

Isocyanide migration from an axial to an equatorial position in the synthesis of octahedral cationic carbonyl complexes of manganese(I) containing nitrogen donor chelate ligands

F.J. Garcia Alonso, V. Riera

Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo (Spain)

and M. Vivanco

Departamento de Química Inorgánica, Universidad de Valladolid, 4700.5 Valladolid (Spain)

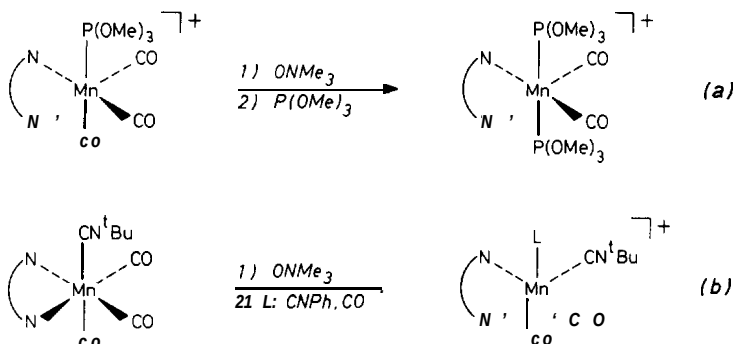
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Abstract

Several manganese carbonyl complexes of the type $[\text{Mn}(\text{CO})_m(\text{CN}^t\text{Bu})_n(\text{L})_p(\text{L}-\text{L})]\text{ClO}_4$ ($m + n + p = 4$; $m = 1-3$; $n = 1-3$; $p = 0, 1$; $\text{L} = \text{P}(\text{OMe})_3$, CNPh ; $\text{L}-\text{L} = 2,2'$ -bipyridine (bipy), 1,10-phenantroline (phen), bis(*t*-butyl)-1,4-diazabuta-2,3-diene ($^t\text{Bu-DAB}$), $\text{N}, \text{N}, \text{N}', \text{N}'$ -tetramethylethylenediamine (tmed)) have been prepared starting either from *fac*- $[\text{Mn}(\text{CO})_3(\text{CN}^t\text{Bu})(\text{L}-\text{L})]\text{ClO}_4$ or *fac*- $[\text{Mn}(\text{CO})_3\{\text{P}(\text{OMe})_3\}(\text{L}-\text{L})]\text{ClO}_4$ and using ONMe_3 as decarbonylating agent. The stereochemistry of the substitution reactions products is discussed in terms of the nature of the possible intermediates.

Introduction

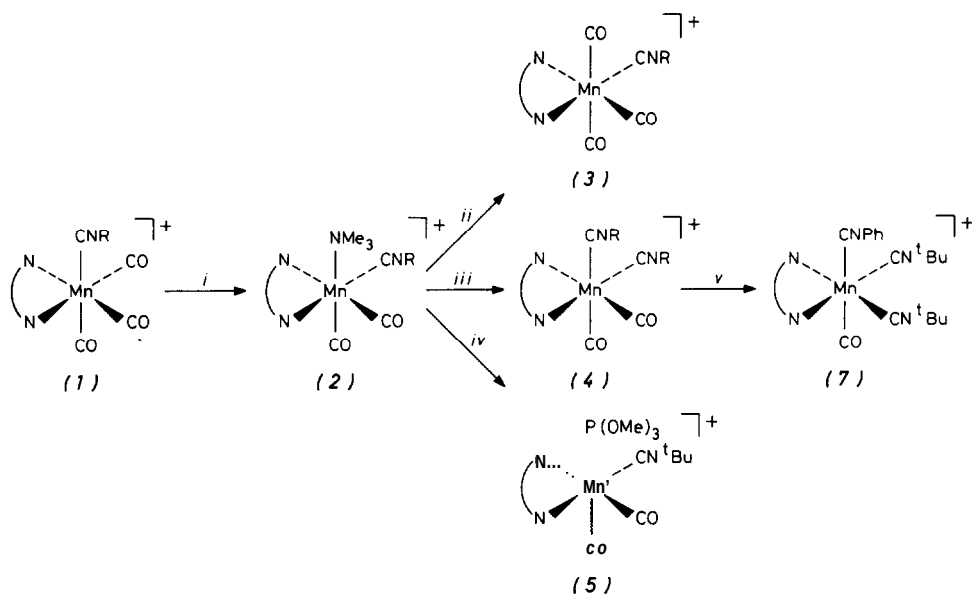
The reaction of the tricarbonyl complex *fac*- $[\text{Mn}(\text{CO})_3\{\text{P}(\text{OMe})_3\}(\text{phen})]\text{ClO}_4$ with ONMe_3 and $\text{P}(\text{OMe})_3$ at room temperature leads to the dicarbonyl *cis,trans*- $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\text{phen})]\text{ClO}_4$ [1] (Eq. a), which had been reported previously [2]. However, under the same conditions the isocyanide derivatives *fac*- $[\text{Mn}(\text{CO})_3(\text{CNR})(\text{N}-\text{N})]\text{ClO}_4$, ($\text{N}-\text{N} = \text{bipy}, \text{phen}$) were found to react with CNR in presence of ONMe_3 to give the dicarbonyl *cis,cis*- $[\text{Mn}(\text{CO})_2(\text{CNR})_2(\text{N}-\text{N})]\text{ClO}_4$ [3]. Moreover, the complex *fac*- $[\text{Mn}(\text{CO})_3(\text{CN}^t\text{Bu})(\text{phen})]\text{ClO}_4$ is known to react with ONMe_3 and subsequently with CNPh or CO to give *cis,cis*- $[\text{Mn}(\text{CO})_2(\text{CNPh})(\text{CN}^t\text{Bu})(\text{phen})]\text{ClO}_4$ or *mer*- $[\text{Mn}(\text{CO})_3(\text{CN}^t\text{Bu})(\text{phen})]\text{ClO}_4$, in which the CN^tBu ligands occupy equatorial positions (Eq. b) [3,4].



In order to investigate the stereochemical aspects of these reactions further we have carried out some additional experiments, the results of which are presented here. A preliminary account has appeared [5].

Results and discussion

The reaction of *fac*-[Mn(CO)₃(CN^tBu)(N-N)]ClO₄ (N-N = bipy (**1a**) and phen (**1b**)) with an excess of ONMe₃ in CH₂Cl₂ at room temperature led to *cis*-[Mn(CO)₂(CN^tBu)(NMe₃)(N-N)]ClO₄(**2**) [3] (reaction i in Scheme 1) (the possibility of a partial substitution of the NMe₃ ligand in **2** by ONMe₃ could not be completely excluded [3]). Although compounds **2** could not be isolated in a pure state, their stereochemistry is suggested to be as shown in Scheme 1, in accordance



Scheme 1. N-N = bipy or phen; (i) ONMe₃; (ii) CO, (iii) CNR; (iv) P(OMe)₃; (v) ONMe₃ and CNPh in refluxing CH₂Cl₂

Table 1

Melting points, conductivities, and analytical data for the new compounds

Compound	M.p. ^a (°C)	Λ_M^b (S cm ² mol ⁻¹)	Analysis [Found (calculated)(%)]		
			C	H	N
<i>cis</i> -[Mn(CO) ₂ {P(OMe) ₃ }(CN ^t Bu)(bipy)]ClO ₄ (5a)	137	146	41.3 (44.2)	4.6 (4.3)	7.2 (7.3)
<i>cis</i> -[Mn(CO) ₂ {P(OMe) ₃ }(CN ^t Bu)(phen)]ClO ₄ (5b)	141	140	(44.2)	(4.4)	6.9 (7.0)
<i>cis</i> -[Mn(CO) ₂ (CN ^t Bu){P(OMe) ₃ }(bipy)]ClO ₄ (6a)	180	136	41.4 (41.8)	4.6 (4.6)	7.1 (7.3)
<i>cis</i> -[Mn(CO) ₂ (CN ^t Bu){P(OMe) ₃ }(phen)]ClO ₄ (6b)	179	138	44.1 (44.2)	4.4 (4.4)	7.1 (7.0)
<i>cis</i> -[Mn(CO)(CNPh)(CN ^t Bu) ₂ (bipy)]ClO ₄ (7a)	148	144	54.6 (54.8)	5.0 (4.9)	11.5 (11.0)
<i>cis</i> -[Mn(CO)(CNPh)(CN ^t Bu) ₂ (phen)]ClO ₄ (7b)	150	143	56.4 (57.0)	4.9 (4.9)	11.4 (11.1)
<i>fac</i> -[Mn(CO) ₃ (CN ^t Bu)(^t Bu-DAB)]ClO ₄ (8a)	165	140	43.6 (44.1)	6.1 (6.0)	8.3 (8.6)
<i>fac</i> -[Mn(CO) ₃ (CN ^t Bu)(tmed)]ClO ₄ (8b)	115	140	38.1 (38.4)	5.8 (5.8)	9.5 (9.6)
<i>mer</i> -[Mn(CO) ₃ (CN ^t Bu)(^t Bu-DAB)]ClO ₄ (10a)		141	43.7 (44.1)	6.1 (6.0)	8.5 (8.6)
<i>cis,cis</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (^t Bu-DAB)]ClO ₄ (11a)	160	138	48.2 (48.5)	7.2 (7.0)	10.2 (10.3)
<i>cis,cis</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (tmed)]ClO ₄ (11b)	173	142	43.2 (43.9)	7.0 (6.9)	11.6 (11.4)
<i>cis,trans</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (^t Bu-DAB)]ClO ₄ (12a)	204	138	48.6 (48.5)	7.4 (7.0)	10.2 (10.3)
<i>cis,trans</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (tmed)]ClO ₄ (12b)	169	144	43.2 (43.8)	6.9 (6.9)	11.3 (11.4)
<i>fac</i> -[Mn(CO)(CN ^t Bu) ₃ (^t Bu-DAB)]ClO ₄ (13a)	134	134	51.2 (52.0)	7.4 (7.9)	11.2 (11.7)
<i>fac</i> -[Mn(CO)(CN ^t Bu) ₃ (tmed)]ClO ₄ (13b)	^d	142	47.8 (48.2)	8.0 (7.9)	12.7 (12.8)
<i>mer</i> -[Mn(CO)(CN ^t Bu) ₃ (^t Bu-DAB)]ClO ₄ (14a)	158	144	52.3 (52.0)	1.8 (7.9)	11.7 (11.7)
<i>mer</i> -[Mn(CO)(CN ^t Bu) ₃ (tmed)]ClO ₄ (14b)	133	140	48.1 (48.2)	8.1 (7.9)	12.9 (12.8)

^a With decomposition. ^b Measured in $5 \times 10^{-4} M$, acetone solution at 25 °C. ^c It isomerizes to **8a**. ^d It isomerizes to **14b**.

with the spectroscopic data for *cis*-[Mn(CO)₂(CN^tBu)(NMe₃)(bipy)]ClO₄ (**2a**) shown in Table 2. Thus, the ¹H NMR spectrum of **2a** exhibits a peak at 1.65 ppm *, which indicates that the CN^tBu ligand occupies an equatorial position. The assignment is consistent with the data in Table 3, which show a correlation between the coordina-

* It should be pointed out that the spectrum of the mixture obtained by adding ONMe₃ to *fac*-[Mn(CO)₃(CN^tBu)(bipy)]ClO₄ also shows a very small peak at 1.22 ppm. This signal probably corresponds to more substituted species, such as *cis,cis*-[Mn(CO)₂(CN^tBu)₂(bipy)]ClO₄ or *fac*-[Mn(CO)(CN^tBu)₃(bipy)]ClO₄, which are always detected by infrared spectroscopy. It has not been possible to avoid these impurities because of the instability of the diacarbonyl complexes **2**.

Table 2

Spectroscopic data for the new compounds

Compound	IR ^a (cm ⁻¹)		¹ H NMR ^b (6 in ppm, <i>J</i> in Hz)	
	$\nu(\text{CN})$	$\nu(\text{CO})$	CN-C(CH ₃) ₃	Other signals
2a	2130, m	1950, s 1880, s	1.65, s	9.03, m; 8.63, m; 8.20, m; 8.00, m; 7.57, m (bipy). 2.90 (br, NMe₃)
5a	2134, s	1986, s 1914, s	1.60, s	9.00 , m; 8.35, m; 8.10, m; 7.70, m; 7.47, m. (bipy). 3.41 (d, P(OCH₃)₃ , <i>J</i> (HP) = 10)
5b	2130, s	1982, s 1910, s	1.65, s	9.34, m; 8.66, m; 8.20, m; 8.11, s; 7.88, m. (phen). 3.31 (d, P(OCH₃)₃ , <i>J</i> (HP) = 10)
6a	2168, m	1971, s 1904, s	1.23, s	9.0, m; 8.74, m; 8.22, m; 7.54, m. (bipy) 3.41 (d, P(OCH₃)₃ , <i>J</i> (HP) = 10)
6b	2157, m	1967, s 1900, s	1.12, s	9.41, m; 8.77, m; 8.21 s; 8.00, m. (phen) 3.32 (d, P(OCH₃)₃ , <i>J</i> (HP) = 10)
7a	2152, s 2105, s 2062, s	1934, s	1.58, s	8.93, m; 8.37, m; 8.08, m; 7.45, m. (bipy) 7.29 (m, CNPh)
7b	2145, s 2097, s 2052, s	1929, s	1.62, s	9.31, m; 8.55, m; 8.04, s; 7.93, m. (phen) 7.30 (m, CNPh)
8a	2198, m	2051, s 1975, s 1942, s	1.54, s	162, s, [(CH ₃) ₃ C-N=CH] ₂ 8.57, s, [(CH ₃) ₃ C-N=CH] ₂
8b	2188, m	2050, s 1960, s 1948, s	1.69, s	2.88, s, br; 2.96, s, br, (tmed)
10a	2152, m	2080, s 1999, s 1950, s	1.57, s	1.60, s; 1.61, s [(CH ₃) ₃ C-N=CH] ₂ 8.61, s; 8.54, s, [(CH ₃) ₃ C-N=CH] ₂
11a	2183, m 2135, s	1982, s 1918, s	1.52, s 1.49, s	1.57, s, br, [(CH ₃) ₃ C-N=CH] ₂ 8.52, s; 8.46, s, [(CH ₃) ₃ C-N=CH] ₂
11b	2172, m 2132, m	1965, s 1907, s	1.66, s 1.48, s	2.80, m, (tmed)
12a	2150, s	1970, s 1905, s	1.42, s	1.59, s, [(CH ₃) ₃ C-N=CH] ₂ 8.56, s, [(CH ₃) ₃ C-N=CH] ₂
12b	2128, s	1971, s 1904, s	1.54, s	2.72, m, (tmed)
13a	2170, s 2118, vs 2060, s	1927, vs	1.49, s (18 H) 1.46, s (9 H)	1.56, s, [(CH ₃) ₃ C-N=CH] ₂ 8.43, s, [(CH ₃) ₃ C-N=CH] ₂
13b	2155, s 2105, s 2040, s	1900, vs	1.63, s (9H) 1.43, s (18 H)	2.64, s, br; 2.74, s, br, (tmed)
14a	2155, sh 2120, vs 2062, sh	1891, s	1.48, s (9 H) 1.40, s (18 H)	1.58, s, [(CH ₃) ₃ C-N=CH] ₂ 8.50, s; 8.46, s, [(CH ₃) ₃ C-N=CH] ₂
14b	2150, w 2092, s 2065, sh	1885, s	1.54, s (18 H) 1.44, s (9 H)	2.76, s, br; 2.68, s, br, (tmed)

^a The IR spectra were recorded in CH₂Cl₂ solution. ^b The ¹H NMR spectra were recorded in CDCl₃ solution.

tion positions of the CN^tBu ligands and the chemical shifts of their protons. In terms of the two-step mechanism proposed for the decarbonylating reactions promoted by ONMe₃[6], the stereochemistry of **2** suggests that the isocyanide

Table 3

Chemical shift of the t-butykcyanide protons

Compound	δ^a {CN-C(CH ₃) ₃ }		Reference
	<i>cis</i> to both N atoms	<i>trans</i> to a N atom	
<i>fac</i> -[Mn(CO) ₃ (CN ^t Bu)(bipy)]ClO ₄	1.28		3 ^b
<i>fac</i> -[Mn(CO) ₃ (CN ^t Bu)(phen)]ClO ₄	1.18		3
<i>mer</i> -[Mn(CO) ₃ (CN ^t Bu)(bipy)]ClO ₄		1.66	3
<i>mer</i> -[Mn(CO) ₃ (CN ^t Bu)(phen)]ClO ₄		1.72	3
<i>cis,trans</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (bipy)]ClO ₄	1.24		9
<i>cis,trans</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (phen)]ClO ₄	1.12		9
<i>cis,cis</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (bipy)]ClO ₄	1.26 (9H)	1.58 (9H)	3
<i>cis,cis</i> -[Mn(CO) ₂ (CN ^t Bu) ₂ (phen)]ClO ₄	1.16 (9H)	1.65 (9H)	3
<i>fac</i> -[Mn(CO)(CN ^t Bu) ₃ (bipy)]ClO ₄	1.26 (9H)	1.54 (18H)	3
<i>fac</i> -[Mn(CO)(CN ^t Bu) ₃ (phen)]ClO ₄	1.20 (9H)	1.62 (18H)	3
<i>mer</i> -[Mn(CO)(CN ^t Bu) ₃ (bipy)]ClO ₄	1.22 (18H)	1.58 (9H)	9
<i>mer</i> -[Mn(CO)(CN ^t Bu) ₃ (phen)]ClO ₄	1.18 (18H)	1.63 (9H)	9

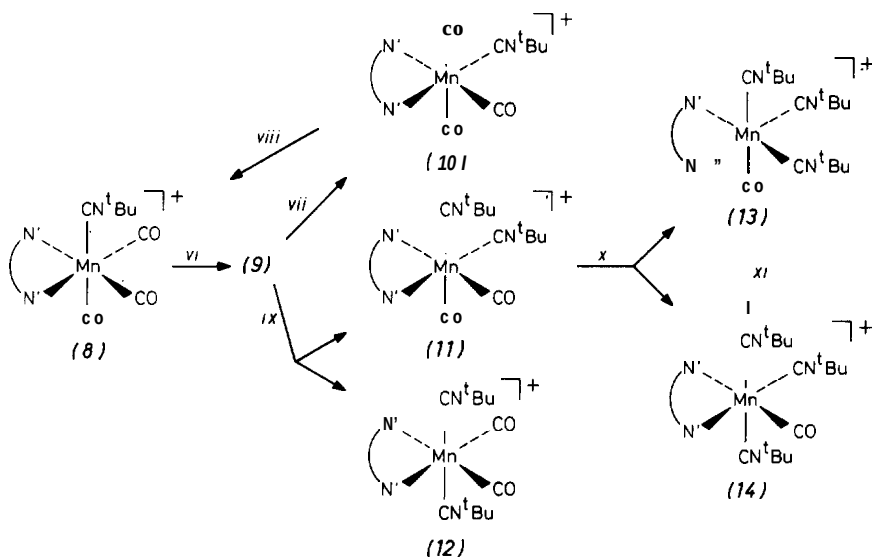
^a All the NMR spectra were recorded in CDCl₃ solution. ^b The reference 3 only includes the preparation of the compounds, the NMR data, however, have been obtained recently in order to make out this Table.

ligand migrates from an axial to an equatorial position in the square pyramid intermediate. This is in accord with the “site preference model” [7], which predicts that an isocyanide ligand (a weaker σ -acceptor than CO) should prefer a basal position in the square pyramid intermediate. Moreover, assuming a dissociative pathway in the substitution of NMe₃ in 2, the formation of *mer*-tricarbonyl complexes 3 (ii in Scheme 1) and the *cis,cis*-dicarbonyl compounds 4 (iii in Scheme 1) [3] further supports the suggestion that there is a stable intermediate containing a basal isocyanide.

The NMe₃ ligand in 2 can also be readily replaced by P(OMe)₃ in CH₂Cl₂ at room temperature to give *cis,cis*-[Mn(CO)₂{P(OMe)₃}(CNR)(N-N)]ClO₄ (5) (iv in Scheme 1). Their analytical and spectroscopic data are collected in Tables 1 and 2. The peaks at 1.60 (5a) and 1.65 ppm (5b) in the ¹H NMR spectra show that the CN^tBu ligands are in equatorial positions, as in the starting complexes.

On the other hand, the dicarbonyls *cis,trans*-[Mn(CO)₂(CNR){P(OMe)₃}(N-N)]ClO₄ (6) (isomers of 5) were obtained by adding ONMe₃ and CN^tBu to a solution of *fac*-[Mn(CO)₃{P(OMe)₃}(bipy)]ClO₄ in CH₂Cl₂. Their analytical and spectroscopic data are collected in Tables 1 and 2. In this case, the ¹H NMR spectra show four groups of signals in the aromatic region, corresponding to equivalent chelated N atoms; the chemical shifts of the CN^tBu protons (1.23 (6a) and 1.12 ppm (6b)) are in the range expected for axial CN^tBu ligands. The stereochemistry of 6a and 6b indicates that, unlike isocyanides, the phosphites do not migrate in these substitution reactions.

The *cis*-isocyanide dicarbonyl complexes *cis,cis*-[Mn(CO)₂(CN^tBu)₂(N-N)]ClO₄ (N-N = bipy or phen, (4)) were found to react with ONMe₃ and CNPh in refluxing CH₂Cl₂ to yield *fac*-[Mn(CO)(CNPh)(CN^tBu)₂(N-N)]ClO₄ (7) (v in Scheme 1). The stereochemistry of the monocarbonyl complexes 7 is suggested on the basis of their ¹H NMR spectra. Thus, the appearance of singlets at 1.58 (7a) and 1.62 ppm (7b) indicate the presence of two equivalent equatorial *tert*-butylisocyanides. On the other hand, the four groups of signals in the aromatic region indicate the equiv-



Scheme 2. $N'-N' = {}^t\text{Bu-DAB}$ or tmed ; (vi) ONMe_3 ; (vii) CO ; (viii) refluxing hexane for **10a**, or stirring at room temperature for **10b**, (ix) CN^tBu ; (x) ONMe_3 and CN^tBu ; (xi) refluxing CHCl_3 , only for **13b**

alence of the two N atoms in the chelates. The stereochemistry of **7a** and **7b** confirms that the isocyanide migration also takes place during the formation of the monocarbonyl compounds $[\text{Mn}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{ClO}_4$.

At this point, it seemed of interest to extend our study to other related carbonyl complexes, containing **bis(t-butyl)-1,4-diazabuta-1,3-diene** (${}^t\text{Bu-DAB}$), and N, N, N', N' -tetramethylethylenediamine (tmed) as nitrogen donor chelates.

The tricarbonyl complexes $\text{fac-}[\text{Mn}(\text{CO})_3(\text{CN}^t\text{Bu})(\text{N}'-\text{N}')]\text{ClO}_4$ ($\text{N}'-\text{N}' = {}^t\text{Bu-DAB}$ (**8a**) and tmed (**8b**)), reacted in CH_2Cl_2 with ONMe_3 in the absence of other ligands to give mainly the dicarbonyl derivatives of formula $\text{cis-}[\text{Mn}(\text{CO})_2(\text{CN}^t\text{Bu})(\text{NMe}_3)(\text{N}'-\text{N}')]\text{ClO}_4$ ($\text{N}'-\text{N}' = {}^t\text{Bu-DAB}$ (**9a**) and tmed (**9b**)) (vi in Scheme 2)*. Because of the presence of an excess of ONMe_3 and partial decomposition of the products, they could not be isolated and so have not been fully characterized. However, from their IR spectra (CH_2Cl_2 , cm^{-1} ; $\nu(\text{CN}) = 2130 \text{ s}$, $\nu(\text{CO}) = 1945 \text{ s}$, 1876 s , (**9a**); $\nu(\text{CN}) = 2133 \text{ s}$, $\nu(\text{CO}) = 1955 \text{ s}$, 1866 s (**9b**)) it is clear that they contain an isocyanide ligand and a *cis*-dicarbonyl arrangement.

Irrespective of the stereochemistry of **9**, bubbling CO through a CH_2Cl_2 solutions of this product gave the tricarbonyl complexes $\text{mer-}[\text{Mn}(\text{CO})_3(\text{CN}^t\text{Bu})(\text{N}'-\text{N}')]\text{ClO}_4$ (**10**) (vii in Scheme 2). The complex **10a** ($\text{N}'-\text{N}' = {}^t\text{Bu-DAB}$), was fully characterized (see Tables 1 and 2), but complex **10b** ($\text{N}'-\text{N}' = \text{tmed}$) could not be isolated in a pure state because of its rapid isomerization to the corresponding *fac*-isomer **8b** (viii in Scheme 2) and it was identified only by IR spectroscopy on the product of a reaction carried out at 0°C (CH_2Cl_2 , cm^{-1} ; $\nu(\text{CN}) = 2117 \text{ s}$, $\nu(\text{CO}) = 1939 \text{ s}$, 1868 s). The *mer* to *fac* isomerization also occurs in the case of the compound **10a**, but only at the higher temperature of refluxing hexane.

* It is possible that small amounts of $[\text{Mn}(\text{CO})_2(\text{CN}^t\text{Bu})(\text{ONMe}_3)(\text{N}'-\text{N}')]\text{ClO}_4$ were also formed, since the reaction was carried out in presence of an excess of ONMe_3 [3,8].

While the reaction of *cis*-[Mn(CO)₂(CN'Bu)(NMe₃(N-N))]ClO₄ (2) with CN'Bu afforded *cis,cis*-[Mn(CO)₂(CN'Bu)₂(N-N)]ClO₄ (4) as a single product [3] (iii in Scheme 1), the reaction of 9 with CN'Bu in CH₂Cl₂ at room temperature gave a mixture of two isomers *cis,cis*-[Mn(CO)₂(CN'Bu)₂(N'-N')]ClO₄ (11) and *cis,trans*-[Mn(CO)₂(CN'Bu)₂(N'-N')]ClO₄ (12) (ix in Scheme 2). These were isolated by careful fractional crystallization from CH₂Cl₂/EtOH and fully characterized (Tables 1 and 2). The ¹H NMR and IR spectra of the crude reaction mixture reveal that there is a preponderance of the *cis,cis*-complexes. In addition, we observed that the isomers 11 and 12 cannot be interconverted under the conditions in which they are generated. This could be an indication that the product 9 is itself a mixture of two isomers.

The results can be explained by assuming that two square-pyramidal intermediates exist in equilibrium in all substitution reactions involving complexes containing N'-N' chelates, in contrast to the single pentacoordinate intermediate proposed for the analogous reactions involving bipy and phen complexes. The intermediate present in higher proportion (A) would have the isocyanide ligand in the base of the square-pyramid, while the other one (B) would have it in the apical position. Thus, in the reaction of 9 with CN'Bu, the species A would give 11 (the main product), whereas the intermediate B would give 12. In the reaction of 9 with CO, however, only the mer-tricarbonyl isomer 10 is formed indicating that the low concentration of CO forces the reaction to proceed only through the intermediate A. Consistently, when 9 was reacted with a very dilute solution of CN'Bu the proportion of the isomer 11 was higher than that obtained when a concentrated solution of the isocyanide was used.

The existence of two intermediates in equilibrium is also supported by the fact that the separate reactions of 8 and 10 with ONMe₃ and CN'Bu gave the same mixture of isomers (11 and 12). Furthermore, the proportion of the isomer 11 in the final mixture could be increased by raising the temperature in the reaction of 8 with ONMe₃ and CN'Bu, suggesting that the ratio of the intermediates A and B is temperature dependent.

Again there is a marked contrast between the reactions of *cis,cis*-[Mn(CO)₂(CN'Bu)₂(N-N)]ClO₄ (4) and *cis,cis*-[Mn(CO)₂(CN'Bu)₂(N'-N')]ClO₄ (11) with ONMe₃ and CNR. Thus while the former gave *fac*-[Mn(CO)(CNR)₃(N-N)]ClO₄ (7) as single product [3] (v in Scheme 1), the latter gave a mixture of *fac*-[Mn(CO)(CN'Bu)₃(N'-N')]ClO₄ (13) and *mer*-[Mn(CO)(CN'Bu)₃(N'-N')]ClO₄ (14) (x in Scheme 2), which could be separated by fractional crystallization. Although the complex *mer*-[Mn(CO)(CN'Bu)₃(tmed)]ClO₄ (14b) always crystallizes contaminated with 13b, it could be prepared pure by heating the corresponding *fac*-isomer 13b in refluxing CHCl₃ (xi in Scheme 2). In the substitution reactions involving complexes containing N'-N' chelates, the formation of the mixture of 13 and 14 further supports the existence of two intermediates differing in the coordination position of the isocyanide ligand.

Experimental

All reactions were carried out under nitrogen, and except for those involving complexes containing tmed, in the dark. The IR spectra were recorded with Perkin-Elmer 599 and Perk&Elmer 883 spectrometers, and calibrated by reference

to the 1602 cm^{-1} band of the polystyrene. The NMR spectra were recorded on Varian FT-80 and Bruker AC 80 instruments, with TMS as internal reference. The compounds *fac*-[Mn(CO)₃(CN^tBu)(N–N)]ClO₄, (N–N = bipy and phen) [3], *cis,cis*-[Mn(CO)₂(CN^tBu)₂(N–N)]ClO₄ [3], *fac*-[Mn(CO)₃{P(OMe)₃}(N–N)]ClO₄ [2], *fac*-[Mn(CO)₃(^tBu-DAB)Br] [10], ONMe₃ [11], CN^tBu [12], CNPh [12] and ^tBu-DAB [13] were prepared by published methods.

Preparation of *cis,cis*-[Mn(CO)₂{P(OMe)₃}(CN^tBu)(N–N)]ClO₄ (N–N = bipy (5a), phen (5b))

A mixture of *fac*-[Mn(CO)₃(CN^tBu)(N–N)]ClO₄ (1) (0.63 mmol), ONMe₃ (0.047 g, 0.63 mmol) and P(OMe)₃ (0.082 g, 0.69 mmol) in CH₂Cl₂ (40 cm³) was stirred at room temperature for 1.5 h. The solution was evaporated to dryness, the residue washed with light petroleum, and the product crystallized from CH₂Cl₂/Et₂O at –20°C to give orange crystals. Yields 60% (5a) and 62% (5b).

Preparation of *cis,trans*-[Mn(CO)₂{P(OMe)₃}(CN^tBu)(N–N)]ClO₄ (N–N = bipy (6a), phen (6b))

To a solution of *fac*-[Mn(CO)₃{P(OMe)₃}(N–N)]ClO₄ (0.58 mmol) in CH₂Cl₂ (40 cm³) were added ONMe₃ (0.044 g, 0.58 mmol) and CN^tBu (0.050 g, 0.60 mmol), and the mixture was stirred for 1 h. After evaporation of the solvent, the residue was washed with light petroleum to give a solid, which was recrystallized from CH₂Cl₂/EtOH to afford yellow orange crystals. Yields 65% (6a), and 63% (6b).

Preparation of [Mn(CO)(CN^tBu)₂(CNPh)(N–N)]ClO₄ (N–N = bipy (7a), phen (7b))

A mixture of *cis,cis*-[Mn(CO)₂(CN^tBu)₂(N–N)]ClO₄ (0.47 mmol), ONMe₃ (0.035 g, 0.47 mmol) and CNPh (0.052 g, 0.50 mmol) was refluxed in CH₂Cl₂ (40 cm³) for 5 h. The liquid was evaporated off under vacuum and the residue washed with light petroleum. Recrystallization from CH₂Cl₂/EtOH gave dark red crystals. Yields 55% (7a) and 53% (7b).

Preparation of *fac*-[Mn(CO)₃(tmed)Br]

A solution of [Mn(CO)₃Br] (1 g, 3.64 mmol) and tmed (0.6 cm³, 3.97 mmol) in hexane (60 cm³) was refluxed for 30 min. The product separated out yellow solid. Yield 95%. M.p. 140°C. Anal. Found: C, 32.3; H, 4.9; N, 8.4. Calcd: C, 32.3; H, 4.8; N, 8.4%. IR spectra (CH₂Cl₂, in cm^{–1}), $\nu(\text{CO}) = 2039 \text{ s}, 1935 \text{ s}, 1898 \text{ s}$. ¹H NMR spectra (CDCl₃, δ in ppm): 2.61 (s, CH₂), 2.90 (s, CH₃), 2.96 (s, CH₃).

Preparation of *fac*-[Mn(CO)₃(CN^tBu)(N'–N')]ClO₄ (N'–N' = ^tBu-DAB (8a) tmed (8b))

A mixture of *fac*-[Mn(CO)₃(N'–N')Br] (0.77 mmol) and Ag ClO₄ (0.177 g, 0.85 mmol) in CH₂Cl₂ (60 cm³) was stirred for 1 h in the dark, then filtered to remove the AgBr. To the filtrate was added CN^tBu (0.071 g, 0.85 mmol), and the mixture was refluxed for 30 min. After removal of the solvent, the residue was washed with light petroleum to give a yellow solid. Yields 85% (8a) and 87% (8b).

Preparation of *mer*-[Mn(CO)₃(CN^tBu)(^tBu-DAB)]ClO₄ (10a)

To a solution of *fac*-[Mn(CO)₃(CN^tBu)(^tBu-DAB)]ClO₄ (8a) (0.25 g, 0.51 mmol) in CH₂Cl₂ (40 cm³) was added ONMe₃ (0.096 g, 1.28 mmol), and the resulting

mixture was stirred for 5 mm. The solution was washed **successively** with water to remove the excess of ONMe_3 , dried over MgSO_4 , and filtered. CO was bubbled through the filtrate for 1 h. After removal of the solvent, the residual oil was washed with light petroleum to give a solid. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -20°C affords yellow orange crystals. Yield 38%.

Preparation of *cis,cis*-[Mn(CO)₂(CN^tBu)₂(N'-N')]*ClO*₄ (N'-N' = ^tBu-DAB (11a), *tmed* (11b)) and *cis,trans*-[Mn(CO)₂(CN^tBu)₂(N'-N')]*ClO*₄ (N'-N' = ^tBu-DAB (12a), *tmed* (12b))

To a solution of *fac*-[Mn(CO)₃(CN^tBu)(N'-N')]*ClO*₄ (8) (0.82 mmol) in CH_2Cl_2 (40 cm³) were added ONMe_3 (0.061 g, 0.82 mmol) and CN^tBu (0.136 g, 1.63 mmol), and the mixture was stirred at room temperature for 2 h (^tBu-DAB) or 5 h (*tmed*). After removal of the solvent, the residue was washed with light petroleum. Recrystallization of the crude product from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ gave first the *cis,trans*-isomers 12, orange crystals of 12a (yield 15%) or yellow crystals of 12b (yield 19%). **Successive recrystallizations** afforded the *cis,cis*-isomers 11, red crystals of 11a (yield 32%) and yellow crystals of 11b (yield 53%).

Preparation of *fac*-[Mn(CO)(CN^tBu)₃(^tBu-DAB)]*ClO*₄ (13a) and *mer*-[Mn(CO)(CN^tBu)₃(^tBu-DAB)]*ClO*₄ (14a)

Although the complexes 13 and 14 could be obtained starting from the *cis,cis*-[Mn(CO)₂(CN^tBu)₂(N'-N')]*ClO*₄ (11), it was more convenient to prepare them from *fac*-[Mn(CO)₃(CN^tBu)(N'-N')]*ClO*₄ (8), since in this way the isolation of the dicarbonyl complexes 11 and 12 was avoided.

(A) **From *fac*-[Mn(CO)₃(CN^tBu)(^tBu-DAB)]*ClO*₄ (8a).** A mixture of *fac*-[Mn(CO)₃(CN^tBu)(^tBu-DAB)]*ClO*₄ (8a) (0.25 g, 0.51 mmol), ONMe_3 , (0.096 g, 1.28 mmol) and CN^tBu (0.127 g, 1.53 mmol) in CH_2Cl_2 (30 cm³) was stirred at room temperature for 3 days. The liquid was evaporated to dryness and the residue was washed with light petroleum. Crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -20°C gave first *cis,trans*-[Mn(CO)₂(CN^tBu)₂(^tBu-DAB)]*ClO*₄ (11a) (yield 20%), and then, after addition of light petroleum, deep-red crystals of *fac*-[Mn(CO)(CN^tBu)₃(^tBu-DAB)]*ClO*₄ (13a) (yield 40%), and finally deep-red crystals of *mer*-[Mn(CO)(CN^tBu)₃(^tBu-DAB)]*ClO*₄ (14a) (yield 6%).

(B) **From *cis,cis*-[Mn(CO)₂(CN^tBu)₂(^tBu-DAB)]*ClO*₄ (11a).** A mixture of *cis,cis*-[Mn(CO)₂(CN^tBu)₂(^tBu-DAB)]*ClO*₄ (11a) (0.20 g, 0.37 mmol), ONMe_3 (0.036 g, 0.48 mmol), and CN^tBu (0.063 g, 0.76 mmol) in CH_2Cl_2 (30 cm³) was stirred for 3 days at room temperature. After removal of the solvent, the residue was washed with light petroleum and the crude product recrystallized from $\text{CH}_2\text{Cl}_2/\text{light petroleum}$ to give first 13a (42%) and then 14a (9%).

Preparation of *fac*-[Mn(CO)(CN^tBu)₃(*tmed*)]*ClO*₄ (13b)

(A) **From *fac*-[Mn(CO)₃(CN^tBu)(*tmed*)]*ClO*₄ (8b).** To a solution of *fac*-[Mn(CO)₃(CN^tBu)(*tmed*)]*ClO*₄ (8b) (0.20 g, 0.46 mmol) in CH_2Cl_2 (30 cm³) were added ONMe_3 (0.086 g, 1.15 mmol) and CN^tBu (0.136 g, 1.63 mmol), and the mixture was stirred at room temperature for 15 days. The solution was then filtered to remove the insoluble decomposition products, and the solvent then evaporated off and the residue washed with light petroleum. Recrystallization of the crude

product from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ gave first yellow-orange crystals of the 13b (35%) and then mixtures of 13b and 14b

(B) From *cis,cis*-[$\text{Mn}(\text{CO})_2(\text{CN}^i\text{Bu})_2(\text{tmed})$] ClO_4 (11b). A mixture of *cis,cis*-[$\text{Mn}(\text{CO})_2(\text{CN}^i\text{Bu})_2(\text{tmed})$] ClO_4 (11b) (0.20 g, 0.41 mmol), and CN^iBu (0.063 g, 0.76 mmol) in CH_2Cl_2 (30 cm^3) was stirred for 10 days at room temperature. The solution was evaporated to dryness and the residue was washed with light petroleum. The crude product was recrystallized from CH_2Cl_2 /light petroleum to give mainly 13b (37%).

It should be noted that in this reaction the presence of ONMe_3 is unnecessary.

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