An Exception to the General Mechanism of CO Insertion into the Alkyl–Manganese Bond

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Two-electron donor ligands L enter *trans* (and not *cis* as in other manganese examples) to the acyl group in the reaction of *fac*-[Mn(CO)$_3$(bipy)(Me)] **1** with L to give *cis,trans*-[Mn(CO)$_2$(L)(bipy)(COMe)] **2**; the reaction of **1** with *CO (CO 99% enriched in ^{13}C) gives *cis,trans*-[Mn(CO)$_2$(*CO)(bipy)(COMe)] **4**, ruling out the formation of the possible intermediate *cis,cis*-[Mn(CO)$_2$(L)(bipy)(COMe)] **3**.

Carbonylation reactions play an important role in stoichiometric and catalytic organic and organometallic synthesis, both in the laboratory and industry. As a consequence, insertion reactions of CO into metal–alkyl bonds have been thoroughly investigated. After a large number of detailed studies, frequently using manganese carbonyl complexes as appropriate models, it is commonly accepted[1] that in these reactions the alkyl group migrates to an adjacent CO, and the incoming ligand L occupies a coordination site *cis* to the resulting acyl. (The initial product can eventually isomerize to a new complex, in which the acyl group and the ligand L are mutually *trans*.) However, a few exceptions are known; thus, it has been found that in the formation of several octahedral acyl complexes of Fe, Ru, Rh and Ir,[2] the incoming ligand enters in the coordination sphere *trans* to the acyl group, which is said to have a strong *trans*-directing effect. We present here results which support that also in the formation of certain manganese acyl complexes, containing 2,2′-bipyridine (bipy) as chelate ligand, the entering ligand occupies a position *trans* to the acyl group.

The methyl complex *fac*-[Mn(CO)$_3$(bipy)(Me)] **1**† which is

† Selected spectroscopic data for the new compounds: ν(CO)/cm^{-1}, NMR chemical shifts relative to internal Me$_4$Si (^{13}C) or external 85% H_3PO_4 (aq.) (^{31}P). Compound **1**: ν(CO) (CH_2Cl_2) 1988s and 1889s; ^{13}C NMR (CD_2Cl_2, 243 K) δ 228.9 (s, 2 C, CO) and 212.6 (s, 1 C, CO). Compound **2a**: ν(CO) (CH_2Cl_2) 1912s, 1844s and 1582w; ^{31}P NMR (C_6D_6, 25 °C) δ 176.6; ^{13}C NMR ($CDCl_3$, 25 °C) δ 287.0 (s, 1C, COMe) and 229.0 (s, 2C, CO). Compound **2b**: ν(CO) (CH_2Cl_2) 1897s, 1824s and 1571w; ^{31}P NMR (C_6D_6) δ 30.3; ^{13}C NMR (CD_2Cl_2) δ 286.4 (s, 1C, COMe) and 232.1 (s, 2C, CO). Compound **2c**: ν(CN) (CH_2Cl_2) 2074m; ν(CO) (CH_2Cl_2) 1916s, 1858s and 1580w; ^{13}C NMR ($CDCl_3$) δ 289.3 (s, 1C, COMe) and 228.5 (s, 2C, CO). Compound **2d**: ν(CO) (CH_2Cl_2) 1999s, 1910s, 1889s and 1598w; ^{13}C NMR ($CDCl_3$) δ 280.9 (s, 1C, COMe), 225.0 (s, 2C, CO) and 212.6 (s, 1C, CO).

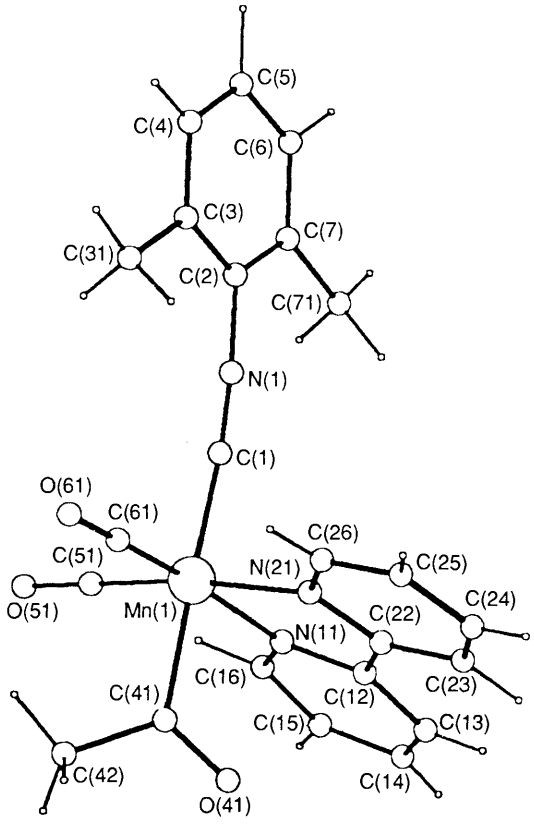


Fig. 1 Perspective view of the structure of *cis,trans*-[Mn(CO)$_2$(CN-2,6-Me$_2$C$_6$H$_3$)(COMe)] **2c**. Selected bond lengths (Å) and angles (°). Mn–N(11) 2.037(2), Mn–N(21) 2.029(2), Mn–C(1) 1.898(3), Mn–C(41) 2.056(3), Mn–C(51) 1.782(3), Mn–C(61) 1.767(3); N(11)–Mn–C(1) 96.0(1), N(21)–Mn–C(1) 91.8(1), N(11)–Mn–C(41) 84.0(1), N(21)–Mn–C(41) 86.3(1), C(1)–Mn–C(41) 178.0(1), N(11)–Mn–C(61) 171.9(1), N(21)–Mn–C(51) 172.8(1), Mn–C(1)–N(11) 174.9(3).

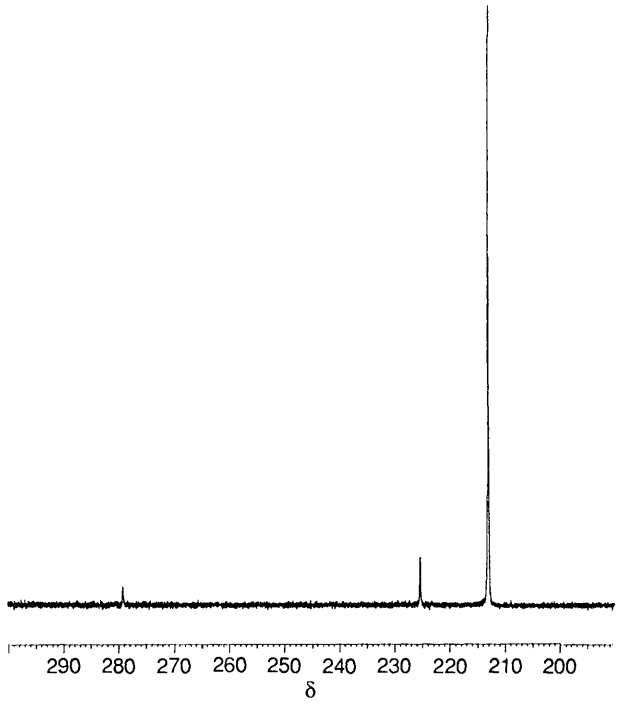


Fig. 2 ^{13}C NMR spectrum of **4** in the CO region. (CD$_2$Cl$_2$, −30 °C). δ 279.1 (s, 1C, COMe), 225.2 (s, 2C, CO *cis* to the acyl group) and 213.0 (s, 1C, *CO, *trans* to the acyl group).

easily obtained by reducing *fac*-[Mn(CO)$_3$(bipy)(Br)][3] with sodium amalgam in tetrahydrofuran and then adding methyl iodide, reacts with two-electron donor ligands L to give *cis*-dicarbonyl complexes *cis,trans*-[Mn(CO)$_2$(L)(bipy)-(COMe)]† (L: P(OMe)$_3$, **2a**; PEt$_3$, **2b**; CN-2,6-Me$_2$C$_6$H$_3$, **2c**) or *fac*-[Mn(CO)$_3$(bipy)(COMe)] (L: CO, **2d**).

The structure proposed for compounds **2a–d** is in accordance with their spectroscopic data,† and in the case of **2c**, it has been confirmed by an X ray diffraction study‡ (see Fig. 1).

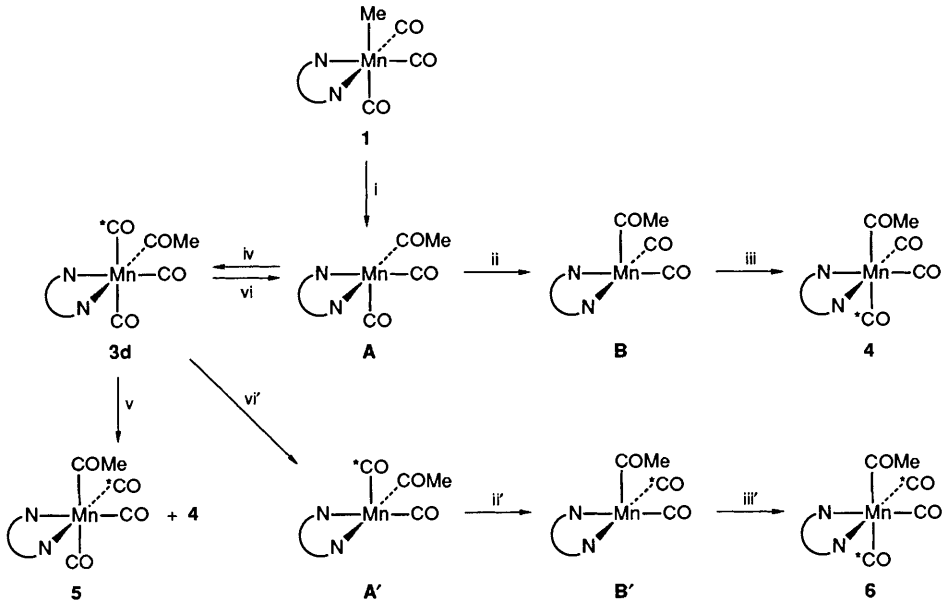
Apparently the geometry of **2** is a consequence of the fact that the incoming ligand enters in the manganese coordination sphere *trans* to the acyl group, and not the result of an isomerization of a hypothetical *cis,cis* intermediate complex such as *cis,cis*-[Mn(CO)$_2$(L)(bipy)(COMe)] **3**, which is the expected product according to the most commonly accepted mechanism[1] for carbonyl insertion into metal–alkyl bond. In fact, **2a** is the only complex containing P(OMe)$_3$ detected by ^{31}P NMR spectroscopy, from the reaction of **1** with P(OMe)$_3$ at −40 °C.

Moreover, the reaction of *fac*-[Mn(CO)$_3$(bipy)(Me)] **1** with *CO (CO 99% enriched in ^{13}C) gives the tricarbonyl *cis,trans*-[Mn(CO)$_2$(*CO)(bipy)(COMe)] **4**, the ^{13}C NMR of which, in the CO region, is shown in Fig. 2. The formation of **4** is only possible if the entering *CO occupies initially a position *trans* to the acyl group, and rules out the possibility of the CO ligand entering *cis* to the acyl group, as it is shown in Scheme 1. This Scheme presents the possible mechanisms for the reaction of **1** with *CO. Thus, after methyl migration (i in Scheme 1), the five coordinated intermediate **A** could either isomerize to **B** or add a molecule of *CO to give **3d**. In the first case, L would enter *trans* to the acyl group to give **4**, the observed product (iii in Scheme 1). In the second, **3d** would evolve to an equimolecular mixture of the isotopomers **4** and **5** if an intramolecular mechanism is operating (v in Scheme 1), or to a mixture of **4** and **6** in equal amounts if the formation of the tricarbonyls follows an intermolecular pathway (vi, ii, iii and vi′, ii′, iii′, respectively in Scheme 1); however, a 1:1 mixture of isotopomers (**4** plus **5** or **4** plus **6**) is incompatible with the observed ^{13}C NMR spectrum shown in Fig. 2.

Following similar arguments, it is possible to show that the formation of **4** would also imply that the incoming ligand L enters *trans* to the acyl group, even if the first step in the reaction of **1** with L were actually an insertion of a CO ligand into the manganese–methyl bond. In the same way, if a concerted mechanism were operating in our system, it is easy to see that the ligand L should also enter *trans* to the acyl group in order to explain the observed results.

On the other hand, in each of the complexes **2a–d** the L ligands are replaced under very mild conditions by other ligands L′ (L = L′ = P(OMe)$_3$, PEt$_3$, CN-2,6-Me$_2$C$_6$H$_3$ and CO), indicating that the acyl group has a strong *trans*-labilizing

‡ *Crystal data* for compound **2c**: $C_{23}H_{19}MnN_3O_3$, M = 440.36, triclinic, space group $P\bar{1}$, a = 7.355(7), b = 9.072(1), c = 16.137(9) Å, α = 95.33(4), β = 95.2(1), γ = 95.87(2)°, V = 1061(1) Å^3, Z = 2, D_c = 1.38 g cm^{-3}, μ(Mo-Kα) = 0.62 mm^{-1}; crystal dimensions 0.50 × 0.25 × 0.03 mm^3. T = 293 K; measuring range $0 < 2\theta < 50°$; 3881 unique reflections, 2681 observed with $I > 3\sigma(I)$. Semiempirical and empirical absorption corrections were applied. Anisotropic temperature factors for non-hydrogen atoms; 314 refined parameters R = 0.036, R_w = 0.038. Maximum shift/error = 0.01, maximum residual electron density = 0.31 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 Possible mechanisms for the reaction of **1** with *CO (CO 99% enriched in ^{13}C)

influence.§ The relationship between the *trans*-labilizing influence and a *trans*-directing effect of the acyl groups has been pointed out previously[2a] and has been observed in other examples in which the entering ligand occupies a position *trans* to the acyl.[2]

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§ It is known that *N,N'*-chelate ligands like bipy have a strong *cis*-labilization effect. However, the simple presence of the bipy ligand does not explain the very mild conditions in which these reactions take place. For example, the substitution of a CO *cis* to the bipy or phen ligand in *fac*-tricarbonyl complexes of manganese(I) require more forcing conditions[4a] or the use of a decarbonylating agent like $ONMe_3$.[4b]

References

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