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Preliminary communication

A NEW ROUTE TO *mer*-TRICARBONYLS OF MANGANESE(I) CONTAINING N-DONOR CHELATE LIGANDS

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Summary

It has been shown that new *mer*-tricarbonyls *mer*-$[Mn(CO)_3L(tmed)]ClO_4$, (tmed = *N,N,N',N'*-tetramethylethylenediamine, L = $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$) can be readily obtained from the reaction between *fac*-$Mn(CO)_3(tmed)Br$, $AgClO_4$, and L at room temperature, whereas at 0°C *fac*-isomers are produced. The opposite is the case for L = CN-t-Bu; *mer*-$[Mn(CO)_3(CN\text{-}t\text{-}Bu)(tmed)]ClO_4$ is observed at 0°C, and the *fac*-isomer is stable at 25°C.

Recently [1] we isolated the first two *mer*-tricarbonyls of manganese(I) containing N-donor chelate ligands, *mer*-$[Mn(CO)_3(CN\text{-}t\text{-}Bu)(N\text{-chelate})]ClO_4$, (N-chelate: 2,2′-bipyridine, bipy, 1,10-phenanthroline, phen) by decarbonylating the *fac*-isomer with $ONMe_3$ and then bubbling CO through the solution. This method is apparently only useful when the third ligand is CNR. Up to now no other *mer*-tricarbonyl of manganese(I) with N-chelate ligands have been reported, and, indeed, *mer*-tricarbonyls of d^6 metals such as chromium(0) and molybdenum(0) containing N-chelate ligands are very scarce, and kinetic reasons have been advanced to account for their inaccessibility [2]. In continuation of our work in this field we have found that by use of tmed (which is more bulky than bipy and phen) as the N-chelate it is possible not only to generate *mer*-tricarbonyls with CNR by the $ONMe_3$ route but also *mer*-$[Mn(CO)_3L(tmed)](ClO_4)$ (L = phosphites) in a straightforward way.

$Mn(CO)_5Br$ reacts with tmed in refluxing hexane to give *fac*-$Mn(CO)_3(tmed)Br$ (**1** in Scheme 1) as a yellow precipitate [3].

Halide abstraction from **1** with $AgClO_4$, followed by addition of the ligand L gives the yellow *mer*-$[Mn(CO)_3L(tmed)]ClO_4$, (L = $P(OMe)_3$, **3a**; $P(OEt)_3$, **3b**; $P(O\text{-}i\text{-}Pr)_3$, **3c**) in good yield (60%) [4]. The isolation of the *mer*-tricarbonyls was

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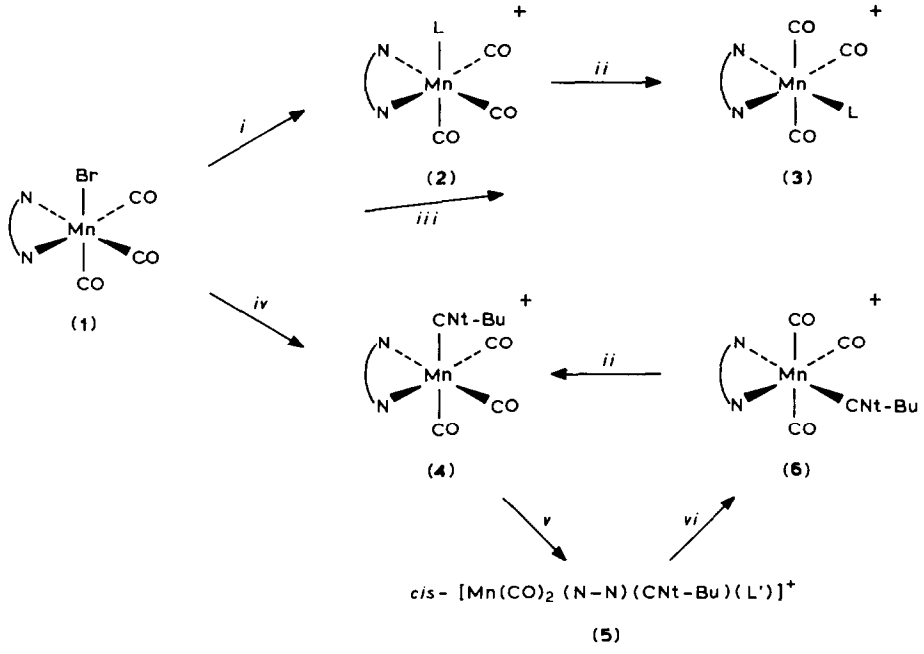

SCHEME 1. N–N: tmed. (i) $AgClO_4$ and L at 0°C; (ii) stirring at room temperature (r.t.); (iii) $AgClO_4$ and L at r.t.; (iv) $AgClO_4$ and CN-t-Bu; (v) $ONMe_3$; (vi) CO.

somewhat surprising, since the expected products were the *fac*-isomers, in view of the *cis*-labilizing effect of the N atoms of the tmed. Indeed, when the reaction was repeated at 0°C, *fac*-$[Mn(CO)_3L(tmed)]ClO_4$, (L = $P(OMe)_3$, **2a**, $P(OEt)_3$, **2b**; $P(O\text{-}i\text{-}Pr)_3$), **2c**) were formed (yield 66%) [5]. They isomerize to the *mer*-complexes **3** in CH_2Cl_2 solution at room temperature.

Complex **1** gives *fac*-$[Mn(CO)_3(CN\text{-}t\text{-}Bu)(tmed)]ClO_4$ (**4**) by replacement of Br by ClO_4 followed by addition of CN-t-Bu [6]. When **4** is stirred with $ONMe_3$, a *cis*-dicarbonyl is formed, (ν(CO) (cm^{-1}): 1937s, 1863s; ν(CN) (cm^{-1}): 2124 m), probably *cis*-$[Mn(CO)_2(CN\text{-}t\text{-}Bu)(tmed)L']ClO_4$ (**5**) (L' = NMe_3, sometimes NMe_3 can be replaced by $ONMe_3$) [7,8]. Complex **5** could not be isolated, since it decomposed during the work up. Bubbling of CO through a CH_2Cl_2 solution of **5** at room temperature gave the *fac*-tricarbonyl **4**, but at 0°C *mer*-$[Mn(CO)_3(CN\text{-}t\text{-}Bu)(tmed)]ClO_4$ (**6**) was obtained [9], contaminated with small amounts of the *fac*-tricarbonyl **4**. Purification of **6** was not possible because of its rapid isomerization to the *fac*-tricarbonyl **4**. Similar isomerization, at higher temperatures, was observed for *mer*-$[Mn(CO)_3(CN\text{-}t\text{-}Bu)(bipy)]ClO_4$ and *mer*-$[Mn(CO)_3(CN\text{-}t\text{-}Bu)(phen)]ClO_4$ [1].

The greater thermal stability of **4** than of **6**, and the fact that **1** does not change its geometry in refluxing hexane, suggest that the dominant influence on the isomerization of *fac*-$[Mn(CO)_3L(tmed)]ClO_4$ (**2**) (L = phosphites) to the corresponding *mer*-complexes **3** is not electronic but steric.

The complexes have been fully characterized by elemental analysis (C,H,N) and by IR and ^1H NMR spectroscopy. The ^1H NMR spectra of pure samples of

fac-tricarbonyls **2**, recorded at room temperature, always reveal the presence of small quantities of the *mer*-isomers **3**.

The possibility of obtaining new *mer*-tricarbonyls containing other bulky N-chelates and extending the studies to other metals is now being explored.

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References and notes

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2 G.R. Dobson, K.I. Asali and N.S. Binzet, 183rd Am. Chem. Soc. Meeting, March/April, 1982, ref. 57.
3 For **1**. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2039s, 1935s, 1898s. Yield 95%.
4 For **3a**. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2071w, 1965s, 1941m. ^1H NMR ($CDCl_3$, δ in ppm, J in Hz). δ(tmed): 2.88,s (16H). $\delta(P(OCH_3)_3)$: 3.84,d; J(PH): 10.4 (9H).
For **3b**. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2068w, 1962s, 1937m. ^1H NMR ($CDCl_3$, δ in ppm, J in Hz). δ(tmed): 2.88, s; (16H). $\delta P(OCH_2CH_3)_3$: 1.38, t; J(HH) 6.3 (9H). $\delta(P(OCH_2CH_3)_3)$: 4.10, q, d; $J(HH) = J(PH) = 6.3$ (6H).
For **3c**. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2068w, 1961s, 1933m. ^1H NMR ($CDCl_3$, δ in ppm, J in Hz). δ(tmed): 2.80,s (16H). $\delta(P(OCH(CH_3)_2)_3)$: 1.30, d; J(HH) 6.0 (18H). $\delta(P(OCH(CH_3)_2)_3)$: 4.96, m (3H).
5 For **2a**. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2050s, 1955s, 1935s. ^1H NMR ($CDCl_3$, δ in ppm, J in Hz). δ(tmed): 2.90, s (10H), and 2.99, s (6H). $\delta(P(OCH_3)_3)$: 4.00, d; J(PH) 11.0 (9H).
For **2b**. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2048s, 1952s, 1936s. ^1H NMR ($CDCl_3$, δ in ppm, J in Hz). δ(tmed): 2.90, s (10H) and 2.99, s (6H). $\delta(P(OCH_2CH_3)_3)$: 1.43, t; J(HH) 7.0; (9H). $\delta(P(OCH_2CH_3)_3)$: 4.30, q, d; $J(HH) = J(PH) = 7.0$; (6H).
For **2c**. IR (CH_2Cl_2, cm^{-1}). ν(CO): 2045s, 1952s, 1938s. ^1H NMR $CDCl_3$, δ in ppm, J in Hz). δ(tmed): 2.91, s (10H) and 2.99, s (6H). $\delta(P(OCH(CH_3)_2)_3)$: 1.50, d; J(HH) 6.3; (18H). $\delta(P(OCH(CH_3)_2)_3)$: 4.85, m (3H).
6 For **4**. IR (CH_2Cl_2, cm^{-1}). ν(CN): 2188m. ν(CO): 2050s, 1960s, 1948s. ^1H NMR ($CDCl_3$, δ in ppm) δ(tmed): 2.88, s (8H) and 2.96, s (8H). $\delta(CNC(CH_3)_3)$: 1.69, s (9H).
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8 P.O. Nubel, S.R. Wilson and T.L. Brown, Organometallics, 2 (1983) 515.
9 For **6**. IR (CH_2Cl_2, cm^{-1}). ν(CN): 2168m. ν(CO): 2070w, 1975s, 1950m.