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ACYLATION OF PYRROLYLTRICARBONYLMANGANESE. STRUCTURE OF THE ACYLATION PRODUCT

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Summary

The acylation of pyrrolyltricarbonylmanganese (PTM) is studied. The reaction proceeds in an unusual manner; introduction of an acetyl group into the α-position of the PTM pyrrolyl ligand is accompanied by extensive rearrangement of bonds resulting in the formation of a binuclear complex

$(\pi\text{-}C_4H_4N)Mn(CO)_3(CH_3COC_4H_3N)Mn(CO)_3$

(I)

Coordination of the acetylpyrrolyl ligand to the manganese atom is of the chelate type and involves atoms of heterocyclic nitrogen and of acetyl oxygen. The ligand, therefore, is not a five-electron but a three-electron donor. The manganese atom is additionally coordinated to three carbonyl groups and one molecule of the initial PTM (by a donor—acceptor bond through a nitrogen atom), thus acquiring a 18-electron shell. A scheme for complex I formation is proposed.

Introduction

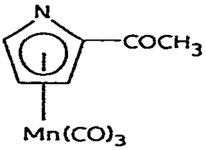
Pyrrolyltricarbonylmanganese was obtained by Pauson et al. [1] in 1964, since then, however, little data has been published relating to its reactivity [2,3].

Recently we succeeded in carrying out the first substitution reaction in the PTM pyrrolyl ligand, namely, hydrogen isotope exchange (HIE) with acids [4, 5]. The reactivity of PTM in this reaction is comparable to the reactivity of ferrocene (the HIE rate of ferrocene is only 1.5 times higher in the same conditions [4]).

We thought it interesting to study the behavior of PTM in another electrophilic substitution reaction typical of ferrocene. Accordingly we acylated PTM with acetic anhydride in the presence of phosphoric acid, conditions that are typical of ferrocene acylation.

Results and discussion

We expected to obtain, by analogy with ferrocene, monoacylated PTM



(II)

However elemental analysis of the product did not conform with II, but corresponded to I:

$$(C_4H_4N)Mn(CO)_3 \xrightarrow[H_3PO_4]{(CH_3CO)_2O} \underset{(I)}{C_{16}H_{10}Mn_2N_2O_7}.$$

Compound I was obtained as dark-orange crystals, with a melting point of 124°C, that readily dissolve in chlorine-containing solvents. It is stable in the solid state and decomposes in solution.

The structure of the complex was unambiguously determined by X-ray structural analysis. Crystals are monoclinic, a 8.972(2), b 8.317(1), c 24.467(5) Å, β 97.38(2)°, V 1810.5(5) Å^3, M 452.2, d_{exp} 1.66, d_{cal} 1.66 g/cm^3 for Z 4, μ(λ-Mo-K_α) 15.1 cm^{-1}, space group $P2_1/c$.

As mentioned above, the structure of complex I (Fig. 1) was totally unexpected. Only some of the initial PTM molecules are acylated (in an α-position to the pyrrolyl nucleus) and the nature of the coordination changes qualitatively: instead of the π-analogue of cyclopentadienyl, α-acetylpyrrolyl is coordinated by the chelate type through the nitrogen atom of the heterocycle and the oxygen of the acetyl group and acts as a three-electron donor. The Mn(2) atom acquires a 18-electron shell by forming a donor—acceptor bond with N(1) (using its unshared electron pair) of the unsubstituted pyrrolyl nucleus which is a π-ligand of Mn(1). Thus, complex I is binuclear although a metal—metal bond is absent (the Mn(1)—Mn(2) distance of 3.840(1) Å greatly exceeds the doubled covalent radius of Mn (2.76 Å [6]).

Coordination of Mn(1) is near-octahedral (the π-pyrrolyl ligand occupies three coordination positions) and the geometry of this fragment is practically the same as of the $C_5H_5Mn(CO)_3$ complex [7], since Mn(1) is symmetrically linked with the five-membered ring and with three carbonyl groups; indeed, the Mn(1)—C(ring) distance is 2.132—2.160 Å (2.144(5) Å in average), whereas the Mn(1)—N(1) distance is 2.120(4) Å, i.e. is only slightly shorter. The Mn(1)—C(O) bond lengths are equal within experimental error and their average value of 1.790(6) Å is close to the usually accepted value (this is also true of the carbonyl groups at Mn(2) atom). The π-pyrrolyl ligand is planar (maximum devia-

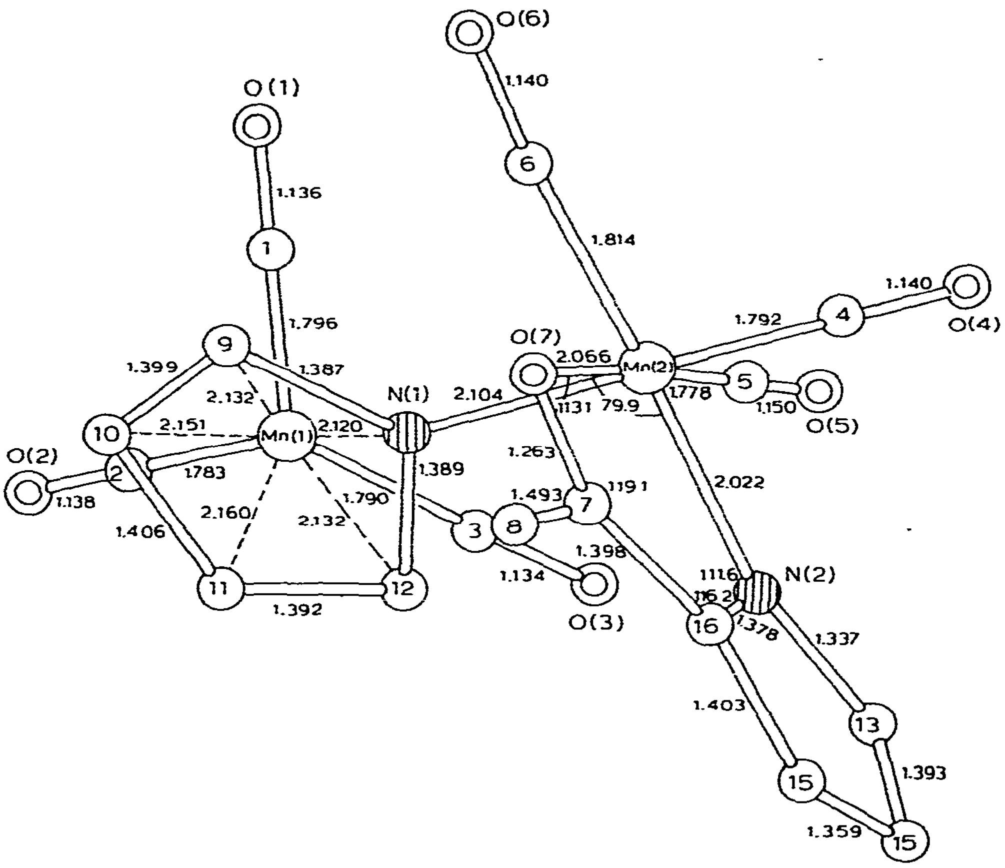


Fig. 1. Structure of complex I.

tion from the mean plane is 0.009 Å) and bond lengths correspond to the total delocalisation of π-electrons.

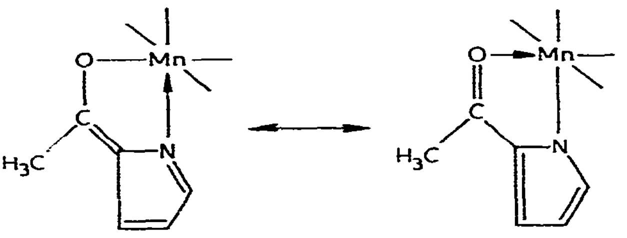
It should be noted that complex I is the first structurally studied complex in which the pyrrolyl system is a $\pi(\eta^5)$-ligand at a transition metal atom.

Mn(2) has a slightly distorted octahedral coordination. The five-membered metallocycle is practically planar (with accuracy of 0.007 Å) as is the pyrrolyl ring condensed with it. The dihedral angle between these two planes is 0.2°, i.e. atoms of the acetylpyrrolyl ligand and Mn(2), on the whole, form a planar system tilted to the plane of the unsubstituted π-pyrrolyl ligand at an angle of 67.0°.

As expected, the lengths of the formally donor—acceptor Mn(2)—N(1) bond (2.104(4) Å) and of the Mn(2)—N(2) σ-bond (2.022(4) Å) are different: the first is close to the sum of covalent radii of Mn (1.38, [6]) and of N (0.70 Å, [8]) and to the usually observed length of Mn—N bonds (amine) (for instance, 2.111 [9] and 2.110 Å [10] in two modifications of $Mn(CO)_4(NH_2CH_3)$(CO-NHCH$_3$)), while the latter is considerably shorter. The Mn(2)—N(1) bond is not entirely coplanar to the π-pyrrolyl plane, forming an angle of 7.9°.

The Mn(2)—O(7) and O(7)—C(7) distances (2.066(3) and 1.263(6) Å, respectively) in the chelate ring are comparable with those established in $Ph_2P[C_6H_3(CO)Mn(CO)_4]Mn(CO)_3\ PPh_3$ (2.05 and 1.27 Å, [11]) and in $(\pi\text{-}C_5H_5)Ir\text{-}\mu\text{-}[C(C_6H_5)O]\text{-}\mu\text{-}[C(CH_3)O]\text{-}\mu\text{-}(PPh_2)Mn(CO)_3 \cdot \frac{1}{2}C_6H_6$ (2.034 and 1.258 Å [12]), in which the carbonyl groups are also coordinated through oxygen to the metal atom forming metalocycles.

It is interesting that the distribution of bond lengths in the α-substituted σ-pyrrolyl nucleus considerably differs from that in the π-nucleus (where all bonds are practically of the same length). This probably indicates a considerable contribution of structure A:



(A) (B)

Mass spectrometric, IR and NMR spectrometric data confirm the structure of complex I.

The M^+ molecular ion at m/e 452 is absent from the mass spectrum of complex I. The heaviest ion is observed at m/e 368 and corresponds to the $(M - 3CO)^+$ fragment ion. Further fragmentation completely agrees with the proposed structure of complex I (Table 1).

The IR spectrum of complex I has six absorption bands in the region of carbonyl modes at 1920, 1945, 1966, 1982, 2033 and 2053 cm^{-1} that correspond to the vibrations of the six carbonyl groups linked with the two manganese

TABLE 1

MASS SPECTRUM OF COMPLEX I

M *m/e*	Int. (%) [a]	Ion
368	11.6	$[(C_4H_4N)Mn(CH_3COC_4H_3N)Mn(CO)_3]^+$
284	25.3	$[(C_4H_4N)Mn(CH_3COC_4H_3N)Mn]^+$
205	11.4	$[(C_4H_4N)Mn(CO)_3]^+$
177	8.2	$[(C_4H_4N)Mn(CO)_2]^+$
163	31.7	$[(CH_3COC_4H_3N)Mn]^+$
149	18.9	$[(C_4H_4N)Mn(CO)]^+$
121	63.3	$[(C_4H_4N)Mn]^+$
109	22.9	$[(CH_3COC_4H_3NH]^+$
94	27.3	$[(COC_4H_3NH]^+$
67	13.4	$[C_4H_4NH]^+$
66	15.3	$[C_4H_4N]^+$
55	100.0	$[Mn]^+$

[a] Masses of fragment ions with intensities below 3% are omitted.

atoms. The PTM spectrum exhibits only two bands in the carbonyl region at 1952 and 2038 cm^{-1} [13]. Splitting of the low-frequency *E*-type band in the PTM fragment and in the $Mn(CO)_3$ group linked with the chelate ring into two components is due to a decrease in the local symmetry of complex I. As a result, all six possible absorption bands are observed in the carbonyl region. An additional band is observed in the 1546 cm^{-1} region which we assigned to the carbonyl of the acetyl group. Its considerable down-field shift is probably due to coordination with the manganese atom in the chelate ring.

The PMR spectrum of complex I is presented in Fig. 2. Methyl protons (CH_3CO) display a signal with δ 2.30 ppm (intensity 3). Proton signals of the π- and σ-pyrrolyl ligands are exhibited at lower field positions. The signal of β-protons in the spectrum of initial PTM are shifted up-field compared with the signal of the α-protons [3]. Consequently we assigned the signal with δ 5.00 ppm (intensity 2) to β-hydrogens of the π-pyrrolyl ligand and signals with δ 5.60 and 5.75 ppm (intensity ratio, 1 : 1) to α-protons. The presence of two signals of the α-hydrogen atoms of the π-pyrrolyl ligand in the PMR spectrum of complex I indicates that they are diastereotopic due to the assymetry of complex I. In the σ-pyrrolyl ligand all hydrogen atoms display separate signals with chemical shifts of δ 6.32, 7.00 and 7.42 ppm (intensity ratio, 1 : 1 : 1).

The ^{13}C {^1H} NMR spectrum also agrees with the proposed structure of compound I (Fig. 3). It is significant that we were able to establish that not only the α-carbon-atoms (chemical shifts of δ 108.47 and 109.38 ppm) but also β-carbons are diastereotopic (85.45 and 86.44 ppm) in the π-pyrrolyl ring.

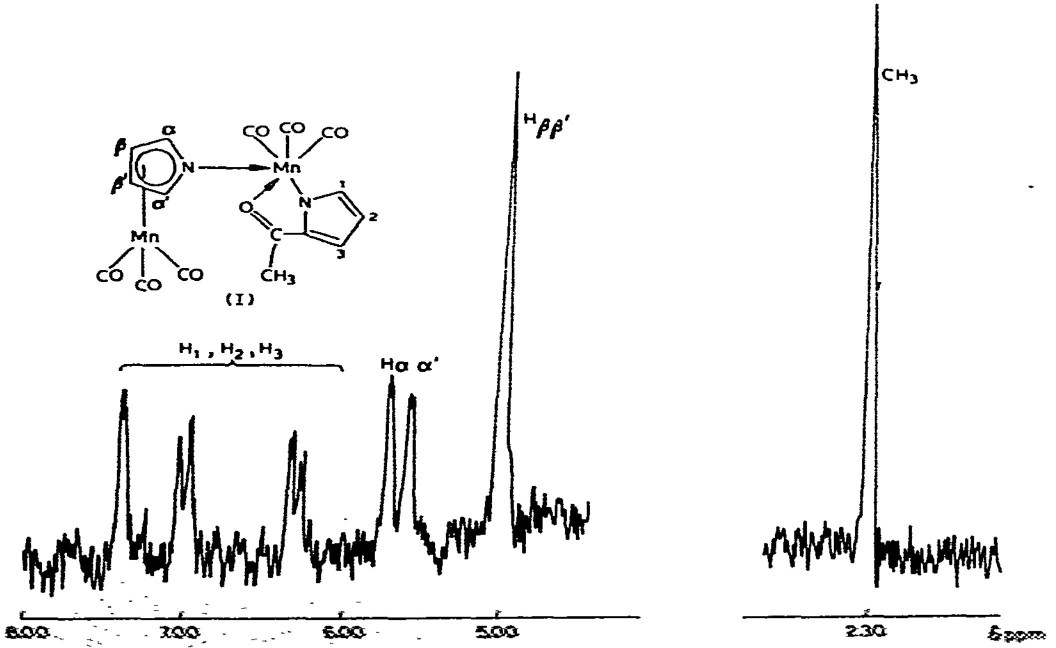
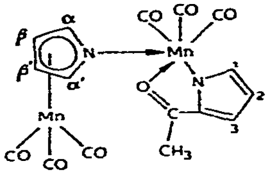


Fig. 2. PMR spectrum of complex I.



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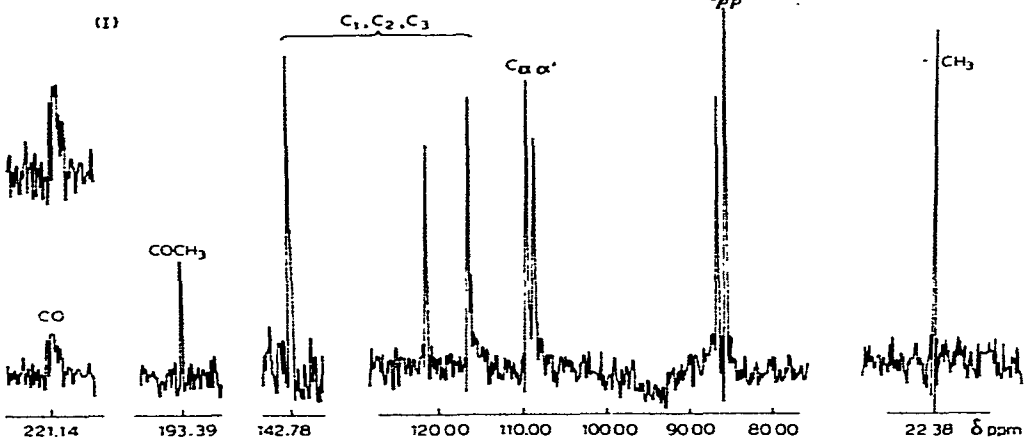


Fig. 3. ^{13}C NMR spectrum of complex I.

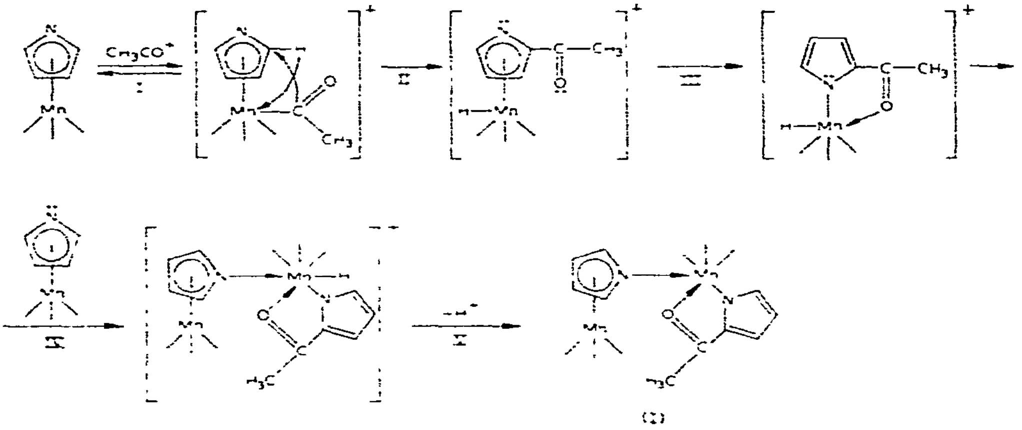
The signals of the four carbons in the acetylated σ-pyrrolyl ligand are exhibited at lower field positions. The key atom signal is superimposed on one of the carbon nuclei signals of the same ligand and only three signals with chemical shifts of δ 116.40, 121.46 and 142.78 ppm are observed. Carbon nuclei of the acetyl group produce two signals with chemical shifts of δ 22.38 (CH_3 group) and 193.39 ppm (CO group). The signal from the carbon nuclei of the six carbonyl groups is represented by a multiplet, the center of which exhibits a chemical shift of δ 221.14 ppm.

Taking into account the capacity of the Mn atom in PTM to coordinate with electrophilic agents [5], the formation of the binuclear complex I can be described by Scheme 1. The first stage involves addition of the acylium ion to the manganese atom of PTM; the acylium ion is then transferred to the ring (stage II). At stage III the 7-coordinated π-complex is rearranged into a 6-coordinated σ-complex, which interacts with the base (stage IV) (electron pair on nitrogen of PTM). The charged complex is stabilised by ejecting a proton (stage V) forming complex I. It is quite possible that certain stages occur simultaneously.

It should be noted that two other products of PTM acylation were established, $HMn(CO)_5$ and $Mn_2(CO)_{10}$ which were identified by mass spectrometric analysis. Formation of these compounds is probably due to decomposition of PTM in acid medium (in the presence of H_3PO_4).

Thus, we have established that PTM can be acylated under mild conditions and introduction of the acetyl group into the π-pyrrolyl ligand is accompanied by extensive rearrangement of bonds resulting in formation of the binuclear

SCHEME 1. PTM acetylation



(I)

complex I. Complex I contains all types of bonds characteristic of complex organometallic compounds: π-, σ-, donor—acceptor bonds and a chelate ring. It is of interest that the molecule of initial PTM acts as a two-electron ligand in this compound.

Experimental

An inert atmosphere (Ar) was maintained throughout the synthesis. PTM was prepared according to [4].

1.2 ml (12.8 mmol) of acetic anhydride and 0.12 ml (2.2 mmol) of 85% H_3PO_4 in 2 ml of CH_2Cl_2 were added to a solution of 0.36 g (1.8 mmol) of PTM in 4 ml of methylene chloride. The reaction mixture was stirred for 1.5 h at room temperature and then ice and a saturated $NaHCO_3$ solution were added for neutralisation. The mixture was extracted with CH_2Cl_2 and the solvent was removed under vacuum. The residue was chromatographed on alumina. Compound I was eluted with CH_2Cl_2, the mixture of $HMn(CO)_5$ and $Mn_2(CO)_{10}$ with ether. Evaporation of the first eluate under reduced pressure, followed by drying in high vacuum and crystalisation from heptane with a small addition of CH_2Cl_2 gave 0.07 g (18% yield) of compound I. Elemental analysis: found C, 42.69; H, 2.35; N, 6.37; Mn 24.53. $C_{16}H_{10}Mn_2N_2O_7$ calcd.: C, 42.50; H, 2.23; N, 6.20; Mn, 24.30%.

Mass spectra were obtained on a Ms-30/Ds-50 instrument. IR spectra were recorded in CCl_4 on a UR-20 spectrophotometer. PMR spectra were measured in CCl_4 on a Perkin—Elmer R-20 spectrometer with working frequency of 60 MHz. ^{13}C NMR spectra we recorded in CH_2Cl_2 on a Bruker HX-90 spectrometer (working frequency 22.63 MHz).

X-ray structural analysis was carried out on a Syntex-P2$_1$ automated diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scanning $2\theta_{max}$ 44°). 2289 independent reflections were measured, 1770 reflections with $I \geqslant 1.96\sigma(I)$ were used; no absorption corrections were introduced. The structure was solved by the heavy atom method and refined in the full-matrix anisotropic

(isotropic for H atoms revealed by difference synthesis) approximation, R 0.037 R_w 0.028 (R factor was 0.058 for all 2289 reflections).

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