239. The Synthesis and Structure of Pentacarbonyl (5*H*-dipyrrolo[1,2-*c*:2′,1′-e]imidazol-5-yl)manganese

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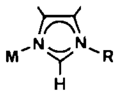
Summary

The dipyrroloimidazolyl ligand is found to bind the pentacarbonylmanganese group to its central ring *via* a carbon-metal σ-bond. This bonding mode differs greatly from that of known imidazole complexes and from the pentahapto mode encountered with the isoelectronic fluorenyl ligand. The X-ray structure of the title compound is reported.

The binding of transition metals to imidazole, disguised as histidine, benzimidazole, and purines, plays a prominent role in the biochemistry of transition metals [1]. If a free pair of electrons is available at the pyridine-type N-atom of imidazole, binding preferentially occurs at this site (see **1**). Complexes have been reported in which the metal (*e.g.*) Ru(II), Ru(III), Fe(O), and Cr(O) is bound to the sp^2-hybridized C(2)-atom of imidazole (see **2**) [2]. In these cases, the heterocyclic entity can be regarded as a carbene or as a C-bound amidine ligand. In contrast to the pyrrole ring [3], the imidazole unit generally shows little propensity to coordinate as an oligohapto π-type ligand.

We have reported earlier on the synthesis of 5*H*-dipyrrolo-[1,2-*c*:2′,1′-*e*]imidazole (**3**) [4]. The present study deals with the interaction possibilities between this novel heterocycle and transition metals. Binding of the entity to a metal obviously cannot occur by any of the modes mentioned above. Both N-atoms are blocked by the pyrrolo annellation, and coordination to the central C-atom C(5) in the sp^2-state would lead to an antiaromatic π-system.



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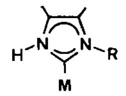

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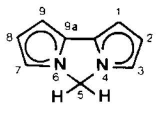

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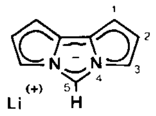

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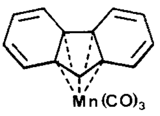

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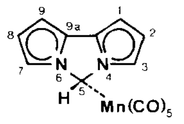

6

M = Metal

The 5*H*-dipyrrolo[1,2-*c*:2′,1′-*e*]imidazole (**3**) and its heteroaromatic anion **4** are isoelectronic with fluorene and the fluorenyl anion, respectively. The latter has been found to bind transition metals to the central ring in a pentahapto mode. Thus, bromopentacarbonylmanganese gives tricarbonyl(η^5-fluorenyl)manganese (**5**) upon reaction with fluorenyl sodium [5]. The analogous reaction with the heteroaromatic anion **4** leads, however, to a different result.

Results and Discussion. – The lithium salt **4** [4] was allowed to react at –78°C in tetrahydrofurane with pentacarbonylchloromanganese. Chromatographic isolation at room temperature gave the title compound **6** as bright yellow monoclinic crystals in 18% yield. It was accompanied by decacarbonyldimanganese (10%) and free 5*H*-dipyrrolo[1,2-*c*:2′,1′-*e*]imidazole (**3**; 23%).

Compound **6** melts in a sealed capillary at 123–125°C without decomposition and can be sublimed at *ca.* 100°C/10^{-4} Torr without loss of CO. However, when heated rapidly in a combustion tube in the presence of V_2O_5, the compound explodes. In contact with air, **6** decomposes within a day to give a grey amorphous powder.

The C_s-symmetry of **6** was readily deduced from the ^{1}H-NMR spectrum. Three of the four resonances are of double intensity and similar in their chemical shifts to the corresponding signals of the dipyrroloimidazole **3** *(Table 1)*. The central hydrogen atom (H–C(5)) of the organomanganese compound, however, appears at lower field than the methylene group of **3**. For the purpose of comparison, NMR data of the lithium salt **4** are included in *Table 1*. All its ^{1}H-NMR shifts are shifted to higher field than those of the organomanganese compound **6**. This feature clearly accounts for the delocalization of negative charge over the entire π-system of **4**.

With the exception of carbon atom C(5), the ^{13}C-NMR shift values of **6** again resemble those of the parent dipyrroloimidazole **3** *(Table 1)*. The deshielding of C(5) directly bound to the metal has precedence in (η^1-allyl)- [6] and benzylpentacarbonylmanganese [7] (*cf.* [8–10]). An interesting observation is the large C,H coupling constant ($^1J_{H,C(5)}$) of 163.1 Hz. Only, when compared to the equally large value of 156.0 Hz found for the central methylene group of **3**, can sp^3-hybridization be admitted for C(5).

Table 1. *Selected ^{1}H- and ^{13}C-NMR Parameters of the Organomanganese Compound* **6**, *5*H-*Dipyrroloimidazole* **3** *and its Lithium Salt* **4**

^{1}H-NMR, δ [ppm]	**6**[a])	**3**[a])	**4**[a])
H–C(1), H–C(9)	5.98	6.03	5.80
H–C(2), H–C(8)	6.26	6.24	6.14
H–C(3), H–C(7)	6.86	6.81	6.71
H–C(5),	6.58	5.70	5.65
$^1J_{H,C(5)}$[Hz]	163.1	156.0	

^{13}C-NMR, δ[ppm]	**6**[a])	**3**[a])	**4**[b])
C(1), C(9)	95.87	96.8	89.65
C(2), C(8)	113.3	113.1	108.8
C(3), C(7)	113.6	115.1	109.2
C(5)	67.59	62.1	83.39
C(9a), C(9b)	129.0	130.2	129.7
$(CO)_5$	209.6 (br.)		

[a]) In CD_2Cl_2, relative internal TMS, at 8.46 tesla.

[b]) In (D_8)THF, relative internal TMS, at 2.3 tesla.

The ^{13}C-NMR spectrum of **6** provides limited information about the number and nature of the carbonyl groups. At room temperature, a dissymmetric signal strongly broadened by the quadrupole momentum of the metal and presumably also by dynamic effects [7] [11] appears at 209.6 ppm.

The IR spectrum recorded in hexane is more informative. It shows three strong CO-stretching fundamentals at 2003, 2018, and 2025 cm^{-1}. They are accompanied by two weak bands at 2061 and 2116 cm^{-1}. This pattern strongly resembles that of other pentacarbonylmanganese complexes [12].

The precise structure of the title compound was finally made certain by X-ray-structure determination[1]). The result is depicted in the *Figure*. Selected geometric parameters are given in *Table 2*. Corresponding computed data (MINDO-3 [13]) of the parent dipyrroloimidazole **3** is included for comparison.

Table 2. *Selected Geometric Parameters with e.s.d.'s of* **6** (X-ray). Computed data (MINDO-3) for the free dipyrroloimidazole **3** are given in parentheses for comparison.

Distances [Å]			Bond angles [°]		
	6	**3**		**6**	**3**
Mn–C(5)	2.181(5)	–	N(4)–C(5)–N(6)	98.9(3)	(105.1)
Mn–C(10)	1.876(6)[a])	–	N(4)–C(5)–H	109(5)[a])	(112.7)
Mn–C(12)	1.854(6)[a])	–	N(4)–C(5)–Mn	115.9(3)[a])	–
Mn–C(14)	1.854(7)	–	Mn–C(5)–H	107(5)	–
N(4)–C(5)	1.465(6)[a])	(1.431)	C(5)–Mn–C(10)	89.0(2)[a])	–
N(4)–C(9b)	1.382(6)[a])	(1.421)	C(5)–Mn–C(12)	85.0(2)[a])	–
C(5)–H	1.02(9)	(1.136)	C(5)–Mn–C(14)	177.0(2)	–

[a]) Mean values with respect to the pseudo-C_s symmetry of **6**.

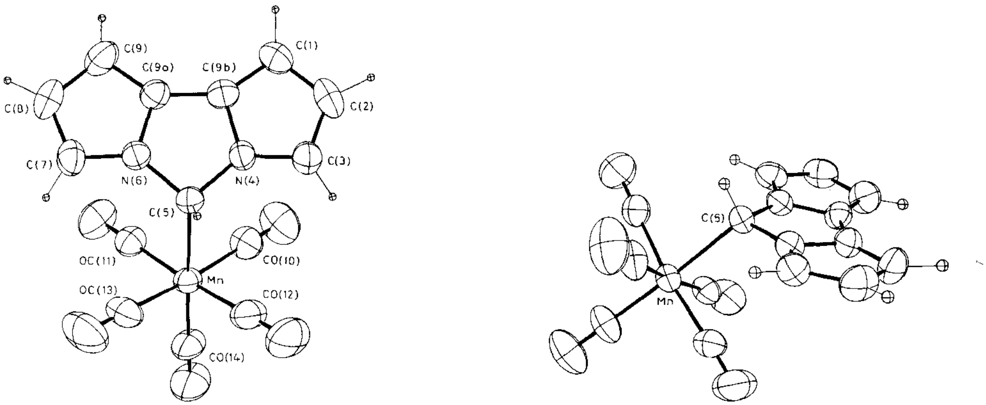

Figure. *X-ray structure of pentacarbonyl(5*H*-dipyrrolo[1,2-*c*:2',1'-*e*]imidazol-5-yl)manganese* (**6**) *in top and side view*

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[1]) Observed and calculated structure factors may be obtained on request from *G. B.* Crystallographic data has been deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England.

From the *Figure* it is seen that the heterocyclic ligand is nearly planar; the mean deviation from the best plane is 0.04 Å. The two N-atoms clearly are out of bonding distance for the manganese centre (N-Mn distance: 3.112(4) Å). The bond-angle deviation of C(5) from ideal sp^3-hybridization is substantial. The metal is kept in a slightly distorted octahedral ligand sphere. Its bonding to the heterocycle occurs *via* a σ-bond to C(5). The Mn-C(5) distance (2.181(5) Å) is compatible with the corresponding value found for methylpentacarbonyl manganese by electron scattering (2.185 Å) [14]. The two basal carbonyl groups CO(12) and CO(13) are slightly bent towards the dipyrroloimidazolyl ligand – a feature which the title compound shares with pentacarbonylhydrido manganese [15]. The apical carbonyl group (CO(14)) is found opposite to the heterocyclic ligand (bond angle C(5)-Mn-CO(14): 177.0(2)°).

From our findings, it becomes evident that dipyrroloimidazolide shows a basically differing behaviour from that of the isoelectronic fluorenyl anion. It is too poor an acceptor to allow for efficient backdonation and accompanying carbonyl extrusion from the metal centre. Since the more traditional binding modes of imidazole derivatives are obstructed for electronic or structural reasons, the ligand accommodates the metal simply by a Mn,C σ-bond. this feature, however, is rarely encountered in heterocyclic complexes of transition metals.

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Experimental Part

Crystallographic Data. $C_{14}H_7MnN_2O_5$, monoclinic, $P2_1/n$, $a = 10.311(1)$, $b = 9.294(1)$, $c = 15.382(3)$ Å; $Z = 4$, $d_c = 1.535$ g·cm^{-3}, $\mu = 8.88$ cm^{-1}, $F(000) = 680$. The lattice parameters and intensities were measured at r.t. on an automatic four-circle *Philips PW1100* diffractometer with graphite monochromated MoK_α radiation. Of the 2284 independent reflections recorded (ω-2θ scan), 1635 had $|F_o| > 3\sigma(F_o)$ and $|F_o| > 6$. The structure was solved by direct methods (MULTAN 80 [16]) and refined by full-matrix least-squares (XRAY 76 [17]). No absorption correction was made. All H-atoms were located from a ΔF and refined with blocked isotropic temperature factors ($U = 0.063$ Å^2). The atomic scattering factors and f' and f'' (for Mn atom) are from *Cromer & Waber* [18]. The final R factor, based on 1635 observed reflections was 0.040 ($wR = 0.057$ with $w = \exp[18.0(\sin\theta/\lambda)^2]$ [19].

*Pentacarbonyl(5*H*-dipyrrolo[1,2-*c*:2',1'-*e*]imidazol-5-yl)manganese* (**6**). At −78°, 5 ml (9.1 mmol) of 1.82M BuLi in hexane were added under N_2 and with stirring to 1.22 g (8.47 mmol) of **3** [4] in 30 ml of anh. THF. The mixture was allowed to warm to 0° and then recooled to −78°. In small portions, 1.7 g (7.38 mmol) of solid [$Mn(CO)_5Cl$] were added. The solvents were removed *i.v.* and replaced by 50 ml of dioxane/Et_2O 1:1. After addition of 100 mg of solid NH_4Cl, the solution as passed over a short silica-gel column. The deep yellow mixture remaining after solvent removal was taken up in the minimum of toluene. Column chromatography on silica gel (hexane/Et_2O 2:1) gave, in the order of increasing retention time, 144 mg (10%) of [$Mn_2(CO)_{10}$], 449 mg (18%) of **6** and 280 mg (23%) of **3**. **6**: yellow crystals, m.p. 123–125° (from hexane at 0°, $d = 1.53$ g·cm^{-3}. IR: see text. ^{1}H-NMR (360 MHz, C_6D_6): 6.65 (br. *d*, $^3J = 2.8$, H–C(3), H–C(7)); 6.44 ($\sim t$, H–C(2), H–C(8)); 6.23 (br. *d*, $J = 3.1$, H–C(1), H–C(9)); 5.70 (*s*, H–C(5)). ^{13}C-NMR: see *Table 1*. MS (70 eV): 338 (3, M^+), 210 (3), 198 (4), 143 (100, $M^+ - Mn(CO)_5$), 116 (12).

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