

Preliminary communication

**Isomerization of cationic carbonyls of manganese(I)
with *N*-donor chelate ligands promoted by reduction**

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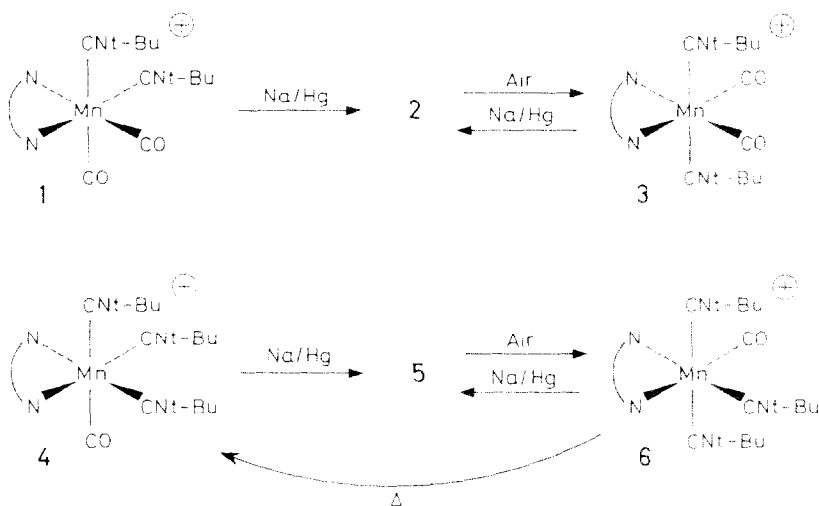
(Received November 27th, 1986)

Abstract

The carbonyls *cis,cis*-[Mn(CO)₂(CN-t-Bu)₂(N–N)]ClO₄ and *fac*-[Mn(CO)(CN-t-Bu)₃(N–N)]ClO₄, (N–N = 2,2'-bipyridine, bpy, and 1,10-phenantroline, phen), are isomerized to *cis,trans*- and *mer*-complexes respectively by reduction in acetonitrile with sodium amalgam and subsequent oxidation by air. The structure of *fac*-[Mn(CO)(CN-t-Bu)₃(bpy)]ClO₄ has been determined by X-ray diffraction.

Considerable attention has been focused on redox processes involving structural changes [1]. Among these, isomerizations occurring as a consequence of a reduction are scarcer than those promoted by oxidation and to the best of our knowledge only two cases have been reported in which reductions involving octahedral 19 electron species lead to isomerization. In the first [2], the reduction of monocarbene complexes alters the conformation of a phenyl ring in the carbene ligand; in the second [3], *trans*-[Co(iminoacetato)₂][–] undergoes isomerization to the *cis*-complex.

On the other hand, metal complexes containing polypyridyl ligands such as bpy or phen have been extensively used for experiments in photochemical energy storage [4] and more recently to catalyze the reduction of CO₂ to CO [5]. In continuation of our work on the derivatives of *fac*-[Mn(CO)₃(CNR)(N–N)]ClO₄, (CNR = CN-t-Bu, CNPh; N–N = bpy, phen) [6], we describe here the first isomerizations of 18 electron manganese octahedral carbonyls promoted by reduction.



Scheme 1

Stirring at room temperature of solutions of *cis,cis*-[Mn(CO)₂(CN-*t*-Bu)₂(bpy)]ClO₄ (**1** in Scheme 1) [6] in acetonitrile with sodium amalgam causes the initially brown colour to turn to deep-blue. Under N₂ this solution does not change its colour, but in the air it turns brown, and *cis,trans*-[Mn(CO)₂(CN-*t*-Bu)₂(bpy)]ClO₄ (**3a**), can be isolated from it in good yield (60%) [7 *]. **3a** is reduced by sodium amalgam in MeCN to give a deep-blue solution, from which, after exposure to air, **3a** can be recovered. So far, we have not been able to isolate any neutral or anionic compound from these deep-blue solutions. From the literature [5,8], it seems probable that the blue species could be a neutral radical [Mn(CO)₂(CN-*t*-Bu)₂(bpy)] (**2a**) (either an isomer or a mixture of isomers). **2a** would be oxidized to **3a** by the air. The same procedure gave *cis,trans*-[Mn(CO)₂(CN-*t*-Bu)₂(phen)]ClO₄ (**3b**). The intermediate species **2b** is green and not as stable as **2a**.

Similarly *fac*-[Mn(CO)(CN-*t*-Bu)₃(N-N)]ClO₄ (N-N = bpy, **4a**; phen, **4b**) [6] react in an inert atmosphere with sodium amalgam in MeCN to give green-blue solutions, which are also stable under N₂ for some hours, but turn dark-brown in the air. From the dark-brown solutions *mer*-[Mn(CO)(CN-*t*-Bu)₃(N-N)]ClO₄ (N-N = bpy, **6a**; phen, **6b**) were isolated in good yield (65%) [9 *]. **6a** and **6b** are reversibly reduced with Na/Hg in MeCN; the intermediate **5** in Scheme 1 could be the neutral green-blue radical [Mn(CO)(CN-*t*-Bu)₃(N-N)][•] (one isomer or a mixture).

Only one structure of octahedral manganese(I) monocarbonyls has been determined by X-ray diffraction [10]. In order to establish the geometry of one of the monocarbonyl isomers, the crystal structure of complex **4a** was determined [11 *]. The structure is shown in Fig. 1, together with the more relevant bond distances and angles. The coordination around the manganese atom displays a distorted oc-

* Asterisk indicates a note in the list of references.

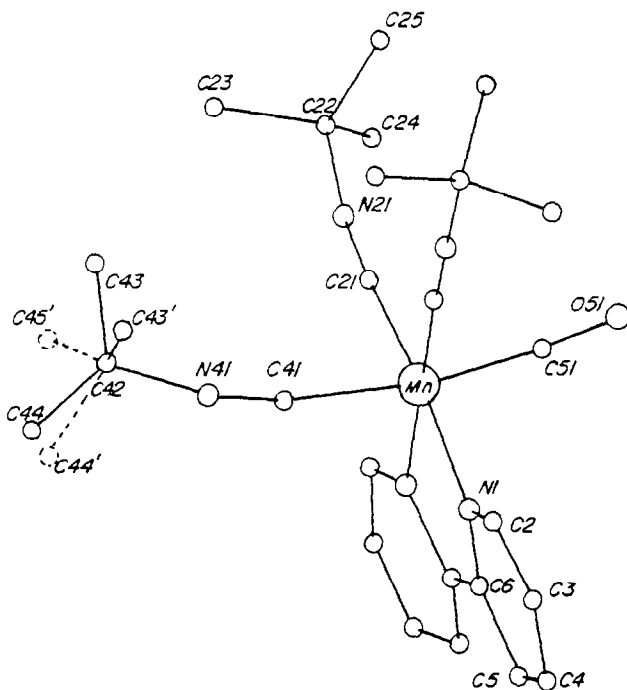


Fig. 1. Structure of the cation $fac\text{-}[\text{Mn}(\text{CO})(\text{CN}\text{-}t\text{-Bu})_3(\text{bpy})]^+$ (**4a**), with the atom numbering scheme. Relevant bond distances (Å), and angles, ($^\circ$): Mn–N(1): 2.058(3); Mn–C(21): 1.876(4); Mn–C(41): 1.971(5); Mn–C(51): 1.808(5); N(21)–C(21): 1.176(5); N(41)–C(41): 1.147(7); C(51)–O(51): 1.151(6). N(1)–Mn–C(21): 174.2(1); Mn–C(21)–N(21): 179.2(3); Mn–C(41)–N(41): 171.7(5).

tahedral geometry with the three isocyanide ligands in mutually *cis* positions, in accord with spectroscopic data. Bond distances and bond angles fall in the expected ranges.

The *fac*-complex **4** seems to be the thermodynamically stable monocarbonyl isomer, since the *mer*-monocarbonyl **6** isomerizes to **4** when heated in CH_2Cl_2 . No thermal interconversion is observed between the dicarbonyls **1** and **3**.

Acknowledgements. We thank the Spanish C.A.I.C.Y.T. for financial support, and the University of Barcelona for a grant.

References and notes

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- For **3a**. ^1H NMR: δ (CN-*t*-Bu) 1.24 ppm, s. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CN})$ 2145 s; $\nu(\text{CO})$ 1975s, 1912s. For **3b**. ^1H NMR: δ (CN-*t*-Bu) 1.12 ppm, s. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CN})$ 2140 s; $\nu(\text{CO})$ 1975s, 1912s.
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- 9 For **6a**. $^1\text{H NMR}$: δ (CN-t-Bu) (ppm) 1.22 s (18H), 1.56 s (9H). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CN})$ 2160 m, 2117 s, 2067 m, sh; $\nu(\text{CO})$ 1893 s.
For **6b**. $^1\text{H NMR}$: δ (CN-t-Bu) (ppm) 1.22 s (18H), 1.58 s (9H). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CN})$ 2160 m, 2115 s, 2068 m, sh; $\nu(\text{CO})$ 1893s.
- 10 M. Laing and P.M. Treichel, *J. Chem. Soc., Chem. Commun.*, (1975) 746.
- 11 Crystal data for **4a**. $\text{C}_{26}\text{H}_{35}\text{N}_3\text{OMn}$, ClO_4 , $F_w = 587.97$, monoclinic, a 15.311(3), b 12.264(2), c 8.285(2) Å, β 93.62(2)°, V 1552.6(9) Å³, $P2_1/m$, D_x 1.257 g cm⁻³, $Z = 2$, $F(000) = 616$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 5.75 cm⁻¹. Room temperature. The intensities of 2578 independent reflections were determined on a Philips PW1100 four circle diffractometer (with θ in the range 2–25°) and 2525 were assumed as observed by application of the condition $I \geq 2.5 \sigma(I)$. Lorentz-polarization but no absorption corrections were made. Graphite monochromatized Mo-K α radiation and the ω -scan technique were used. The structure was solved by direct methods, using the MULTAN system of computer programs (Univ. of York, England, and Univ. Louvain, Belgium) and refined by full-matrix least-squares, using SHELX76 computer program (Univ. of Cambridge). The final value of R was 0.066 ($R_w = 0.079$) for all observed reflections.