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π-COMPLEXES AS LIGANDS IN TRANSITION METAL COMPOUNDS

IV *. METALLATION OF π-PYRROLYLTRICARBONYLMANGANESE

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Summary

The metallation of π-pyrrolyltricarbonylmanganese (PTM) with n-butyllithium has been studied. The metallizing agent has been shown to attack the carbonyl group of PTM, forming a trinuclear complex (I) as a reaction product. The complex contains the initial and the CO group-metallated molecules of PTM as n-ligands. The possible routes of formation of I are discussed.

Introduction

The first papers devoted to studying the reactivity of π-pyrrolyltricarbonylmanganese (PTM) were only published in the early 1970's, although Pauson and co-workers had synthesized this complex as far back as 1964 [1]. Up to now, the participation of PTM in isotopic hydrogen exchange and protonation in acid media [2,3], acetylation [4], reactions with halogens [5], metal carbonyls [6,7], and diphenylketene [8] have been reported. While systematically investigating the reactivity of PTM, we have studied its behaviour in metallation reactions. This paper deals with the interaction of PTM with n-butyllithium.

Results and discussion

It is known that metallation of π-cyclopentadienyltricarbonylmanganese (CTM) can proceed in two directions: in the cyclopentadienyl ring or at the CO group. The direction of attack by a metallizing agent depends to a great extent on the reaction conditions (a decrease of temperature and an increase of the

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* For part III see ref. 7.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$ FOR Mn AND $\times 10^3$ FOR OTHER ATOMS) AND PARAMETERS OF TEMPERATURE FACTORS [a]

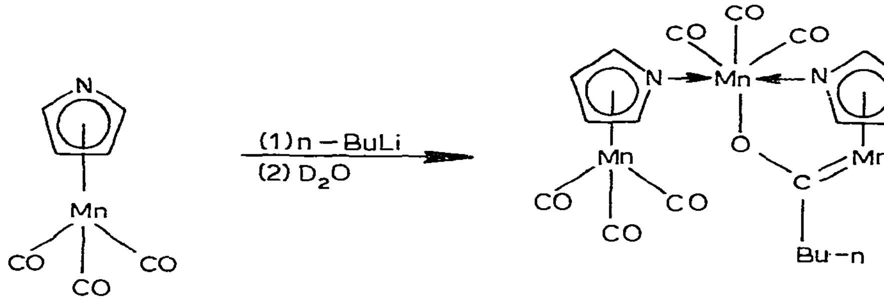
Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	776(7)	7562(4)	7469(2)	5.0(3)	4.0(3)	3.5(3)	0.7(3)	−0.5(2)	−0.2(3)
Mn(2)	−2988(7)	8117(4)	9819(3)	5.2(3)	4.0(3)	4.1(3)	−0.4(3)	0(3)	−1.1(3)
Mn(3)	−2591(7)	8707(4)	8277(3)	5.1(3)	3.4(3)	5.2(3)	−0.4(3)	−0.6(3)	0.4(3)
Atom	x	y	z	B_{iso} (Å^2)	Atom	x	y	z	B_{iso} (Å^2)
O(1)	−158(4)	700(2)	634(1)	8.9(8)	C(6)	−365(3)	722(2)	910(1)	3.0(7)
O(2)	324(3)	665(2)	690(1)	7.6(7)	C(7)	−365(6)	848(3)	743(3)	9(1)
O(3)	142(3)	949(2)	701(1)	7.0(7)	C(8)	−437(5)	927(3)	833(2)	5.8(9)
O(4)	−630(4)	860(2)	970(1)	8.6(8)	C(9)	−186(5)	980(3)	804(2)	6(1)
O(5)	−319(3)	670(2)	1081(1)	7.7(7)	C(10)	−409(4)	614(2)	912(1)	3.9(8)
O(6)	−341(2)	745(2)	855(1)	4.8(5)	C(11)	−264(5)	544(3)	933(2)	7(1)
O(7)	−409(4)	837(2)	694(2)	10.2(9)	C(12)	−315(6)	439(4)	943(2)	9(1)
O(8)	−547(3)	974(2)	833(1)	5.8(6)	C(13)	−176(6)	386(3)	974(2)	9(1)
O(9)	−132(4)	1053(3)	785(1)	10.1(9)	C(14)	−58(4)	684(3)	810(2)	4.8(8)
N(1)	−53(3)	787(2)	823(1)	4.2(6)	C(15)	102(4)	652(2)	826(2)	4.4(8)
N(2)	−156(3)	892(2)	925(1)	3.9(6)	C(16)	203(4)	729(3)	845(2)	4.9(9)
C(1)	−73(5)	727(3)	681(2)	7(1)	C(17)	106(5)	813(3)	843(2)	6.0(9)
C(2)	207(6)	700(3)	714(2)	8(1)	C(18)	−236(5)	958(3)	967(2)	6.2(9)
C(3)	107(4)	869(3)	719(2)	5.6(9)	C(19)	−157(4)	937(3)	1030(2)	5.6(9)
C(4)	−409(5)	843(3)	974(2)	5.6(9)	C(20)	−63(4)	847(2)	1030(3)	4.4(8)
C(5)	−322(4)	733(3)	1042(2)	5.3(9)	C(21)	−51(5)	823(3)	959(2)	5.9(9)

[a] The anisotropic temperature factor is $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots 2B_{23}klb^*c^*)]$.

solvent coordinating strength favour metallation in the ring) [9,10].

Since our aim was to use the metallation of PTM to synthesize various derivatives of this complex, we chose the conditions under which metallation of CTM proceeds mainly in the cyclopentadienyl ring [9,10]. The metallation was performed in THF at —60 or —70°C with n-butyllithium as metallizing agent. The reaction mixture was decomposed with D_2O in order to detect the location of lithium.

We found, quite unexpectedly, that under the above conditions n-BuLi attacks not the pyrrolyl ring, but the carbonyl group of PTM, yielding the trinuclear complex I, not containing deuterium. The structure of I was established by an X-ray diffraction analysis.



(1)

Complex I is yellow crystalline compound with a decomposition temperature of about 152°C, readily soluble in acetone and CH_2Cl_2, and insoluble in hexane. It is stable in the solid state but decomposes gradually in solution.

Crystals of I are monoclinic with lattice parameters at 20°C, *a* 8.503(1), *b* 13,657(3), *c* 21.185(4) Å, β 100.84(2)°, *V* 2416(1) Å^3, M = 606.22 ($C_{21}H_{17}N_2O_9Mn_3$), d_{calc} 1.66 g/cm^3, Z = 4, space group $P2_1/n$. Unfortunately, because of the poor quality of the crystals, the results are not accurate enough to discuss the molecular dimensions in detail, but the general stereochemical features of the molecule I are determined quite reliably. Atomic, positional and thermal parameters are given in Table 1, bond angles in Table 2, and the geometry of the molecule, with bond lengths, is shown in Fig. 1.

The Mn(1) atom has an 18-electron shell and coordination typical for π-pyrrolyl complexes of manganese, $(\eta^5\text{-}C_4H_4N)Mn(CO)_3(C_4H_3NCOCH_3)Mn(CO)_3$ (II) [4], $(\eta^5\text{-}C_4H_4N)Mn(CO)_3(\eta^5\text{-}C_5H_5)Re(CO)_2$ (III) [6] and $[(\eta^5C_4H_4N)Mn(CO)_3]_2Mn(CO_3)I$ (IV) [5], whose structures we have determined earlier, i.e. it is bonded to three carbonyl groups and to a η^5-pyrrolyl ligand. The Mn(2) atom is bonded to two CO groups and a carbene-like ligand, since the length of the Mn(2)—C(6) bond to this ligand, equal to 1.96(3)Å, is appreciably shorter than the standard length of the Mn—C(sp^3) σ bond (ca. 2.15 Å) [11], but exceeds the usual length of the Mn—CO bond (ca. 1.8 Å [12]). The distance C(6)—C(10), equal to 1.52(4) Å, corresponds to a single C(sp^2)—C(sp^3) bond. The distance C(6)—O(6), equal to 1.25(4) Å, is much shorter than the standard length of a single C(sp^2)—O bond (1.31 Å) and exceeds only slightly the standard length of a double C=O bond (1.22 Å) [13].

Taking into account the values determined for the Mn—C(6) and C(6)—O(6)

TABLE 2

BOND ANGLES

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
C(1)Mn(1)C(2)	90(2)	N(2)Mn(3)C(9)	93(2)	Mn(2)C(6)C(10)	128(2)
C(1)Mn(1)C(3)	93(2)	C(7)Mn(3)C(8)	82(2)	O(6)C(6)C(10)	111(3)
C(2)Mn(1)C(3)	97(2)	C(7)Mn(3)C(9)	90(2)	Mn(3)C(7)O(7)	172(5)
C(4)Mn(2)C(5)	89(2)	C(8)Mn(3)C(9)	90(2)	Mn(3)C(8)O(8)	172(4)
C(4)Mn(2)C(6)	87(2)	Mn(3)O(6)C(6)	128(2)	Mn(3)C(9)O(9)	176(4)
C(5)Mn(2)C(6)	97(2)	Mn(3)N(1)C(14)	123(2)	C(6)C(10)C(11)	115(3)
O(6)Mn(3)N(1)	83.5(9)	Mn(3)N(1)C(17)	129(2)	C(10)C(11)C(12)	113(3)
O(6)Mn(3)N(2)	86.0(9)	C(14)N(1)C(17)	108(3)	C(11)C(12)C(13)	107(4)
O(6)Mn(3)C(7)	91(2)	Mn(3)N(2)C(18)	120(2)	N(1)C(14)C(15)	105(3)
O(6)Mn(3)C(8)	90(1)	Mn(3)N(2)C(21)	121(2)	C(14)C(15)C(16)	111(3)
O(6)Mn(3)C(9)	179(2)	C(18)N(2)C(21)	115(3)	C(15)C(16)C(17)	106(3)
N(1)Mn(3)N(2)	85(1)	Mn(1)C(1)O(1)	171(4)	N(1)C(17)C(16)	110(3)
N(1)Mn(3)C(7)	97(2)	Mn(1)C(2)O(2)	173(4)	N(2)C(18)C(19)	105(3)
N(1)Mn(3)C(8)	174(2)	Mn(1)C(3)O(3)	174(3)	C(18)C(19)C(20)	109(3)
N(1)Mn(3)C(9)	96(2)	Mn(2)C(4)O(4)	176(3)	C(19)C(20)C(21)	109(3)
N(2)Mn(3)C(7)	175(2)	Mn(2)C(5)O(5)	169(3)	N(2)C(21)C(20)	101(3)
N(2)Mn(3)C(8)	95(2)	Mn(2)C(6)O(6)	119(2)		

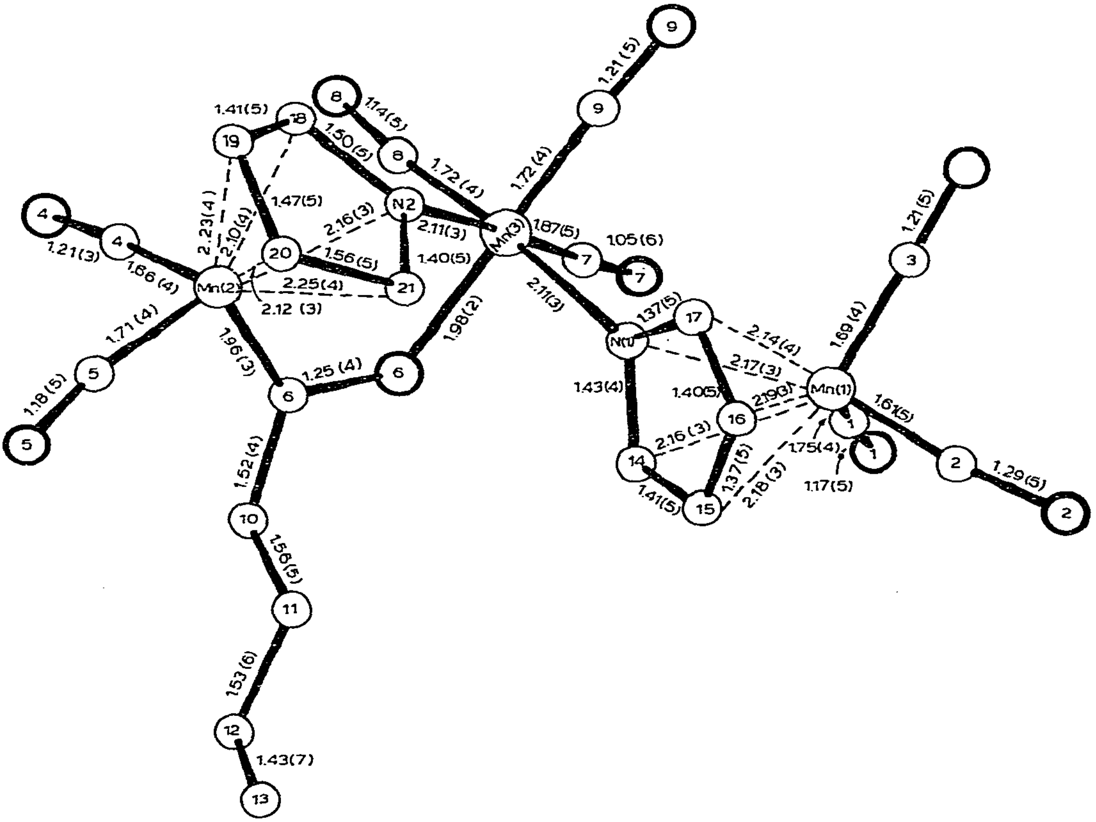
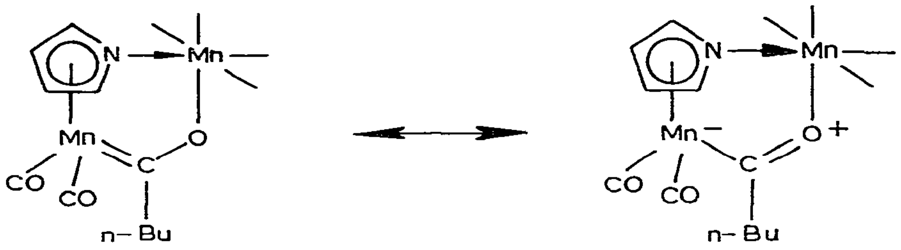


Fig. 1. The geometry of the molecule I.

bond lengths, the structure of complex I in the Mn(2) region can be represented by a resonance of two canonical forms:



The coordination of the central Mn(3) atom is *fac*-octahedral: the metal atom is bonded to three CO groups, participates in a donor-acceptor interation with nitrogen atoms of two *cis*-situated pyrrolyl ligands and forms a σ-bond with O(6) of a carbene-like ligand, the length of the latter bond (1.98(2) Å) being somewhat shorter than the sum (2.04 Å) of single-bonded covalent radii of Mn [14] and O [15].

The lengths of the two donor-acceptor Mn(3)—N(1) and Mn(3)—N(2) bonds are equivalent (2.11(3) Å) and differ only slightly both from those found in II (2.104 Å) and IV (2.115 and 2.118 Å) and from the sum (2.08 Å) of single-bonded covalent radii of Mn [14] and N [15].

Data from elemental analysis and mass, IR, and PMR spectra are consistent with the structure established for complex I.

The IR spectrum of complex I (in CH_2Cl_2) in the region of carbonyl vibrations contains the following absorption bands, corresponding to eight terminal CO groups: 1867s, 1922(sh), 1940vs, 1980s (br), 2013 (bending), 2023(sh), 2032s, 2039(sh), 2055s, and 2105w cm^{-1}. The poor resolution of some

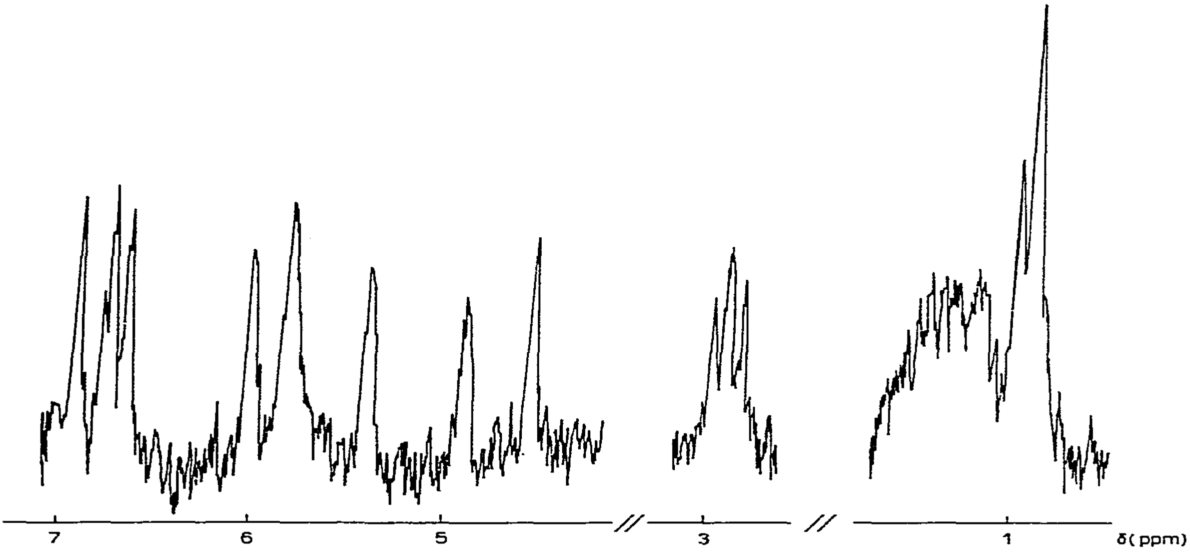
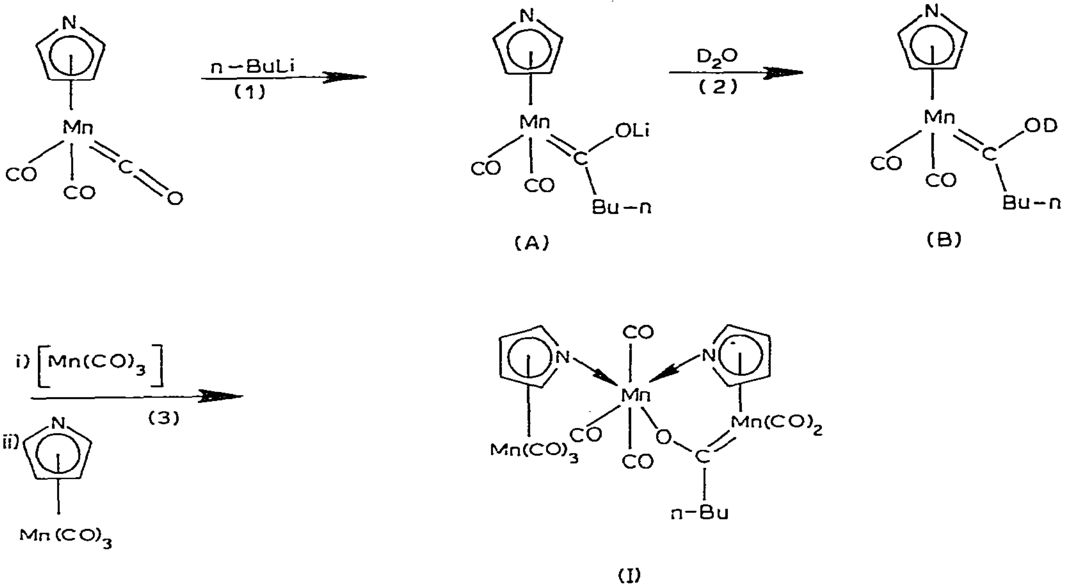


Fig. 2. The NMR spectrum of complex I.

SCHEME 1



carbonyl bands and their superposition resulting in shoulders and distortions, considerably complicates the IR spectrum of I and makes band assignments unreliable. It can only be noted that the weak absorption at 1400 cm^{-1} seems to correspond to the C—O vibration in a cyclic fragment of I (Mn—C—O—Mn).

The PMR spectrum of I (in acetone-d_6, Fig. 2) reveals in a strong field three signals from n-butyl group protons at δ 0.9 (3H), 1.3 (4H), and 2.9 (2H) ppm, and eight signals of equal intensity (1H) in a weak field at δ 4.5, 4.9, 5.4, 5.8, 6.0, 6.6, 6.7, and 6.9 ppm, corresponding to protons of the two pyrrolyl rings in I. These data show the non-equivalence of the pyrrolyl protons due to the asymmetric structure of the trinuclear complex I.

The mass-spectrum of I (12 eV), showing the presence of a molecular ion with *m/e* 606 and fragments, is consistent with the X-ray-determined structure of I and no deuterium is detected in pyrrolyl ligands of the complex analyzed.

Formation of the trinuclear complex I by interaction of PTM with n-BuLi is, apparently, a complex process (Scheme 1), whose first stage represents lithiation of the CO ligand with formation of the carbene complex A. Interaction of A with D_2O should yield the enol complex B. Formation of the trinuclear complex I can be represented as resulted from coordination of the fragment $[Mn(CO)_3]$* with the enol complex B and a PTM molecule. But, as such, this fragment can be absent in the reaction medium and interaction of the enol

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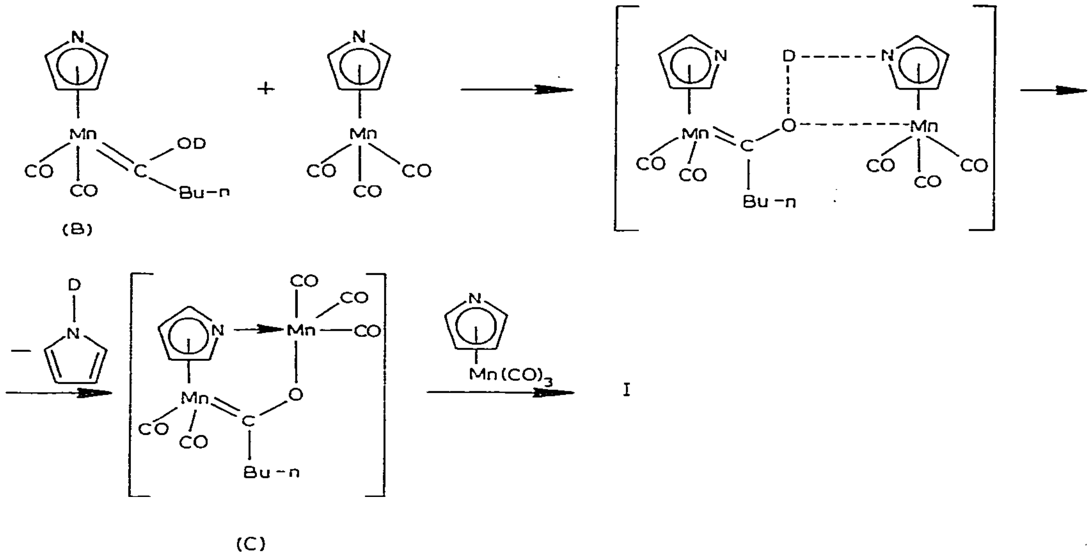
* It should be noted that upon metallation of a phosphorus analogue of PTM (phosphacymantrene) under identical conditions a nucleophilic attack at the heteroatom of the complex was observed, accompanied by destruction of the π-bond Mn—phospholyl and formation of P—butylphosphole [16]. It is not excluded that in the case of PTM such a process is also possible and, then, in addition to metallation of the CO ligand, the attack of n-BuLi at the nitrogen atom of PTM molecule will give rise to decomposition of the complex, yielding *N*-butylpyrrole and the fragment $[Mn(CO)_3]$.

SCHEME 2



complex B, which, apparently has a mobile deuteron, with the PTM molecule (Scheme 2) can result in elimination of *D*-*N*-pyrrole *, and formation of a coordinatively-unsaturated intermediate C. The latter builds up its 16-electron shell to an 18-electron one via coordination with a new PTM molecule, yielding complex I.

Formation of complex I supports the proposal that unreacted PTM is present in the reaction medium. To confirm this, we metallated PTM with 1.5—2-fold excess of n-BuLi, assuming that the whole amount of initial PTM would participate in the reaction already at the first stage. It turned out that in fact no complex I is formed under these conditions.

The above schemes for the formation of the trinuclear complex I undoubtedly require an additional experimental foundation and, therefore, we intend to study the metallation of PTM in more detail.

Experimental

Complex I was synthesized and isolated under argon. All solvents were carefully dried and distilled under argon prior to use.

PTM was prepared by the known procedure [2].

A hexane solution of n-BuLi (2 ml, 0.85 *N*) was added dropwise to the solution of PTM (0.7 g or 3.4 mmol) in 30 ml THF at —60 to —70°C under stirring for 5—10 minutes. After stirring for 30—40 minutes at this temperature, the mixture was brought to room temperature and decomposed with D_2O (10—15 ml). The addition of 10—15 ml of benzene resulted in separation of the mixture to an organic layer, which was isolated, and an aqueous layer, which was extracted with benzene. The extracts were dried over $MgSO_4$, and

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* It should be noted that both *D*-*N*-pyrrole and *N*-butylpyrrole seem to polymerize under the reaction conditions and therefore attempts at their identification were unsuccessful.

the solvent was removed in vacuo. The oily residue was dissolved in CH_2Cl_2 and passed rapidly through a thin silica gel layer. After removing the solvent, the residue was washed with hexane to separate the unreacted PTM and recrystallized from a mixture of hexane and CH_2Cl_2. Yellow crystals of complex I (0.1 g or 15% as calculated for 3 PTM molecules) were obtained with a decomposition temperature of about 152°C.

Elemental analysis. Found: C,41.25; H, 2.70; N, 4.28; Mn, 27.31. $C_{21}H_{17}N_2$-O_9Mn_3calcd.: C, 41.58; H, 2.80; N, 4.62; Mn, 27.23%:

Lattice parameters of I and intensities of 1130 reflections with $I \geqslant 2\sigma$ were measured with a 4-circle Hilger & Watts automatic diffractometer (λ Cu-K_α, graphite monochromator, $\theta/2\theta$ scan, $\theta \leqslant 57°$) without correction for absorption. The structure was solved by a direct method using the MULTAN programme and refined by the least-squares method in a full-matrix anisotropic (Mn atoms)-isotropic approximation, $R = 0.108$, $R_G = 0.111$.

Mass spectra were recorded with a MS-30/DS-50 spectrometer; IR spectra were measured with a UR-20 spectrophotometer; PMR spectra were recorded with a RYa-2309 (90 MHz) spectrometer.

References

1 K.K. Joshi, P.L. Pauson, A.R. Qazi and W.H. Stubbs, J. Organometal. Chem., 1 (1964) 471.

2 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.

3 V.N. Setkina, N.I. Pyshnogreava, P.V. Petroskii, N.E. Kolobova and D.N. Kursanov, Dokl. Akad. Nauk, 220 (1975) 123.

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

5 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu. T. Struchkov and D.N. Kursanov, J. Organometal. Chem., 186 (1980) 331.

6 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu. T. Struchkov and D.N. Kursanov, J. Organomet. Chem., 157 (1978) 431.

7 N.I. Pyshnograeva, V.N. Setkina and D.N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., in press.

8 W.A. Herrmann, I. Schweizer, P.S. Skell, M.L. Ziegler, K. Weidenhammer and B. Nuber, Chem. Ber., 112 (1979) 2423.

9 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and Yu. V. Makarov, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 686.

10 N.E. Kolobova and Yu. V. Makarov, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 2529.

11 M.R. Churchill, Perspectives in Struct. Chem., 3 (1970) 92.

12 B.P. Biryukov and Yu. T. Struchkov in Itogi Nauki. Kristallokhimiya, Vol. 6, VINITI, Moscow 1971, p. 148.

13 L.E. Sutton (Ed.), Tables of interatomic distances and configuration in molecules and ions, Suppl. 1956—1959, Chemical Society, London, 1965.

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

15 L. Pauling, The Nature of the Chemical Rond, Cornell Univ. Press, Itaca, N.Y., 3rd edn., 1960.

16 F. Mathey, A. Mitschler and R. Weiss, J. Amer. Chem. Soc., 100 (1978) 5748.