Chemistry of bicymantrenyl

7.* Mercuration of bicymantrenyl and reactions with aprotic acids

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Bicymantrenyl, $(CO)_3MnC_5H_4C_5H_4Mn(CO)_3$, can be mercurated under the action of 8 moles of mercury trifluoroacetate in CH_2Cl_2 to give an octamercuric derivative. Mono- and diphosphine derivatives of bicymantrenyl react with mercury trifluoroacetate and with tin tetrachloride to give adducts at one or two manganese atoms.

Key words: bicymantrenyl, mercuration, mercury trifluoroacetate, tin tetrachloride, IR spectra.

In continuation of the study of bicymantrenyl (BCM, **1**) chemistry,[1—5] we investigated the reactions of compound **1** and its mono- and diphosphine derivatives with mercury trifluoroacetate $Hg(CF_3COO)_2$. Under the action of 8 moles of $Hg(CF_3COO)_2$ in CH_2Cl_2, BCM, similarly to cymantrene (CMT), undergoes mercuration of C—H bonds, and octa(trifluoroacetoxymercurio)bicymantrenyl (**2**) is the final product. Reactions of exhaustible mercuration of all C—H bonds of Cp rings under the action of mercury acetate or trifluoroacetate are known for CMT[6,7] and ferrocene and its derivatives.[8,9] Octamercurio derivative **2** enters standard reactions of C—Hg bond cleavage. For example, initial complex **1** is quantitatively recovered under the action of dilute HCl, and octaiodobicymantrenyl (**3**) is synthesized by treatment with iodine. When compound **2** is boiled with anhydrous $CuCl_2$ in acetone, mercury is replaced by chlorine; however, unlike the pentamercurio derivative of CMT, which gives pentachloro- or pentabromocymantrene in the reaction with $CuCl_2$ or $CuBr_2$,[7] in the case of BCM, a mixture of compounds consisting, according to the mass spectrometry data, mainly of hexa- and heptachlorobicymantrenyl with a minor amount of the octachloro derivative was isolated. Incomplete replacement of mercury by chlorine can be due to steric hindrances to substitution in α-positions 2 and 5 as compared with sterically nonhindered β-positions 3 and 4. We have previously shown[2—4] that both acylation and metallation of BCM occur predominantly in more accessible β-positions, and the ratio of products of β/α-substitution is (4—6) : 1.

We monitored the mercuration of BCM by IR spectroscopy in the ν(CO) vibration region (Table 1) and observed that at the initial stage, unstable intermediate **4** is formed in the reaction mixture (Scheme 1). It is characterized by frequencies ν(CO) 2015 (br) and 2070 cm^{-1} that are strongly shifted toward high wave numbers as compared to the spectrum of complex **1** ($\Delta\nu$ = 75 and 45 cm^{-1}, respectively). Two bands corresponding to intermediate **4** coincide with the absorption bands of a similar intermediate observed previously in the mercuration of CMT.[6] The position and shape of the bands indicate that in both cases, they belong to the $Mn(CO)_3$ fragments to which an acceptor group has attached. Intermediate **4** is the kinetically controlled product: it is rapidly formed, but is unstable in solution. Its bands are observed in the IR spectrum approximately 5—15 min after the beginning of the reaction, their intensity decreases, and after 1.5—2 h they completely disappear. The intensity of the bands that belong to the final product, octamercurio complex **2**, at 1720 ($O(C{=}O)CF_3$), 1960 (br), and 2037, 2045 (sh) cm^{-1} (ν(CO)) and to trifluoroacetic acid formed during mercuration (a doublet at 1790, 1810 cm^{-1}) increases simultaneously.

Unlike bicymantrenyl, its phosphine derivatives $(CO)_3MnC_5H_4C_5H_4Mn(CO)_2(PPh_3)$ (**5**) and $(PPh_3)(CO)_2MnC_5H_4C_5H_4Mn(CO)_2(PPh_3)$ (**6**) react with $Hg(CF_3COO)_2$ in a different manner. When 1 or 2 moles of $Hg(CF_3COO)_2$ acts on complexes **5** and **6** in CH_2Cl_2, mercury adds at one or both Mn atoms, and bonds of the Cp ring are not mercurated. No CF_3COOH is yielded during the reaction, and its bands are absent in the IR spectrum of the reaction mixture. Thermostable mono- or bis-adducts **7** and **8**, characterized by elemental analysis and containing one $Hg(CF_3COO)_2$ molecule per Mn atom, were isolated from the solution. Their characteristic feature is very easy cleavage with elimination of the $Hg(CF_3COO)_2$ molecule and formation of initial complexes **5** and **6** (identified by TLC and

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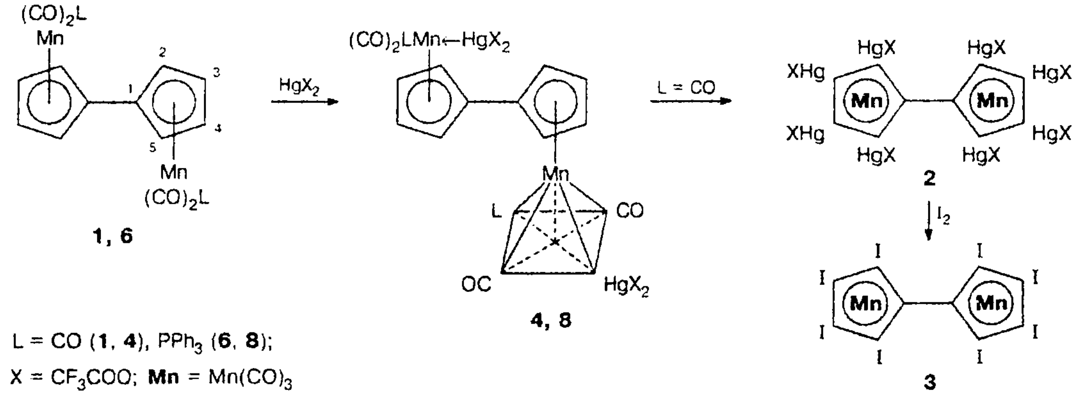
Scheme 1



L = CO (**1**, **4**), PPh_3 (**6**, **8**);
X = CF_3COO; **Mn** = Mn(CO)$_3$

Table 1. IR spectra (in CH_2Cl_2) of initial compounds, intermediates, and mercuration products

Compound	ν(CO)/cm^{-1} (Δν/cm^{-1})	Assignment
1	1940 br, 2025	Mn(CO)$_3$
2	1960 br, 2037, 2045 sh (20, 13)	Mn(CO)$_3$
3	1958 br, 2035, 2045 sh (18, 10)	Mn(CO)$_3$
4	2015 br, 2070 (75, 45)	Mn(CO)$_3$—Hg(OCOCF$_3$)$_2$
5	1870, —,*	Mn(CO)$_2$PPh$_3$
	1945 br, 2025	Mn(CO)$_3$
7	1998,**	Mn(CO)$_2$PPh$_3$—Hg(OCOCF$_3$)$_2$
	1960 br, 2030	Mn(CO)$_3$
5+SnCl$_4$	1960 br, 2038 (15, 13),	Mn(CO)$_3$
	1990, 2030 sh (120, 90*)	Mn(CO)$_2$PPh$_3$—SnCl$_n$
6	1870, 1935	Mn(CO)$_2$PPh$_3$
8	1965, 2008, 2030 sh (95, 73)	Mn(CO)$_2$PPh$_3$—Hg(OCOCF$_3$)$_2$
6+SnCl$_4$	1890, 1950 (20, 15),	Mn(CO)$_2$PPh$_3$
	1988, 2025 (118, 90)	Mn(CO)$_2$PPh$_3$—SnCl$_n$
6+HgCl$_2$	1985, 2020 (115, 85)	Mn(CO)$_2$PPh$_3$—HgCl$_2$
6+SnBr$_4$	1970 sh, 2020 (100, 85)	Mn(CO)$_2$PPh$_3$—SnBr$_4$

* The band of symmetrical vibration ν(CO) in Mn(CO)$_2$PPh$_3$ at ~1935—1940 cm^{-1} is disguised by the intense band at 1945 cm^{-1} that belongs to Mn(CO)$_3$.

** The band of antisymmetrical vibration ν(CO) in adduct **7** is disguised by the band that belongs to Mn(CO)$_3$.

spectral methods) under the action of acids (HCl, CF_3COOH) or upon dissolution in coordinating solvents (acetone, acetonitrile, DMSO, and others). This cleavage is precisely characteristic of donor-acceptor adducts of mercury salts with carbonyl complexes of metals containing metal—mercury bonds. Cleavage under the action of coordinating solvents is related to the fact that Hg^{II} form with them stable complexes with coordination through the oxygen or nitrogen atom.

To prove the structure of the reaction products, we used IR spectroscopy in the region of ν(CO) vibrations. This method is widely used in the chemistry of metal-carbonyl complexes, because ν(CO) bands are very intense and highly characteristic, and their position depends strongly on changes in the ligand environment of the metal.

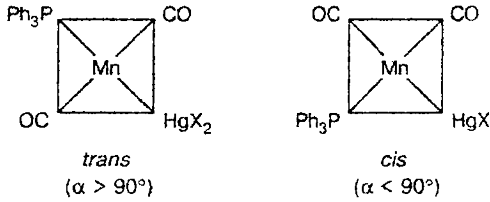
In diphosphine complex **6**, two Mn(CO)$_2$(PPh$_3$) fragments are equivalent, and four CO ligands give two absorption bands with equal intensities at 1870 and 1935 cm^{-1} (antisymmetrical and symmetrical vibrations, respectively, local symmetry C_s). It is known that the following correlation is fulfilled for the M(CO)$_2$ or M(CO)$_2$L fragments:

$$I_{as}/I_s = \tan^2(\alpha/2), \qquad (1)$$

where I_{as} and I_s are the intensities of bands of antisymmetrical and symmetrical vibrations of CO, respectively; and α is the OC—M—CO angle.[10,11] Equation (1) makes it possible to estimate the OC—M—CO angle from the experimentally measured ratio of intensities and draw conclusions about the structures of the complexes.

The equal intensities of both ν(CO) bands in the IR spectrum of complex **6** indicate that the OC—Mn—CO angle is close to 90°, as in almost all structurally characterized CMT derivatives. Upon coordination with $Hg(CF_3COO)_2$ and transformation of complex **6** into adduct **8**, the bands at 1870 and 1935 cm^{-1} disappear, and in the IR spectrum two new bands appear at 1965 and 2008 cm^{-1} (sh 2030 cm^{-1}), shifted toward high wave numbers by 95 and 73 cm^{-1}, respectively, and the band of the antisymmetrical vibration (1965 cm^{-1}) is 2.4 times more intense than the band of the symmetrical vibration (2008 cm^{-1}). The strong increase in the ν(CO) frequencies is related to the fact that an electron-acceptor group was attached to the metal atom, and the change in the ratio of intensities of the bands from 1 to 2.4 indicates that during transformation into adduct **8** the OC—Mn—CO angles increase from 90° to ~108—112°. When any ligand, for example, mercury salts HgX_2, is coordinated with the $M(CO)_2(PPh_3)$ fragment, two geometric isomers, *cis-* and *trans-*, can be formed on the metal atom (Scheme 2). In these isomers, the ratio of intensities of bands and OC—M—CO angles should be inverse (in the case of the *cis*-isomer, $\alpha < 90°$ and the band of symmetrical vibration is more intense; for the *trans*-isomer, $\alpha > 90°$ and the band of antisymmetrical vibration is more intense).

Scheme 2



It follows from the experimental data (decomposition of adducts **7** and **8** under the action of acids or coordinating solvents, change in the ratio of intensities) that in the reaction of diphosphine complex **6** with $Hg(CF_3COO)_2$, one $Hg(CF_3COO)_2$ molecule adds to each Mn atom, and only the *trans-trans*-isomer in which OC—Mn—CO angles should be >90° is formed. We have previously shown that the mononuclear complex $CpMn(CO)_2PPh_3$ easily adds one $Hg(CF_3COO)_2$ molecule to the Mn atom and gives the dimer $[Cp(CO)_2(PPh_3)Mn—Hg(OC(O)CF_3)_2]_2$, which was characterized structurally.[6] According to the X-ray diffraction data, the OC—Mn—CO angle in this complex is equal to 109.3°. Based on analogy in the IR spectra (the direction and shift of frequencies, the ratio of intensities), we may suggest that adduct **8** has a similar structure and is formed due to the addition of the strong Lewis acid $Hg(CF_3COO)_2$ at the metal atoms, which (in complexes of this type) are the centers with the highest basicity. In this reaction, complex **6** exhibits the properties of an organometallic Lewis base (the concept of basicity of transition metal complexes has been developed considerably in the eighties[12,13]).

The formation of *cis*-isomers during coordination of phosphine complexes with mercury salts is improbable because of steric hindrances: bulky PPh_3 and $Hg(CF_3COO)_2$ ligands in *cis*-isomers should be near each other, which creates steric hindrances. Monophosphine complex **5** adds only one $Hg(CF_3COO)_2$ molecule (at the $Mn(CO)_2PPh_3$ fragment in which the basicity of the Mn atom is higher than that in $Mn(CO)_3$) due to the donating PPh_3 ligand. However, in this case, the pattern in the IR spectrum is complicated because the bands of $Mn(CO)_2$ are partially disguised by more intense bands of $Mn(CO)_3$.

The results obtained suggest the following scheme of the reaction of BCM with $Hg(CF_3COO)_2$ (see Scheme 1). Most likely, when complexes **1** and **6** are treated with the aprotic acid $Hg(CF_3COO)_2$, at first mercury adds to the center with the highest basicity, the metal atom. However, the stability of the adducts formed differs sharply and depends on the ligand environment of Mn. In the case of complex **1**, which contains no donating ligands and in which the basicity of the Mn atom is low, intermediate **4** is formed. It is unstable and rapidly enters the secondary reaction of mercuration of Cp rings to yield CF_3COOH, and the final product is octamercurio derivative **2**. In the case of diphosphine complex **6** (and similarly, **5**), the attack of $Hg(CF_3COO)_2$ is also directed to the metal atom, and strong and stable adducts **8** (similarly to **7**) with Mn—Hg bonds are formed due to coordination. Their higher stability, as compared to that of intermediate **4**, is due to the higher basicity of the manganese atom because of the presence of phosphine ligands.

We also studied the reactions of BCM with tin tetrachloride by IR spectroscopy. Similarly to cymantrenyl, BCM does not react with $SnCl_4$. Phosphine complexes **5** and **6** react with $SnCl_4$ in CH_2Cl_2 with coordination of tin at the Mn atom in the $Mn(CO)_2PPh_3$ fragments, which results in a strong increase in the ν(CO) frequencies (by 90—110 cm^{-1}, *i.e.*, 20—30 cm^{-1} higher than for the coordination with $Hg(CF_3COO)_2$). The change in the ratio of intensities shows that only the *trans*-isomer is formed of two possible isomers in this case as well. The picture of changes in the IR spectra during the reactions of $SnCl_4$ with complexes **5** and **6** coincides completely with the previously studied[14] spectral changes for the reaction of $SnCl_4$ with the mononuclear complex $CpMn(CO)_2PPh_3$. However, in the reaction of diphosphine complex **6** with $SnCl_4$ even at an excess of the latter, only one Mn atom participates in the coordination with tin. When $SnCl_4$ is added to complex **6** in CH_2Cl_2, in the IR spectrum, the ν(CO) bands at 1870 and 1935 cm^{-1} disappear and four new bands appear. Two of them are strongly shifted toward high wave numbers ($\Delta\nu$ = 118 and 90 cm^{-1}), and the ratio of their intensities is ~2.5 : 1, which corresponds to an increase in the OC—Mn—CO angle in the adducts with tin from 90° to 112—116° due to the coordination of tin to the metal atom. Two other bands are shifted much more weakly ($\Delta\nu$ = 20 and 15 cm^{-1}) and correspond to the $Mn(CO)_2PPh_3$ fragment that is not coordinated with a tin atom. Based on the strong shift of frequencies in the IR spectra, we may assume that the products of coordination of complexes **5** and **6** with stannic chloride may have a ionic structure similar to that of the salt-like complex$[Cp(CO)_2PPh_3Mn—SnCl_3]^+SnCl_5^-$, whose structure was solved by X-ray diffraction.[14] The absence of coordination of tin at the second Mn atom is related, most likely, to the presence of the positive charge that prevents electrophilic attack at another metal atom. During hydrolysis or dissolution in acetone, adducts with tin chloride are instantly cleaved to give initial compounds **5**, **6** and hydrolysis products of $SnCl_4$.

Diphosphine complex **6** forms adducts at the metal atom and with weaker aprotic acids $Hg(OAc)_2$, $HgCl_2$, and $SnBr_4$; however, in these cases, the intensity of ν(CO) bands corresponding to the coordination products in the IR spectrum is low, and the equilibrium in the solution is shifted toward the initial complex.

Experimental

Initial BCM and its phosphine derivatives were prepared by the previously described procedure.[15] Experiments were carried out in an inert atmosphere.

Octa(trifluoroacetoxymercurio)bicymantrenyl (2). $Hg(CF_3COO)_2$ (0.86 g, 2 mmol) was added by portions with vigorous stirring to a solution of compound **1** (0.10 g, 0.25 mmol) in anhydrous CH_2Cl_2 (30 mL). The solution gained an intense orange color, and the IR spectrum exhibited bands of complex **2** and intermediate **4** and ν(CO) bands of CF_3COOH that formed (doublet at 1790, 1810 cm^{-1}). The solution was stirred for 2 h and left to stand overnight. The color of the solution changed to yellow, and in the IR spectrum the bands of intermediate **4** disappeared, but the bands of complex **2** and CF_3COOH remained. The solution was filtered, and CH_2Cl_2 was removed *in vacuo*. The yield was 96% (0.70 g). Complex **2** is a yellow-orange powder, stable in air, with a temperature of decomposition >120 °C (without melting). Found (%): C, 13.48; H, 0; Hg, 55.40; Mn, 3.48; F, 16.62. $C_{32}F_{24}Hg_8Mn_2O_{22}$. Calculated (%): C, 13.22; H, 0; Hg, 55.20; Mn, 3.78; F, 15.69. When the reaction is carried out at the ratio $Hg(CF_3COO)_2$: BCM = 1 : 1, inseparable mixtures of mono- and polymercury derivatives are formed.

Octaiodobicymantrenyl (3). Complex **2** (0.50 g, 0.17 mmol) was added gradually to a solution of iodine (0.38 g, 1.49 mmol) and NaI (0.57 g, 3 mmol) in water (40 mL). After stirring for 6 h, the precipitate was filtered off, and the aqueous layer was extracted with CH_2Cl_2. The extract was concentrated and added to the precipitate. The resulting solution was chromatographed on a column with Al_2O_3 using a toluene—heptane mixture as an eluent. Complex **3** (0.15 g, 75%) was yielded as a pale yellow powder stable in air with decomp. temperature >100 °C. Found (%): C, 15.27; H, 0; Mn, 7.39. $C_{16}I_8Mn_2O_6$. Calculated (%): C, 15.28; H, 0; Mn, 7.78. An attempt at direct determination of iodine did not give correct data.

Reaction of complex 2 with $CuCl_2$. A solution of complex **2** (0.8 g, 0.275 mmol) in acetone (8 mL) was added dropwise with stirring to a solution of anhydrous $CuCl_2$ (1.86 g, 13.78 mmol) in acetone (40 mL). The mixture was refluxed for 3.5 h, then the precipitate of CuCl (0.48 g) that formed was filtered off, and acetone was removed *in vacuo*. The residue was washed with 10% HCl (3×20 mL) and water, dissolved in CH_2Cl_2, and dried, and the solvent was removed. To separate a minor amount of products of acetone chlorination, the residue was chromatographed on Al_2O_3, using a benzene—heptane (1 : 2) mixture as an eluent. After removal of the solvent and recrystallization from hexane, light-yellow needle-like crystals, which are well soluble in hexane, were obtained (IR (CH_2Cl_2), ν(CO): 1968 br, 2038, 2044 sh). According to the data of elemental analysis and mass spectrometry, the crystals are a mixture of compounds with six and seven Cl atoms, $C_{10}H_2Cl_6Mn_2(CO)_6$ and $C_{10}HCl_7Mn_2(CO)_6$, containing only traces of the $C_{10}Cl_8Mn_2(CO)_6$ complex. The mass spectrum exhibits peaks of molecular ions with *m/z* 683, 681, 679, 677 (for the complex $C_{10}Cl_8Mn_2(CO)_6$), sets of 9—10 peaks of molecular ions with *m/z* 654—644 (for $C_{10}HCl_7Mn_2(CO)_6$) and 620—610 (for $C_{10}H_2Cl_6Mn_2(CO)_6$), and similar sets of the corresponding peaks of fragmentation ions [M − 3 CO] and [M − 6 CO]. The distribution of intensities of individual peaks in sets of molecular ions coincides with that calculated for the molecules indicated containing 6 and 7 Cl atoms. Found (%): C, 30.16; H, <0.3; Cl, 36.45. Calculated for $C_{16}H_2Cl_6Mn_2O_6$ (%): C, 31.32; H, 0.33; Cl, 34.75. Calculated for $C_{16}HCl_7Mn_2O_6$ (%): C, 29.65; H, 0.15; Cl, 38.38. An increase in the duration of boiling or in the amount of $CuCl_2$ did not result in the preparation of the pure octa-substituted product.

η^5,η^5-Fulvalenylpentacarbonyltriphenylphosphinedimanganesemercury trifluoroacetate (7). Mercury trifluoroacetate (0.068 g, 0.16 mmol) was added by several portions with vigorous stirring to a solution of monophosphine complex **5** (0.10 g, 0.16 mmol) in CH_2Cl_2. After a yellow precipitate was formed, the mother liquor was decanted, and the residue was washed with CH_2Cl_2 and dried *in vacuo*. Compound **7** was obtained (0.12 g, 72%) as a bright yellow powder stable in air. Found (%): C, 41.19; H, 2.26; Hg, 19.0. $C_{37}H_{23}F_6HgMn_2O_9$. Calculated (%): C, 41.65; H, 2.17; Hg, 18.8.

η^5,η^5-Fulvalenyltetracarbonylbis(triphenylphosphine)dimanganesebis(mercury trifluoroacetate) (8). Similarly to the synthesis of complex **7**, compound **8** (110 mg, 56%) as a bright yellow powder stable in air was obtained from diphosphine complex **6** (0.096 g, 0.11 mmol) and mercury trifluoroacetate (0.094 g, 0.22 mmol). Found (%): C, 39.87; H, 2.39; Hg, 23.10. $C_{58}H_{38}F_{12}Hg_2Mn_2O_{12}$. Calculated (%): C, 40.32; H, 2.22; Hg, 23.22. Complexes **7** and **8** are virtually insoluble in hexane and benzene. Attempts to dissolve them in acetone and other solvents capable of coordination resulted in their immediate cleavage to yield starting compounds **5** and **6**, which were identified by TLC and IR and mass spectrometry.

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