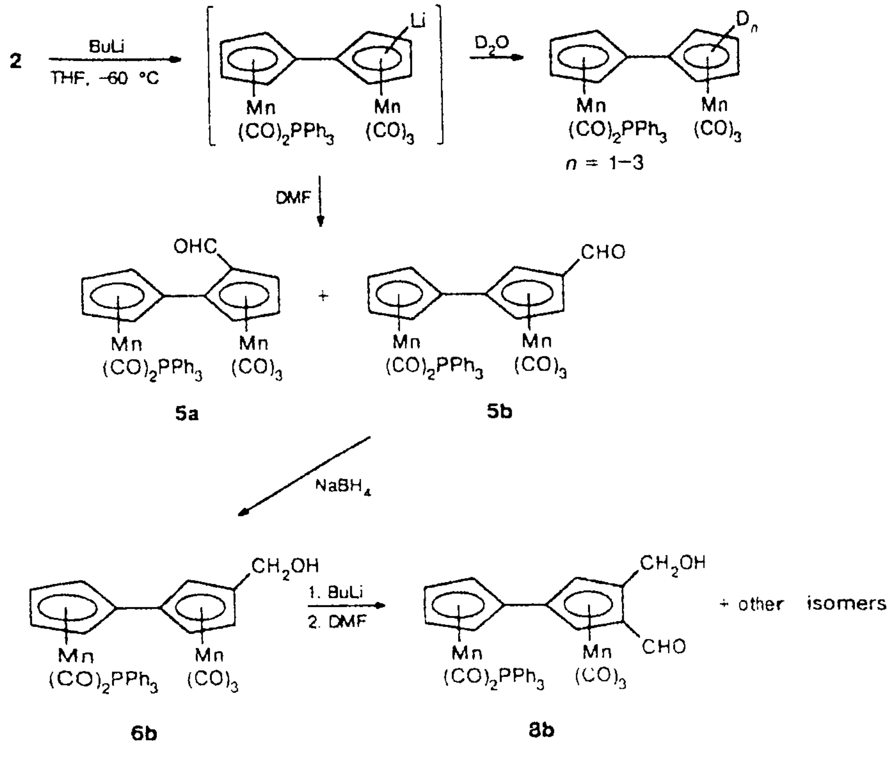
the more donor $Mn(CO)_2PPh_3$ fragment enter into the isotopic exchange with CF_3COOD, and the protons of $C_5H_4Mn(CO)_3$ (as of cymantrene itself) do not participate in the reaction under these conditions.

According to this situation, acetylation of complex **2** by a $MeCOCl—AlCl_3$ mixture results in the formation of a mixture of two ketones **4a,b** containing an acetyl substituent in the α- and β-positions, respectively, of the ring coordinated with $Mn(CO)_2PPh_3$ (see Scheme 1). The reaction is nonselective, and ketone **4b** predominates (the ratio **4b**/**4a** ≈ 5—6). Thus, in reactions of compound **2** with electrophilic reagents (H^+, MeCO), attack of the electrophile is directed only at the $C_5H_4Mn(CO)_2PPh_3$ ring, where the PPh_3 ligand, which is more donor than CO, is coordinated with manganese.

By contrast, metallation of complex **2** by butyllithium occurs only in the $C_5H_4Mn(CO)_3$ ring, because a stronger acceptor, the $Mn(CO)_3$ fragment, increases the mobility of protons in $C_5H_4Mn(CO)_3$ compared to $C_5H_4Mn(CO)_2PPh_3$. Under the action of BuLi followed by hydrolysis of Li-containing derivatives in D_2O, deuterium is only inserted in both positions of the $C_5H_4Mn(CO)_3$ ring, but in different amounts. In the ^1H NMR spectrum of complex **2** isolated after treatment with BuLi and hydrolysis with D_2O, the ratio of the intensities of the four signals is equal to 0.78 : 0.37 : 1.00 : 1.00. It follows that replacement of CO by phosphine in one of the $Mn(CO)_3$ fragments passivates completely the coordinated C_5H_4 ring with respect to attack of BuLi. This makes it possible to selectively synthesize quite different derivatives of complex **2** containing one or several substituents only in the $C_5H_4Mn(CO)_3$ ring.

In fact, treatment of Li-containing derivative **2** with DMF results in a mixture of two aldehydes **5a,b** (Scheme 2). As in the case of compound **1**, metallation in the $C_5H_4Mn(CO)_3$ ring occurs nonselectively involving hydrogen atoms in both nonequivalent positions, although substitution in the β-position, which is sterically more accessible, predominates (the ratio **5b**/**5a** ≈

Scheme 2



10). The reduction of aldehyde **5b** results in the formation of alcohol **6b**. Its analog containing no PPh_3 group, $(CO)_3MnC_5H_4C_5H_3(CH_2OH)Mn(CO)_3$ (**7**), was obtained previously.[8] For comparison, we metallated alcohols **6b** and **7**. It turned out that metallation of compound **7** is not selective, and after hydrolysis in D_2O deuterium is inserted both in position 4 of the $C_5H_3CH_2OH$ ring and in both β-positions of the C_5H_4 ring. However, as follows from the data of ^1H NMR spectroscopy, in metallation of alcohol **6b** followed by hydrolysis with D_2O, deuterium is mainly (>85%) inserted in position 4 adjacent to the CH_2OH substituent of the $C_5H_3(CH_2OH)Mn(CO)_3$ ring and considerably less in positions 2 and 5 of this ring, but deuterium is absent in the $C_5H_4Mn(CO)_2PPh_3$ ring. Hydroxyaldehyde **8b** is the main reaction product in quenching of the Li-containing derivative of alcohol **6b** with DMF. In addition, traces of isomeric hydroxyaldehydes containing a CHO substituent in positions 2 and 5 form (see Scheme 2).

It can be concluded from the results obtained that the reactivity of complex **2** resembles that of cymantrenylferrocene (**3**).[12] For both compounds, the electrophilic attack is directed to the more donor region of the molecule (the $C_5H_4Mn(CO)_2PPh_3$ ring in complex **2** or ferrocenyl in **3**), while the protophilic reagent BuLi detaches a proton from the $C_5H_4Mn(CO)_3$ ring.

All bicymantrenyl derivatives containing a R substituent in positions 2 or 3 are planar chiral. In the general case, due to diastereotopic nonequivalence, seven protons of the $C_5H_4C_5H_3(R)$ fragment correspond to seven individual signals in the ^1H NMR spectrum. These signals can usually be assigned easily on the basis of the differences in their multiplicities. The four protons of the $C_5H_4Mn(CO)_3$ ring form an ABCD system and give four multiplets, and the two protons in α-positions appear as a doublet of triplets; however, due to partial overlapping, each of the signals consists of five lines with nonbinomial distribution of intensities and constants $^1J_{H,H} = 2.6-2.8$ Hz and $^2J_{H,H} = 1.6-1.9$ Hz. The two signals in an upper field correspond to two protons in the β-positions, each has the form of a triplet of doublets (six lines) with the same constants. The four protons of the $C_5H_4Mn(CO)_2PPh_3$ ring also give four individual multiplets, and the two signals in the upper field (usually, protons in β-positions) consist of eight lines (of 12 theoretically possible lines), which is related to the close values of the constants: $^1J_{H,H} \approx {}^1J_{H-Mn-^{31}P} \approx 2.6-2.8$ Hz and partial overlapping of multiplets. For the two signals in a more downfield region, the $^1J_{H-Mn-^{31}P}$ value is considerably lower and does not exceed 0.5—1.0 Hz.

The three protons of the $C_5H_3(R)Mn(CO)_3$ ring form an ABC system and give three signals. When the R substituent is in the α-position (for example, aldehyde **5a**), the H(4) proton appears as a triplet in the upper field with the "near" constant $^1J_{3,4} = {}^1J_{3,5} = 2.8-3.0$ Hz, and the H(3) and H(5) protons appear as two doublets of doublets in a more downfield. By contrast, when the R substituent is in the β-position (aldehyde **5b**), the H(2) proton gives the signal in the downfield region, a triplet with a "far" constant $^2J_{2,4} = {}^2J_{2,5} = 1.7-1.8$ Hz, and the H(4) and H(5) protons give two doublets of doublets in the upper field. Three protons of the $C_5H_3(R)Mn(CO)_3PPh_3$ fragment also correspond to three individual signals, however, their positions and multiplicities can differ, which is related to the ratio of the $J_{H,H}$ and $J_{H-Mn-^{31}P}$ constants for the particular compound.

In the case of ketones **4a,b**, it turned out to be impossible to assign signals on the basis of the one-dimensional ^1H NMR spectrum, and a two-dimensional correlation $^1H-^1H$ NMR (COSY) spectroscopy combined with double resonance $^1H\{^{31}P\}$ was used. The ^1H NMR spectra of compounds obtained are presented in Table 1.

Experimental

All reactions were carried out in an atmosphere of argon. Prior to the reaction, THF was distilled over benzophenone sodium ketyl. ^1H NMR spectra were recorded on Bruker WP-200-SY (200 MHz) and Bruker AMX-400 (400 MHz) instruments. Mass spectra were obtained on a Kratos-MS-890 instrument. IR spectra were recorded on a UR-20 instrument in KBr.

Synthesis of 2- and 3-acetyldifulvalenedimanganesepentacarbonyltriphenylphosphines (4a,b). A solution of complex **2** (0.30 g, 0.47 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a mixture of $AlCl_3$ (0.13 g, 1 mmol) and MeCOCl (1 mL, excess) in anhydrous CH_2Cl_2 (10 mL), and the mixture was stirred for 2 days at room temperature. Then the mixture was boiled for 1 h and decomposed with water after cooling, and the products were extracted with CH_2Cl_2. A dark-red oil (0.29 g) was isolated and chromatographed on a column (27×3 cm) with Al_2O_3. Elution with benzene gave the following fractions: initial complex **2** (0.10 g, 33%); ketone **4a** (0.030 g, 9%). A fraction containing ketone **4b** (0.15 g, 47%) was obtained by elution with benzene—ether (10 : 1) mixture. Ketone **4a** is fine dark-red crystals with m.p. 205—207 °C (from toluene—hexane mixture). Ketone **4b** is reddish crystals with m.p. 162—164 °C (from toluene—hexane mixture). Found (%): C, 62.05; H, 3.90; P, 4.26. $C_{36}H_{25}Mn_2O_6P$. Calculated (%): C, 61.58; H, 3.67; P, 4.55. MS (for both ketones), *m/z*: 682 [M^+], 626 [M−2CO], 542 [M−5CO], 280 [$M-5CO-PPh_3$], 262 [PPh_3], 225 [$M-5CO-PPh_3-Mn$], 170 [M−5CO−2Mn]. IR, ν/cm^{-1}: 1885, 1930 ($Mn(CO)_2PPh_3$); 1945, 2020 ($Mn(CO)_3$); 1680 (C=O).

Synthesis of 2′- and 3′-difulvalenedimanganesepentacarbonyltriphenylphosphinecarbaldehydes (5a,b). A 1.4 *N* solution of BuLi (5 mmol) was added dropwise to a solution of complex **2** (1.50 g, 2.34 mmol) in THF (70 mL) at −65 °C. The solution was stirred for 40 min at −65 °C, then DMF (1.5 mL, excess) was added, and stirring was continued. Two hours after cooling was stopped and after heating to room temperature, the mixture was decomposed by addition of 20% H_3PO_4, poured in water, and the products were extracted with CH_2Cl_2. After treatment and removal of the solvent, a dark-red oil (1.58 g) was obtained. Chromatography on a column with silica gel (30×4 cm) and elution with benzene—heptane

Table 1. ^{1}H NMR spectra of bicymantrenyl derivatives

Compound	Solvent	δ (*J*/Hz)			
		C$_5$H$_3$ ring	C$_5$H$_4$ ring		Other protons*
			H(2′), H(5′)	H(3′), H(4′)	
4a	C$_6$D$_6$	3.454 (q, 1 H, H(4), *J* = 2.8); 4.165 (m, 1 H); 4.658 (dd, 1 H, H(3), H(5))	6.139 (m, 1 H); 4.217 (m, 1 H)	3.948 (m, 1 H); 4.044 (m, 1 H)	1.990 (s, 3 H, CH$_3$)
4b	C$_6$D$_6$	4.995 (q, 1 H, H(2), *J* = 1.8); 4.038, 4.622 (both q, 1 H, H(4), H(5))	4.122 (q, 1 H); 4.172 (q, 1 H)	3.863 (m, 2 H)	1.885 (s, 3 H, CH$_3$)
5a	CDCl$_3$	4.879 (t, 1 H, H(4), *J* = 2.8); 5.413, 5.095 (both dd, 1 H, H(3), H(5))	4.753 (q, 1 H); 4.900 (q, 1 H)	4.101 (m, 1 H); 4.315 (m, 1 H)	9.766 (s, 1 H, CHO)
5b	CDCl$_3$	5.381 (t, 1 H, H(2), *J* = 1.8); 5.433, 5.016 (both dd, 1 H, H(4), H(5))	4.667 (m, 1 H); 4.550 (m, 1 H)	4.148 (m, 1 H); 4.288 (m, 1 H)	9.553 (s, 1 H, CHO)
6b	CDCl$_3$	4.954 (t, 1 H, H(2), *J* = 1.8); 4.816, 4.479 (both dd, 1 H, H(4), H(5))	4.156 (m, 1 H); 4.049 (m, 1 H)	4.548 (q, 2 H)	4.316 (d, 2 H, CH$_2$, *J* = 6.0); 1.748 (t, 1 H, OH, *J* = 6.0)
8b	CDCl$_3$	5.312, 5.096 (both d, 1 H, H(2), H(5) *J* = 1.9)	4.267 (m, 1 H); 4.210 (m, 1 H)	4.661 (m, 1 H); 4.592 (m, 1 H)	δ_A 4.540, δ_B 4.507 (AB-system, CH$_2$, J_{AB} = 2.5); 4.342 (t, 1 H, OH, *J* = 6.7); 9.596 (s, 1 H, CHO)

* Signals of protons from PPh$_3$ are not presented.

(2 : 1) mixture gave the following fractions: initial complex **2** (0.35 g, 23%), aldehyde **5a** (0.06 g, 3.8%), a mixture of **5a** + **5b** (0.31 g, 19%), and aldehyde **5b** (0.80 g, 51%). Aldehyde **5a** is orange crystals with m.p. 165—167 °C (from toluene—hexane mixture). Found (%): C, 61.02; H, 3.54; P, 4.38. $C_{34}H_{23}Mn_2O_6P$. Calculated (%): C, 61.10; H, 3.47; P, 4.63. Aldehyde **5b** is needle-like yellow crystals with m.p. 235—241 °C (from toluene—hexane mixture). Found (%): C, 60.99; H, 3.37; P, 4.57. $C_{34}H_{23}Mn_2O_6P$. Calculated (%): C, 61.10; H, 3.47; P, 4.63. MS (for both aldehydes), *m/z*: 668 [M$^+$], 612 [M−2CO], 528 [M−5CO], 266 [M−5CO−PPh$_3$], 262 [PPh$_3$], 211 [M−5CO−PPh$_3$−Mn], 156 [M−5CO−2Mn]. IR, ν/cm^{-1}: 1875, 1940 (Mn(CO)$_2$PPh$_3$); 1955, 2030 (Mn(CO)$_3$); 1690, 1705 (C=O).

3′-(Hydroxymethyl)difulvalenedimanganesepentacarbonyltriphenylphosphine (6b). NaBH$_4$ (0.2 g, 5 mmol) was added to a solution of aldehyde **5b** (0.80 g, 1.25 mmol) in THF (100 mL) and EtOH (5 mL). After stirring for 50 min, no aldehyde was observed in the reaction mixture (TLC data). Decomposition with a solution of NH$_4$Cl and extraction with ether gave raw alcohol **6b** (0.76 g, 95%) as a yellow oil. After recrystallization from toluene—hexane mixture, large yellow crystals (0.53 g) with m.p. 153—155 °C were obtained. Found (%): C, 60.75; H, 3.73; P, 4.57. $C_{34}H_{25}Mn_2O_6P$. Calculated (%): C, 60.90; H, 3.73; P, 4.63. MS, *m/z*: 670 [M$^+$], 614 [M−2CO], 612 [M−2CO−2H], 528 [M−5CO−2H], 268 [M−5CO−2H−PPh$_3$], 262 [PPh$_3$].

3′-(Hydroxymethyl)difulvalenedimanganesepentacarbonyltriphenylphosphine-4′-carbaldehyde (8b). A 1.4 *N* solution of BuLi (5 mmol) in hexane (3.6 mL) was added to a solution of alcohol **6b** (0.76 g, 1.13 mmol) in THF (40 mL) at −65 °C, then DMF (2 mL, excess) was added. Two hours after cooling was stopped and after heating to room temperature, the mixture was decomposed by addition of 20% H$_3$PO$_4$ and poured in water. After extraction with ether, a yellow oil (0.80 g) was isolated. The oil was chromatographed on a column with silica gel (35×3.5 cm) and eluted with CH$_2$Cl$_2$—petroleum ether (1 : 9) mixture to isolate the following fractions: initial alcohol **6b** (0.26 g, 34%), hydroxyaldehyde **8b** (0.34 g, 43%), and a mixture of other isomers and unidentified compounds (0.07 g). Hydroxyaldehyde **8b** is yellow crystals with m.p. 195—198 °C (from toluene—hexane mixture). Found (%): C, 60.73; H, 3.56; P, 4.35. $C_{36}H_{25}Mn_2O_7P$. Calculated (%): C, 61.17; H, 3.58; P, 4.44. MS, *m/z*: 640 [M−2CO−2H], 556 [M−5CO−2H], 371 [M−5CO−PPh$_2$], 296 [M−5CO−PPh$_3$], 294 [M−5CO−2H−PPh$_3$], 262 [PPh$_3$]. ^{1}H NMR, δ: 5.312, 5.096 (AX-system, 2 H, C$_5$H$_2$(CH$_2$OH)(CHO), J_{AX} = 1.9 Hz); 4.540, 4.507 (AB-system, 2 H, CH$_2$, J_{AB} = 2.5 Hz). (It should be mentioned that diastereotopic nonequivalence of protons of CH$_2$ does not appear in the spectrum of alcohol **6b**, and they form a doublet at 4.316 ppm with *J* = 6.0 Hz.) IR, ν/cm^{-1}: 1875, 1940 (Mn(CO)$_2$PPh$_3$); 1955, 2030 (Mn(CO)$_3$); 1678, 1690 sh (C=O).

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