

## $\pi$ -COMPLEXES AS LIGANDS IN TRANSITION METAL COMPOUNDS

### II \*. BIS-( $\pi$ -PYRROLYLTRICARBONYLMANGANESE)- TRICARBONYLMANGANESE HALIDES

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#### Summary

The trinuclear complexes, bis-( $\pi$ -pyrrolyltricarbonylmanganese)tricarbonyl-halomanganese (halo = I, Br) have been obtained. They comprise two molecules of  $\pi$ -pyrrolyltricarbonylmanganese acting as *N*-ligands at the central manganese atom due to the formation of donor—acceptor Mn—N bonds.

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#### Introduction

Recently we have found that the nitrogen atom in  $\pi$ -pyrrolyltricarbonylmanganese (PTM) is capable of forming a donor—acceptor bond with a transition metal [1]. This property was employed to synthesize binuclear complexes of a new type, wherein the pyrrolyl ring fulfils simultaneously two functions, acting as a  $\pi$ -ligand to a manganese atom and as an *N*-ligand to another metal [2]. These complexes were obtained by substituting a CO-ligand at a particular metal by PTM through intermediate formation of a tetrahydrofuran derivative. Continuing the investigation in this direction, we attempted to replace a CO ligand by PTM in  $\pi$ -cyclopentadienyldicarbonyliodoiron,  $\text{CpFe}(\text{CO})_2\text{I}$ , using the same technique. However, instead of the expected iron complex  $\text{CpFe}(\text{CO})-\text{I}(\text{PTM})$  we isolated an iron-free trinuclear complex I (Scheme 1), the structure of which was unambiguously established by an X-ray diffraction analysis.

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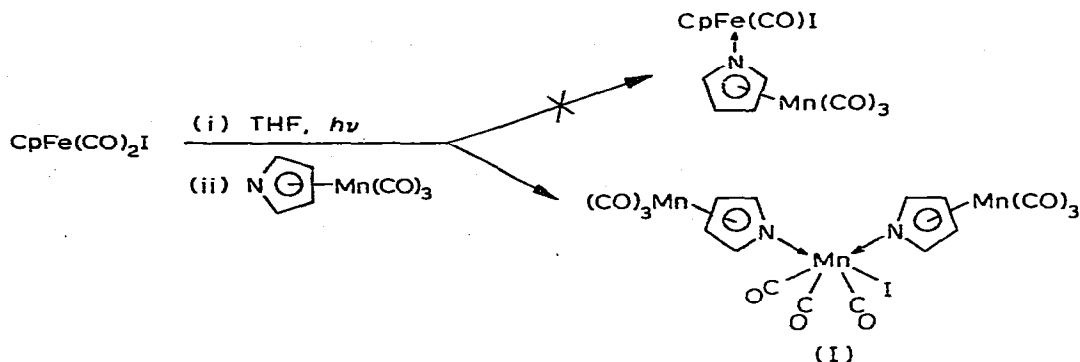
\* Part I, see reference 2.

TABLE 1

ATOMIC COORDINATES ( $\times 10^5$  FOR I AND X  $10^4$  FOR OTHER ATOMS) AND PARAMETERS OF ANISOTROPIC TEMPERATURE FACTORS ( $\times 10^2$ )<sup>a</sup>

Atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
I	2422(7)	13486(5)	21728(6)	502(4)	272(4)	447(4)	45(3)	83(3)	-80(3)
Mn(1)	-3387(2)	3894(1)	1895(1)	338(8)	306(8)	220(7)	28(6)	49(6)	-21(6)
Mn(2)	-673(2)	2386(1)	3405(1)	391(8)	241(7)	240(7)	-8(6)	50(6)	20(6)
Mn(3)	2803(2)	3199(1)	4948(1)	320(8)	276(7)	289(7)	33(6)	60(6)	7(6)
N(1)	-1608(7)	3145(6)	2142(6)	258(38)	259(41)	282(40)	8(30)	63(32)	4(32)
N(2)	846(7)	3294(6)	3589(6)	256(38)	273(38)	234(38)	29(31)	21(33)	2(33)
O(1)	-674(7)	4671(7)	796(7)	550(32)	876(36)	585(50)	324(48)	43(44)	69(49)
O(2)	-4594(9)	2678(9)	2962(8)	659(59)	902(71)	760(63)	-142(51)	391(50)	143(54)
O(3)	-3147(11)	5224(7)	3431(7)	1192(81)	568(54)	525(48)	25(51)	244(52)	-306(46)
O(4)	-2700(10)	1055(6)	3117(7)	753(57)	382(44)	726(59)	-181(41)	323(48)	-101(40)
O(5)	-1879(8)	3432(9)	4850(8)	678(51)	525(46)	304(40)	98(39)	252(38)	-41(39)
O(6)	634(10)	1242(9)	5994(8)	814(62)	610(54)	582(54)	151(45)	-25(49)	356(47)
O(7)	3636(8)	1481(6)	3743(7)	667(52)	301(38)	710(56)	139(38)	281(44)	-28(38)
O(8)	5414(9)	3936(9)	5139(9)	364(48)	670(60)	1035(76)	-111(42)	-5(48)	22(50)
O(9)	2923(9)	2423(8)	6299(7)	770(60)	1004(75)	324(45)	135(50)	182(42)	207(47)
C(1)	-4784(12)	4353(8)	1218(9)	476(65)	467(65)	361(59)	40(56)	124(52)	-39(51)
C(2)	4122(11)	3141(9)	2527(9)	361(59)	569(74)	380(62)	89(52)	116(52)	61(54)
C(3)	-3210(13)	4690(9)	2845(9)	711(82)	474(70)	355(62)	47(59)	125(59)	6(58)
C(4)	-1928(12)	1600(8)	3199(9)	511(65)	345(55)	375(58)	-18(53)	139(51)	-7(47)
C(5)	-1392(11)	3048(9)	4194(9)	416(59)	321(52)	287(54)	-15(45)	65(47)	119(46)
C(6)	164(12)	1696(9)	4448(10)	549(70)	387(58)	435(66)	-30(54)	68(56)	-33(56)
C(7)	3339(10)	2123(8)	3966(8)	390(59)	363(59)	306(55)	16(47)	163(46)	54(50)
C(8)	4386(13)	3580(9)	4825(10)	541(76)	332(57)	537(71)	124(56)	152(59)	98(53)
C(9)	2875(10)	2725(8)	5551(9)	368(58)	394(59)	345(62)	6(45)	29(48)	-13(52)
C(10)	-1421(10)	4011(7)	1921(8)	318(50)	178(42)	420(57)	16(38)	57(44)	101(42)
C(11)	-2171(10)	4224(8)	963(8)	436(59)	342(54)	323(54)	83(47)	143(46)	118(48)
C(12)	-2842(11)	3489(8)	593(8)	428(57)	378(56)	227(49)	139(48)	53(42)	-44(45)
C(13)	-2477(10)	2803(7)	1308(8)	357(53)	308(50)	276(51)	7(41)	64(44)	-117(45)
C(14)	1176(10)	3954(7)	4322(8)	319(52)	382(54)	264(50)	46(43)	37(42)	-112(44)
C(15)	2061(10)	4540(7)	4116(9)	403(59)	230(48)	443(61)	34(44)	46(46)	20(44)
C(16)	2291(10)	4226(7)	3226(9)	428(59)	248(50)	460(62)	12(44)	144(49)	169(47)
C(17)	1536(10)	3463(7)	2940(8)	358(51)	240(48)	274(49)	14(40)	84(42)	-32(39)

<sup>a</sup> The temperature factor is in the form  $T = \exp[-1/4(B_{11}h^2 + \dots + 2B_{23}hk + \dots)]$ .



SCHEME 1

## Results and discussion

### Crystal structure of complex I

The molecular structure of I is shown in Fig. 1, atomic coordinates and temperature factors are given in Table 1 and bond angles in Table 2.

Crystals of I are monoclinic,  $a$  11.040(2),  $b$  14.960(2),  $c$  14.028(2) Å,  $\beta$  106.15(1)°,  $V$  2225.4(9) Å<sup>3</sup>,  $M = 675.99$ ,  $d_{\text{calc}}$  2.017 g/cm<sup>3</sup> for  $Z = 4$ , space group  $P2_1/c$ .

In the complex two molecules of ( $\eta^5\text{-C}_4\text{H}_4\text{N}$ )Mn(CO)<sub>3</sub> act as  $N$ -ligands at the third (central) Mn atom forming donor-acceptor Mn-N bonds. In addition, the central Mn atom is coordinated with the iodine atom and three CO groups, i.e. has an octahedral coordination. As a result, all three Mn atoms acquire a closed 18-electron configuration of an inert gas. As mentioned previously, the

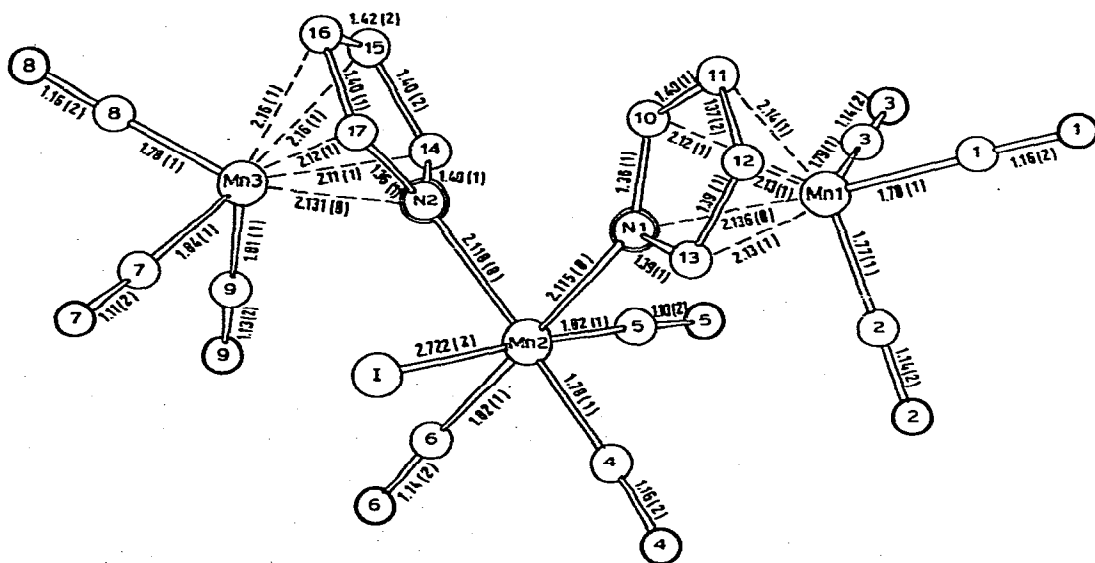


Fig. 1. Structure of complex I.

TABLE 2  
 BOND ANGLES,  $\omega$  ( $^\circ$ )

Angle	$\omega$	Angle	$\omega$	Angle	$\omega$
C(1)Mn(1)C(2)	91.8(6)	C(4)Mn(2)C(5)	90.5(6)	N(1)C(10)C(11)	110.4(9)
C(1)Mn(1)C(3)	88.9(6)	C(4)Mn(2)C(6)	87.3(6)	C(10)C(11)C(12)	106.7(1.0)
C(2)Mn(1)C(3)	89.8(6)	C(5)Mn(2)C(6)	91.7(6)	C(11)C(12)C(13)	107.4(1.0)
IMn(2)N(1)	87.5(2)	C(7)Mn(3)C(8)	91.6(6)	C(12)C(13)N(1)	109.7(9)
IMn(2)N(2)	91.3(2)	C(7)Mn(3)C(9)	89.7(5)	C(13)N(1)C(10)	105.8(8)
IMn(2)C(4)	85.8(4)	C(8)Mn(3)C(9)	89.4(5)	Mn(2)N(1)C(10)	129.2(7)
IMn(2)C(5)	176.1(4)	Mn(1)C(1)O(1)	177.7(1.2)	Mn(2)N(1)C(13)	124.7(6)
IMn(2)C(6)	89.5(4)	Mn(1)C(2)O(2)	177.7(1.2)	N(2)C(14)C(15)	110.1(9)
N(1)Mn(2)N(2)	86.7(3)	Mn(1)C(3)O(3)	178.5(1.2)	C(14)C(15)C(16)	106.2(1.0)
N(1)Mn(2)C(4)	92.5(5)	Mn(2)C(4)O(4)	175.6(1.1)	C(15)C(16)C(17)	106.4(1.0)
N(1)Mn(2)C(5)	91.4(4)	Mn(2)C(5)O(5)	176.8(1.1)	C(16)C(17)N(2)	111.0(9)
N(1)Mn(2)C(6)	176.9(5)	Mn(2)C(6)O(6)	176.6(1.2)	C(17)N(2)C(14)	106.3(8)
N(2)Mn(2)C(4)	177.1(5)	Mn(3)C(7)O(7)	178.6(1.1)	Mn(2)N(2)C(14)	125.3(7)
N(2)Mn(2)C(5)	92.3(4)	Mn(3)C(8)O(8)	179.4(1.2)	Mn(2)N(2)C(17)	127.5(7)
N(2)Mn(2)C(6)	93.3(5)	Mn(3)C(9)O(9)	179.4(1.1)		

molecule ( $\eta^5\text{-C}_4\text{H}_4\text{N}$ )Mn(CO)<sub>3</sub> fulfils a similar function in the previously studied binuclear complexes [( $\eta^5\text{-C}_4\text{H}_4\text{N}$ )Mn(CO)<sub>3</sub>][C<sub>4</sub>H<sub>3</sub>NCOCH<sub>3</sub>]Mn(CO)<sub>3</sub> (II) [1] and [( $\eta^5\text{-C}_4\text{H}_4\text{N}$ )Mn(CO)<sub>3</sub>][ $\eta^5\text{-C}_5\text{H}_5$ ]Re(CO)<sub>2</sub> (III) [2], wherein an unshared electron pair of the N atom participates in coordination bonds with a Mn and a Re atom, respectively. As in the complex II, distances between Mn atoms (Mn(2)—Mn(1) 3.816(2), Mn(2)—Mn(3) 3.890(2) Å) in the complex I substantially exceed the doubled covalent Mn radius (2.76 Å [3]) and do not, therefore, correspond to a metal—metal bond (the Mn—Mn distance in the molecule II is 3.840 Å). The ligand environment of atoms Mn(1) and Mn(3) corresponds to the classic “piano stool” configuration with a practically undistorted C<sub>3v</sub> symmetry of the Mn(CO)<sub>3</sub> fragments (C—Mn—C bond angles ranging from 88.9 to 91.8°). The C and N atoms of the pyrrolyl ligands are equally bonded to the metal atoms, as evidenced by an equivalence of the average Mn—C (2.13(1) Å) and Mn—N (2.134(8) Å) distances, which are comparable to those found in complexes II and III and tricarbonyl(2-methylindolyl)manganese [4] (Mn—C, 2.144, 2.18, 2.16; Mn—N, 2.120, 2.16, 2.16 Å respectively). The pyrrolyl ligands are planar and form a dihedral angle of 119.9° with one another; however, the Mn(2) atom is not precisely in the planes of the cycles since the bonds Mn(2)—N(1) and Mn(2)—N(2) are tilted by 3.6 and 9.3° with respect to the planes of corresponding pyrrolyl ligands (in structures II and III angles between Mn—N and Re—N vectors and cyclic ligands are 7.9 and 6.7°).

No alternation is observed in the distribution of C—C and C—N bond lengths in both heterocycles, indicating a delocalization of  $\pi$ -electrons around all the cyclic system. Average values of bond lengths in the cycles (C—C, 1.40(1); C—N, 1.38(1) Å) agree satisfactorily with those found in II (C—C, 1.399; C—N, 1.388 Å) and III (C—C, 1.42; C—N, 1.41 Å).

As already noted, the Mn(2) atom has a slightly distorted *fac*-octahedral coordination, the Mn—N bond lengths are practically equal (av. 2.116(8) Å) and within accuracy limits do not differ from the Mn—N distance of 2.140 Å in

the molecule II; the Mn—I distance of 2.722(2) Å coincides with the sum of covalent radii of Mn (1.38 Å [3]) and I (1.33 Å [5]). The metal—carbonyl group has a usual geometry with normal lengths of Mn—C (av. 1.80(1) Å) and C—O (1.14(2) Å) bonds.

#### *Physicochemical characteristics of complex I*

The trinuclear complex I forms as brilliant orange-red needles, decomposing at 140°C, and is readily soluble in acetone and chlorine-containing solvents (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>), poorly soluble in benzene and insoluble in hexane. I is stable in the solid state, but gradually decomposes in solutions; it decomposes completely when chromatographed on alumina.

In the IR spectrum of I in CH<sub>2</sub>Cl<sub>2</sub> there are seven absorption bands in the carbonyl group vibration range at 1912m, 1945s, 1970vs, 1980vs, 2028s, 2050vs and 2058s cm<sup>-1</sup> (bands at 1970 and 1980 cm<sup>-1</sup> are poorly resolved). Bands at 1912, 1945 and 2028 cm<sup>-1</sup> we attribute to the CO group vibrations of the Mn(CO)<sub>3</sub>I fragment on the basis of the similarity of these bands with carbonyl bands of the known *fac*-derivatives of pentacarbonyliodomanganese, Mn(CO)<sub>3</sub>IL<sub>2</sub> (L = PPh<sub>3</sub>, AsPh<sub>3</sub>, Py, Dipy) [6] \*. The remaining four bands in the IR spectrum of I (1970, 1980, 2050 and 2058 cm<sup>-1</sup>) correspond to CO group vibrations of two PTM fragments coordinated with the central manganese atom. It is to be noted that an almost identical position of carbonyl absorption bands in the IR spectra of the Mn(CO)<sub>3</sub>I fragment of the complex I and compounds Mn(CO)<sub>3</sub>IL<sub>2</sub> (L = Py, 1906, 1954 and 2037 cm<sup>-1</sup>; L = PPh<sub>3</sub>, 1915, 1955 and 2042 cm<sup>-1</sup>; CHCl<sub>3</sub> [6]) point to a fairly similar donor ability of PTM, Py and PPh<sub>3</sub> ligands. PTM also shows its high donor strength in the complex III, where a substitution of the CO ligand by PTM leads to a shift in the absorption bands of the remaining CO groups by 80 cm<sup>-1</sup> towards the low-frequency region [2].

The PMR spectrum of complex I in acetone-*d*<sub>6</sub> shows three signals with chemical shifts of δ 5.73, 6.74 and 7.18 ppm and a ratio of integral intensities of 2/1/1 respectively. It was natural to assume that two signals of equal intensities refer to α-protons of the two pyrrolyl rings, and that the signal of double intensity to β-protons (according to [7], in PTM the signal at higher field position is due to the β-protons). However the presence of two signals for the α-protons can be due to either of two possible alternatives: i) α-protons of one pyrrolyl ring are not equivalent to α-protons of another ring or ii) α-protons of each of the rings are not mutually equivalent, but are equivalent in pairs. The selection and the explanation of one of the possible alternative requires a reconsideration of the structure of complex I (Fig. 1).

It is of interest to note that although the iodine atom is disposed symmetrically with respect to atoms of nitrogen, I...C distances to α-carbon atoms of the cycles differ greatly: though atoms C(13) and C(17) show the shortened intramolecular contacts I...C(13) of 3.64(1) Å and I...C(17) of 3.52(1) Å, the distances I...C(10) and I...C(14) exceed 4 Å. Thus it is clear that the α-protons of each of the pyrrolyl rings are not equivalent one to another, but are equivalent

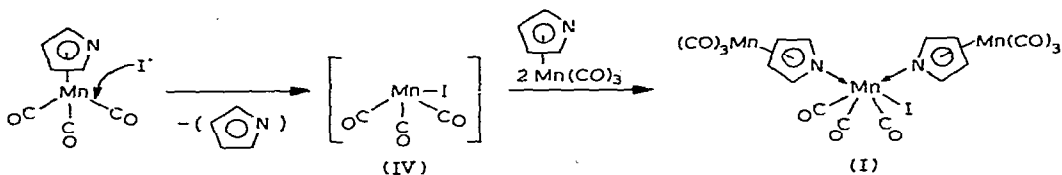
\* As well as compounds Mn(CO)<sub>3</sub>IL<sub>2</sub> [6], complex I was obtained by us also by a direct interaction between PTM and Mn(CO)<sub>3</sub>I.

in pairs, this resulting from a difference in shielding by the iodine atom ( $\Delta\delta = 0.44$  ppm).

### Mechanism of formation of complex I

The formation of a trinuclear complex I instead of the expected  $\text{CpFe}(\text{CO})-(\text{PTM})\text{I}$  (Scheme 1) is rather surprising\* and requires special consideration. An analysis of such an unusual course of this reaction led us to the conclusion that an atomic iodine resulting from UV-irradiation of  $\text{CpFe}(\text{CO})_2\text{I}$  in THF solution is responsible. However, this assumption required experimental checking. To this end, we investigated the interaction of PTM with other iodine-containing complexes of transition metals,  $\text{CpMo}(\text{CO})_3\text{I}$  and  $\text{CpMo}(\text{CO})_2(\text{SbPh}_3)\text{I}$ , and with iodine solutions. These reactions, conducted under conditions similar to the interaction of PTM with the iron complex (Scheme 1), produced the trinuclear complex I. Moreover complex I is also formed by an interaction of PTM with iodine or  $\text{CpFe}(\text{CO})_2\text{I}$ , initiated, not only by an UV-irradiation, but also thermally (refluxing in benzene).

This proved the participation of an iodine atom in the formation of the complex I from PTM\*\*. On the basis of experimental data mentioned above, we suggest a following general scheme of formation of the trinuclear complex I (Scheme 2):



SCHEME 2

The first stage of this reaction is attack of atomic iodine on the PTM molecule at the manganese atom resulting in breaking-off of the  $\pi$ -pyrrolyl ligand and in formation of the coordinatively unsaturated 14-electron intermediate IV. The intermediate IV completes its electron shell to an 18-electron configuration by coordination with two PTM molecules (second stage), thus leading to complex I.

In conclusion, it is to be noted that the above interaction of PTM with iodine has probably a general character for other halogens as well. This is substantial by the formation of a bromide analog of complex I,  $(\text{PTM})_2\text{Mn}(\text{CO})_3\text{Br}$  (V), obtained by interaction of PTM with bromine.

\* It is known from the literature that interaction of  $\text{CpFe}(\text{CO})_2\text{I}$  with two-electron ligands (for example, phosphines and phosphites) usually leads to a substitution of a CO ligand or halogen [8-11]. The process can be initiated both by an UV irradiation and by heating.

\*\* As the present work was being carried out, Alway and Barnett published a paper on the photochemistry of cyclopentadienyldicarbonylhaloiron complexes [12], where the authors conclude that "rupture of the Fe-Hal bond is not an important path of excited-state decay". However, as our experimental data tend to indicate, the formation of the complex I from PTM cannot be explained without the participation of atomic iodine, the more so that the homolysis of the M-I bond occurs, probably, not in the initial complexes ( $\text{CpFe}(\text{CO})_2\text{I}$ ,  $\text{CpMo}(\text{CO})_3\text{I}$ ,  $\text{CpMo}(\text{CO})_2(\text{SbPh}_3)\text{I}$ ), but in the products of the substitution therein of CO groups by THF or PTM.

## Experimental

All the operations involved in the synthesis and the separation of I were carried out in argon. Solvents were thoroughly dried and distilled in a stream of argon prior to use.

PTM,  $\text{CpFe}(\text{CO})_2\text{I}$ ,  $\text{CpMo}(\text{CO})_3\text{I}$ ,  $\text{CpMo}(\text{CO})_2(\text{SbPh}_3)\text{I}$  and  $\text{Mn}(\text{CO})_5\text{I}$  were prepared using known procedures [13–17].

The X-ray diffraction study was performed (2130 reflections with  $I \geq 2\sigma$ ) with an automatic 4-circle diffractometer Synthex P2<sub>1</sub> ( $\lambda$  Mo- $K_\alpha$ , graphite monochromator,  $\theta/2\theta$  scan,  $2\theta_{\text{max}} 45^\circ$ ), absorption not allowed for ( $\mu(\text{Mo-}K_\alpha)$  32.2  $\text{cm}^{-1}$ ). The structure was solved by the standard heavy atom method and refined by the method of least squares in a full-matrix anisotropic approximation,  $R$  0.058,  $R_w$  0.064; H atoms, the positions of which were calculated geometrically, were included in the refinement with fixed positional and temperature ( $B_{\text{iso}}$  5.0  $\text{\AA}^2$ ) parameters.

IR spectra were recorded on a UR-20 spectrophotometer and PMR spectra were recorded on a Perkin-Elmer R 20 (60 MHz) spectrometer.

### 1. Interaction of PTM with $\text{CpFe}(\text{CO})_2\text{I}$

*a) Under UV-irradiation.* 0.3 g (0.99 mmol) of  $\text{CpFe}(\text{CO})_2\text{I}$  in 25 ml of THF was UV irradiated (quartz lamp, 220 W) for 2 hours at  $+5^\circ\text{C}$ . 0.2 g (0.98 mmol) of PTM in 10 ml THF was admixed under stirring to the resultant solution. The reaction mixture was left at  $+5^\circ\text{C}$  for another 4 hours and then left overnight at room temperature. The solvent was removed in a stream of argon. A dark-brown precipitate was washed 3 times with cold hexane (to remove unreacted PTM and partly  $\text{CpFe}(\text{CO})_2\text{I}$ ) and dried in vacuo. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , an equal volume of hexane was added, and the solution was filtered. The solvent was slowly removed in vacuo without heating until crystallization started. A rapid cooling ( $-78^\circ\text{C}$ ) led to sedimentation of a red-brown precipitate, which was filtered off and recrystallized from a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  at room temperature. The yield of I was 0.08 g (36% with respect to PTM). Elemental analysis. Found: C, 30.14; H, 1.26; N, 4.06; I, 18.63.  $\text{C}_{17}\text{H}_8\text{N}_2\text{O}_9\text{Mn}_3\text{I}$  Calcd.: C, 30.20; H, 1.19; N, 4.14; I, 18.77%.

0.14 g (~50%) of unreacted  $\text{CpFe}(\text{CO})_2\text{I}$  were precipitated from the mother solution.

All the subsequent photochemical reactions and isolation of the complex I were carried out as under the item 1a. In all reactions described yields of the complex I were not optimized.

*b) Under heating.* A mixture of 0.2 g (0.98 mmol) of PTM and 0.2 g (0.65 mmol) of  $\text{CpFe}(\text{CO})_2\text{I}$  in 25 ml benzene was refluxed for 16 hours: 0.03 g (14%) of complex I was isolated.

### 2. Interaction of PTM with $\text{CpMo}(\text{CO})_3\text{I}$ under UV-irradiation

0.1 g (0.27 mmol) of  $\text{CpMo}(\text{CO})_3\text{I}$  in 15 ml of THF was UV-irradiated for 3 hours. 0.1 g (0.49 mmol) of PTM was added in 10 ml of THF. 0.02 g (18%) of complex I was obtained.

### 3. Interaction of PTM with $\text{CpMo}(\text{CO})_2(\text{SbPh}_3)\text{I}$ under UV-irradiation

0.3 g (0.43 mmol) of  $\text{CpMo}(\text{CO})_2(\text{SbPh}_3)\text{I}$  in 35 ml of THF was UV irradi-

ated for 3 hours. 0.1 g (0.49 mmol) of PTM in 10 ml of THF was added. 0.02 g (18%) of complex I was obtained.

#### 4. Interaction of PTM with I<sub>2</sub>

*a) Under UV-irradiation.* 0.09 g (0.35 mmol) of I<sub>2</sub> in 15 ml of THF was UV irradiated for 2.5 hours. 0.15 g (0.73 mmol) of PTM in 10 ml of THF was added. 0.05 g (31%) of complex I was isolated.

*b) Under heating.* A mixture of 0.1 g (0.49 mmol) of PTM and 0.06 g (0.24 mmol) of I<sub>2</sub> in 20 ml of benzene was refluxed for 1 hour. 0.05 g (45%) of complex I was obtained.

#### 5. Interaction of PTM with Mn(CO)<sub>5</sub>I

A mixture of 0.38 g (1.86 mmol) of PTM and 0.3 g (0.93 mmol) of Mn(CO)<sub>5</sub>I in 25 ml of n-octane was refluxed for 30 min, resulting in a yellow precipitate. The latter was filtered off and recrystallized from a mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub>. 0.18 g (29%) of complex I was isolated. Unreacted PTM and Mn(CO)<sub>5</sub>I were precipitated from the mother solution.

#### 6. Interaction of PTM with Br<sub>2</sub>

Two drops of Br<sub>2</sub> were added to 0.29 g (1.41 mmol) of PTM in 10 ml of CCl<sub>4</sub> under stirring and cooling with ice to give a green-yellowish precipitate. The latter was filtered off and recrystallized from a mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub>. 0.12 g (40%) of brilliant yellow crystals of the complex V was isolated. Its decomposition point was ~165°C. Elemental analysis. Found: C, 32.44; H, 1.07; N, 4.37; Mn, 26.56; Br, 13.30. C<sub>17</sub>H<sub>8</sub>N<sub>2</sub>O<sub>9</sub>Mn<sub>3</sub>Br Calcd.: C, 32.43; H, 1.27; N, 4.45; Mn, 26.23; Br, 12.71%.

IR-spectrum (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 1912m, 1948vs, 1967vs, 1981vs, 2031s, 2050vs, 2058s.

PMR-spectrum (acetone-d<sub>6</sub>): δ 5.80 (2H); 6.84 (1H); 7.13 (1H) ppm.

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