Journal of Organometallic Chemistry, 157 (1978) 431—436

π-COMPLEXES AS LIGANDS IN TRANSITION METAL COMPOUNDS

I. π-PYRROLYLTRICARBONYLMANGANESE, A NEW TWO-ELECTRON LIGAND

N.I. PYSHNOGRAEVA, V.N. SETKINA *, V.G. ANDRIANOV, Yu.T. STRUCHKOV and D.N. KURSANOV

Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow (U.S.S.R.)

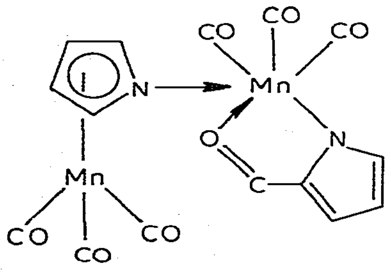
(Received April 3rd, 1978)

Summary

It has been established that the nitrogen atom in π-pyrrolyltricarbonylmanganese can form a donor—acceptor bond with transition metals. This property was used to synthesize novel binuclear complexes in which a pyrrolyl ring performs two functions: a π-ligand to the manganese atom and an *n*-ligand to another metal.

Introduction

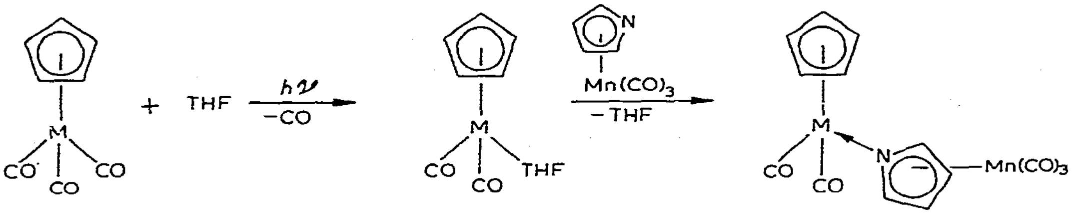
Recently, while studying acylation of pyrrolyltricarbonylmanganese (PTM) we showed [1] that the acylation process is accompanied by extensive rearrangement of bonds in the molecule, resulting in formation of a binuclear complex (I). It is interesting that in this compound the molecule of the initial PTM acts as a two-electron ligand. The capacity of the nitrogen atom in the pyrrolyl ring π-bonded to the manganese atom to coordinate with another transition metal has not been previously reported. This stimulated us to study in greater detail the coordination of PTM with transition metals.



(I)

Results and discussion

For the present study we chose π-cyclopentadienyltricarbonyl complexes of rhenium (CTR) and manganese (CTM), since methods of substituting CO ligands with other two-electron ligands are already sufficiently well developed for these compounds [2,3]. By photochemical replacement of a CO ligand with tetrahydrofuran [3—5] and subsequent interaction of PTM with the tetrahydrofuran complex we were able to obtain π-cyclopentadienyldicarbonyl complexes of rhenium (II) and manganese (III) in which the PTM molecule acted as a two-electron ligand (Scheme 1).



II, M = Re
III, M = Mn

The binuclear complex II was obtained as dark-orange crystals, m.p. 134—136°C, that readily dissolve in methylene chloride. It is stable in the solid state, gradually decomposes in solution and rapidly decomposes when chromatographed on alumina or silica gel.

The structure of this complex was determined by X-ray structural analysis. Crystals of II are monoclinic, $a = 6.349(2)$, $b = 13.653(5)$, $c = 17.128(3)$ Å, $\gamma = 97.55(2)°$, $V = 1471.7(7)$ Å^3, M = 512.4, $d_m = 2.29$, $d_c = 2.31$ g/cm^3 for $Z = 4$, space group $P2_1/b$.

In the binuclear complex II (Fig. 1) both metal atoms have an almost ideal octahedral coordination. π-Pyrrolyl and π-cyclopentadienyl ligands are tridentate, which is typical for monocyclopentadienyl complexes of Group VII transition metals of the type (π-C_5H_5)M(CO)$_3$ and (π-C_5H_5)M(CO)$_2$L, where L is a monodentate ligand [6]. Using its lone electron pair, the nitrogen atom forms a donor—acceptor bond with the Re atom, and the pyrrolyl ring becomes both a π-ligand to Mn and an n-ligand to Re.

Both five-membered cyclic ligands are planar within 0.01—0.03 Å (plane equations: $0.3800x + 0.6052y - 0.6996z = 2.1662$ for the Cp ligand and $-0.2049x + 0.7566y - 0.6309z = -0.8938$ for the pyrrolyl ligand). The Re—N bond is not strictly coplanar with the pyrrolyl ligand forming an angle of 6.7° with it (in I the corresponding angle is 7.9°). The Re—N bond length of 2.194(15) Å does not differ from that found for bonds with amino groups in (Re(CH$_3$NH$_2$)$_4$-(CH$_3$N)Cl)(ClO$_4$)$_2$ [7], although it is slightly shorter than the sum of covalent radii (2.24 Å) of Re (1.54 Å [8]) and N (0.70 Å [9]).

As in complex I, the Mn atom is symmetrically bonded to the heterocyclic ligand: within experimental error the average Mn—C distance of 2.18(2) Å coincides with the Mn—N distance of 2.16(2) Å; C—C and C—N bond lengths are practically equalized in the pyrrolyl ligand (average 1.42(2) Å). The mean

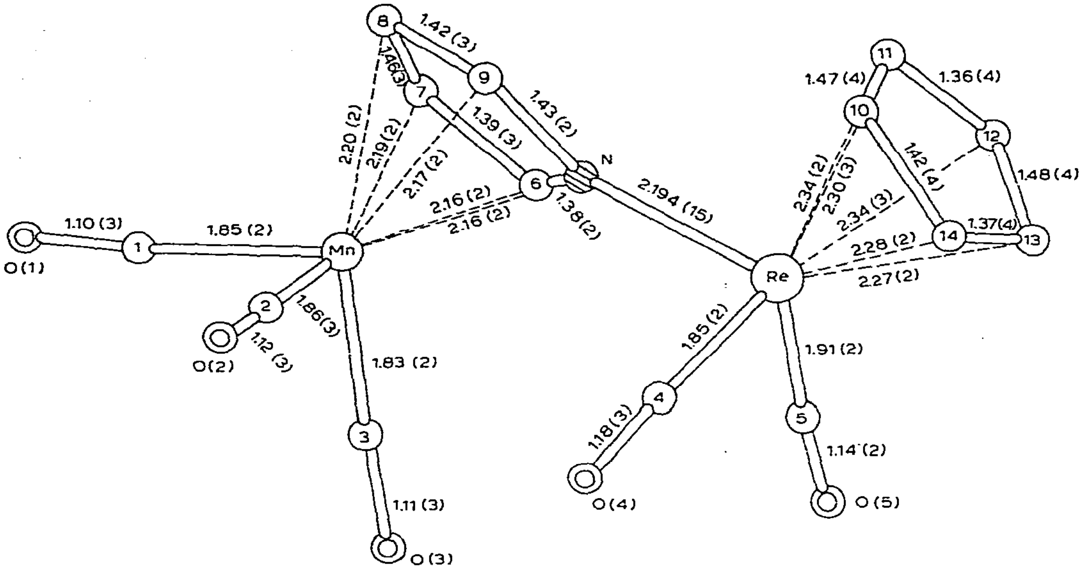


Fig. 1.

Re—C(Cp) distance of 2.31(2) Å coincides with that in monocyclopentadienylrhenium complexes [6]; C—C bond lengths in the Cp ligand are normal (1.36(4)—1.48(4) Å, average 1.42(4) Å). Metal—carbonyl groups Re—C—O and Mn—C—O are linear with normal M—C and C—O bond lengths [10]. Atomic coordinates and anisotropic temperature factors are given in Table 1 and bond angles in Table 2.

Mass-spectrometric, IR and PMR spectroscopic data are in agreement with X-ray analysis of II. The mass spectrum of II (Table 3) exhibits a molecular ion at *m/e* 513. Further fragmentation completely agrees with the proposed structure of II. The IR spectrum of the binuclear complex II in CH_2Cl_2 shows five absorption bands in the carbonyl region at 1836, 1909, 1964, 1973 and 2050 cm^{-1} that correspond to the vibrations of the five carbonyls in the complex. Bands at 1836 and 1909 cm^{-1} belong to the $CpRe(CO)_2$ fragment. Decreasing of local symmetry due to formation of a binuclear complex leads to splitting of the low-frequency *E*-type band in the PTM fragment into two components. As a result, for this fragment three bands at 1964, 1973 and 2050 cm^{-1} are observed in the carbonyl region.

The PMR spectrum of II in $CDCl_3$ reveals only two signals with chemical shifts of δ 5.00 and 6.55 ppm (intensity ratio, 7 : 2) i.e. the signal of the Cp ring overlaps with the signal of β-hydrogens of the pyrrolyl ring (according to [11], in PTM the proton signal displayed at lower field position belongs to α-protons).

The manganese analogue (III) was isolated as a red-orange powder, dec. 90°C. The mass-spectrum of III (Table 4) shows the molecular ion with *m/e* 381 and the corresponding fragment ions, indicating a similarity of structures II and III.

As in the rhenium analogue, the IR spectrum of III (KBr pellets) has five bands in the carbonyl region at 1828, 1907, 1950, 1974 and 2044 cm^{-1}.

The manganese complex is less stable in solution than its rhenium analogue.

(continued on p. 436)

TABLE 1

ATOMIC COORDINATES (X 10^5 FOR Re AND Mn AND X 10^4 FOR OTHER ATOMS) AND ANISOTROPIC TEMPERATURE FACTORS (X 10^2 FOR Re AND Mn AND X 10 FOR OTHER ATOMS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + ...2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	37206(12)	11156(6)	12792(4)	329(3)	273(3)	190(3)	−16(2)	15(3)	15(3)
Mn	18835(43)	11498(21)	34626(15)	315(13)	280(13)	167(11)	−20(10)	3(9)	−13(9)
N	2271(25)	1735(10)	2293(8)	52(9)	18(6)	24(7)	10(6)	3(6)	6(5)
O(1)	92(27)	1125(12)	5055(8)	69(9)	58(9)	23(6)	−8(7)	17(6)	−2(6)
O(2)	5920(27)	511(15)	4033(11)	57(10)	108(15)	72(11)	34(10)	−21(8)	14(10)
O(3)	237(27)	−924(11)	3135(8)	92(11)	35(7)	34(7)	−20(7)	9(7)	−9(6)
O(4)	5912(24)	−370(11)	2176(9)	59(8)	39(8)	56(9)	18(7)	−17(7)	4(7)
O(5)	−61(21)	−434(10)	931(8)	44(7)	42(7)	42(7)	−17(6)	−13(6)	−4(6)
C(1)	757(32)	1093(17)	4457(13)	35(10)	51(12)	41(11)	−16(9)	−3(9)	0(10)
C(2)	4376(41)	713(16)	3819(12)	84(15)	44(11)	22(9)	21(11)	19(10)	4(9)
C(3)	828(34)	−139(15)	3272(10)	60(12)	27(9)	17(8)	−8(8)	7(8)	−1(7)
C(4)	5088(28)	211(16)	1828(13)	20(8)	46(12)	51(12)	4(8)	−5(8)	−38(10)
C(5)	1328(29)	134(14)	1101(10)	38(9)	32(9)	22(9)	1(7)	1(7)	2(7)
C(6)	190(26)	1680(16)	2503(11)	21(8)	41(11)	32(9)	9(8)	−3(7)	4(8)
C(7)	−54(32)	2279(15)	3128(11)	47(11)	39(10)	27(9)	21(9)	10(8)	7(8)
C(8)	1998(35)	2756(14)	3327(10)	64(12)	23(8)	20(8)	0(8)	7(8)	−3(7)
C(9)	3448(32)	2395(13)	2821(10)	59(11)	18(8)	24(8)	−12(8)	−7(8)	−1(7)
C(10)	6431(42)	2298(21)	913(14)	66(15)	62(15)	38(11)	−40(12)	−6(11)	26(11)
C(11)	4482(56)	2726(16)	802(14)	126(23)	20(9)	36(12)	−20(12)	17(14)	2(9)
C(12)	3332(43)	2203(20)	262(16)	73(16)	43(13)	60(15)	18(12)	21(13)	32(12)
C(13)	4665(53)	1469(21)	29(12)	118(21)	80(17)	15(8)	−89(17)	13(11)	13(10)
C(14)	6480(35)	1472(19)	437(13)	43(13)	59(13)	30(10)	−11(10)	9(9)	6(10)

TABLE 2

BOND ANGLES, ω (°)

Angle	ω	Angle	ω	Angle	ω
C(1)—Mn—C(2)	92(1)	C(5)—Re—N	93.8(7)	C(9)—N—C(6)	109(2)
C(1)—Mn—C(3)	92(1)	Re—C(4)—O(4)	178(2)	N—C(6)—C(7)	110(2)
C(2)—Mn—C(3)	88(1)	Re—C(5)—O(5)	175(2)	C(10)—C(11)—C(12)	109(2)
Mn—C(1)—O(1)	176(2)	Re—N—C(6)	129(1)	C(11)—C(12)—C(13)	102(2)
Mn—C(2)—O(2)	175(2)	Re—N—C(9)	122(1)	C(12)—C(13)—C(14)	116(3)
Mn—C(3)—O(3)	178(2)	C(6)—C(7)—C(8)	107(2)	C(13)—C(14)—C(10)	101(2)
C(4)—Re—C(5)	90.8(9)	C(7)—C(8)—C(9)	108(2)	C(14)—C(10)—C(11)	111(2)
C(4)—Re—N	96.7(8)	C(8)—C(9)—N	107(2)		

TABLE 3

MASS SPECTRUM OF COMPLEX II

m/e [a]	% Int.	Ion
513	0.5	M^+
429	4.5	$(M - 3CO)^+$
373	12.9	$(M - 5CO)^+$
318	5.6	$(C_5H_5ReC_4H_4N)^+$
308	13.5	$(C_5H_5Re(CO)_2)^+$
280	66.0	$(C_5H_5Re(CO))^+$
252	36.0	$(C_5H_5Re)^+$
205	5.9	$(PTM)^+$
187	15.9	$(Re)^+$
177	6.7	$(C_4H_4NMn(CO)_2)^+$
149	12.8	$(C_4H_4NMn(CO))^+$
121	63.1	$(C_4H_4NMn)^+$
67	27.5	$(C_4H_4NH)^+$
55	100.0	$(Mn)^+$

[a] The mass spectrum was reduced to ^{187}Re.

TABLE 4

MASS SPECTRUM OF COMPLEX III

m/e	% Int.	Ion
381	3.9	M^+
325	17.6	$(M - 2CO)^+$
241	66.3	$(M - 5CO)^+$
205	15.2	$(PTM)^+$
186	32.8	$(C_5H_5MnC_4H_4N)^+$
177	6.3	$(C_4H_4NMn(CO)_2)^+$
149	18.3	$(C_4H_4NMn(CO))^+$
121	74.3	$(C_4H_4NMn)^+$
120	29.9	$(C_5H_5Mn)^+$
67	12.9	$(C_4H_4NH)^+$
66	26.8	$(C_4H_4N)^+$
65	10.1	$(C_5H_5)^+$
55	100.0	$(Mn)^+$

This is presumably due to the considerably smaller covalent radius of the manganese atom (Mn, 1.38; Re, 1.54 Å [8]) and to the steric hindrances arising from replacement of the CO ligand with bulky PTM.

Hence, we have synthesized a new type of binuclear complexes in which π-pyrrolyltricarbonylmanganese is a two-electron ligand.

Experimental

PTM was prepared according to [12].

Complex II

0.25 g (0.75 mmol) of CTR in 20 ml of abs. THF were photolysed (quartz lamp, 220 W) for 3 h at +5°C under dry argon. To the obtained light yellow solution 0.15 g (0.75 mmol) of PTM in 10 ml of abs. THF were added with stirring and the mixture was then stored overnight at room temperature. The solvent was removed in a flow of argon. The remaining brown oil was washed three times with cooled hexane and dried under vacuum. 0.21 g (55%) of raw product II was obtained as a brown powder. Crystallization from a hexane/CH_2Cl_2 mixture (~10 : 1) was accompanied by intensive decomposition. 0.02 g (5%) of pure II, m.p. 134—136°C, were obtained after triple crystallization.

Complex III

0.2 g (9.8 mmol) of CTM in 20 ml of abs. THF were photolysed for 5 h (under conditions similar to those described for II). 0.2 g (9.75 mmol) of PTM in 10 ml of abs. THF were added to the dark crimson solution formed. The unreacted PTM and CTM were removed by sublimation. 0.18 g (48%) of III was obtained as a red-orange powder, dec. 90°C.

Mass spectra were obtained on a Ms-30/Ds-50 instrument. IR spectra were recorded on a UR-20 spectrophotometer, and PMR spectra were measured on a Perkin—Elmer R-20 spectrometer (working frequency 60 MHz).

An X-ray analysis (2259 reflections with $I \geqslant 2\sigma$) was carried out on a Syntex-$P2_1$ automated diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 54°$); no absorption corrections were introduced. The structure was solved by the heavy atom method and refined by the full-matrix anisotropic least squares technique ($R = 0.062$) with an Eclipse S/200 mini computer using XTL programs.

References

1 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov and D.N. Kursanov, J. Organometal. Chem., 128 (1977) 381.

2 E.O. Fischer and M. Herberhold, Essays in Coordination Chemistry, Birkhauser Verlag, Basel. Vol. 5, 1965, p. 259.

3 A.N. Nesmeyanov, N.E. Kolobova, Yu.V. Makarov, B.V. Lokshin and E.B. Rusach, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 629.

4 W. Strohmeier and F. Muller, Chem. Ber., 100 (1967) 2812.

5 D. Sellman, J. Organometal. Chem., 36 (1972) C27.

6 P.J. Wheatley, Perspectives in Struct. Chem., 1 (1968) 1.

7 R.S. Shandles, R.K. Murmann and E.O. Schlemper, Inorg. Chem., 13 (1974) 1373.

8 V.G. Andrianov, B.P. Biryukov and Yu.T. Struchkov, Zh. Strukt. Khim., 10 (1969) 1129.

9 L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, N.Y., 3rd Edn., 1960.

10 B.P. Biryukov and Yu.T. Struchkov, Itogi nauki. Kristallokhimiya, 6, 148, Viniti, Moscow, 1971.

11 P.L. Pauson, A.R. Qazi and B.W. Rockett, J. Organometal. Chem., 7 (1967) 325.

12 N.V. Kislyakova, N.I. Pyshnograeva, V.F. Sizoy, N.E. Kolobova, V.N. Setkina and D.N. Kursanov, Dokl. Akad. Nauk, 212 (1973) 367.