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SYNTHESIS OF *mer*-TRICARBONYLS OF MANGANESE(I) WITH *N*-DONOR CHELATE LIGANDS

F.J. GARCÍA ALONSO, V. RIERA

Department of Inorganic Chemistry, University of Oviedo, Oviedo (Spain)

F. VILLAFAÑE and M. VIVANCO

Department of Inorganic Chemistry, University of Valladolid, Valladolid (Spain)

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Summary

The first *mer*-tricarbonyl complexes of manganese(I) with *N*-donor chelate ligands, namely *mer*-$[Mn(CO)_3(CNR)(NN)]ClO_4$, where CNR = $CNBu^t$, NN = 1,10-phenantroline (phen) or 2,2′-bipyridine (bipy), have been obtained from the reactions of *fac*-$[Mn(CO)_3(Me_2CO)(NN)]ClO_4$ with isocyanides, CNR. Other members of the $[Mn(CO)_{4-n}(CNR)_n(NN)]ClO_4$ ($n = 1,2,3,4$) series have also been synthesized: viz., *fac*-$[Mn(CO)_3(CNR)(NN)]ClO_4$ (Ia–d) and *cis,cis*-$[Mn(CO)_2(CNR)_2(NN)]ClO_4$ (CNR = $CNBu^t$, CNPh) (IIa–d), *cis,cis*-$[Mn(CO)_2(CNR)(CNR')(NN)]ClO_4$ (CNR = CNPh, CNR′ = $CNBu^t$ and CNR = $CNBu^t$, CNR′ = CNPh) (IIe–f), *fac*-$[Mn(CO)(CNBu^t)_3(NN)]ClO_4$ (IVa–b), and $[Mn(CNPh)_4(NN)]ClO_4$; (NN) represents phen or bipy. (See Scheme 1 and Table 1).

Introduction

In 1979 Treichel and Firsich reported [1] the preparation of a series of mixed complexes of manganese(I) with the bidentate diphosphine dppe (dppe = 1,2-bis(diphenylphosphino)ethane), namely $[Mn(CO)_{4-n}(CNMe)_n(dppe)]^+$ ($n = 1–4$). Since the substitution of a *P*-donor chelate ligand, such as dppe, by an *N*-donor chelate ligand, e.g., bipy, markedly alters the reactivity of the complex [2,3], we became interested in studying the reactions of *fac*-$[Mn(CO)_3(Me_2CO)(NN)]ClO_4$ with isocyanide ligands. In this paper we describe the results of such study, during which the mixed complexes $[Mn(CO)_{4-n}(CNR)_n(NN)]ClO_4$ for $n = 1–4$ have been synthesized (see Scheme 1 and Table 1).

Surprisingly the dicarbonyls $[Mn(CO)_2(CNR)_2(NN)]ClO_4$ (complexes II in Scheme 1) obtained from *fac*-$[Mn(CO)_3(CNR)(NN)]ClO_4$, I, adopt a *cis,cis* geometry in spite of the strong *cis* labilizing effect of both N-atoms of bipy and phen.

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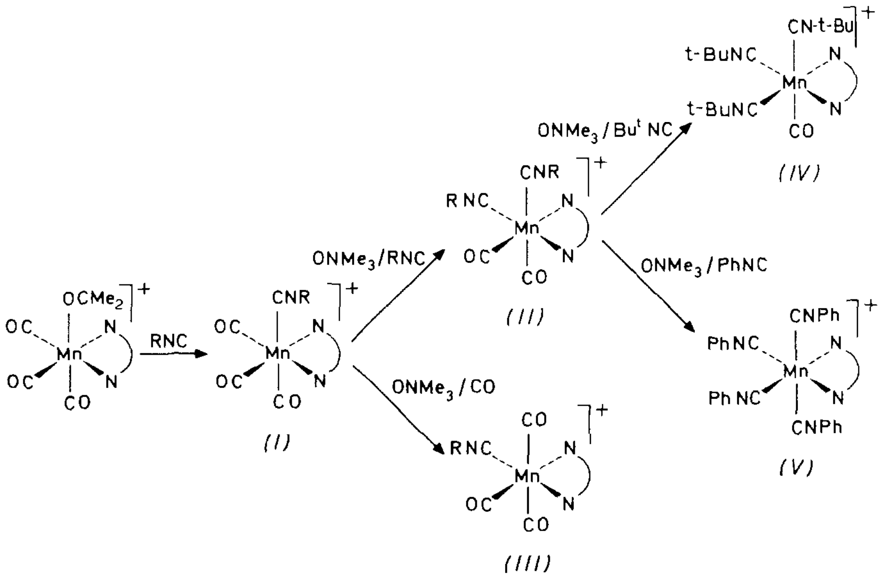

SCHEME 1

Closely related with the production of these *cis,cis*-dicarbonyls (II), is the preparation of the first *mer*-tricarbonyls of manganese(I) with *N*-donor chelate ligands, *mer*-$[Mn(CO)_3(CNR)(NN)]ClO_4$ (III). The synthesis of the *mer*-tricarbonyls is interesting in view of the recent assertion of Dobson et al. [4] about the kinetic inaccessibility of *mer*-tricarbonyl-chromium(0) and -molybdenum(0) complexes with *N*-donor chelate ligands. In fact, to the best of our knowledge no *mer*-tricarbonyls of manganese(I) with *NN* bidentate ligands have been reported, although *mer*-configurations has been proposed for two tricarbonyls of rhenium complexes with phen [5] or containing three *N*-donor ligands [6].

Results and Discussion

The acetone ligand in the complexes *fac*-$[Mn(CO)_3(Me_2CO)(NN)]ClO_4$ [3] was easily replaced by isocyanide ligands at room temperature to give the new cationic species *fac*-$[Mn(CO)_3(CNR)(NN)]ClO_4$ (Ia–d) as orange-yellow crystals.

On refluxing these *fac*-tricarbonyls, I with CNR (mol ratio 1 : 1) in THF, a progressive substitution of CO by CNR was observed. Thus for NN = bipy and CNR = CNPh, the IR spectrum of the solution after 3.5 h showed it to contain a mixture of the initial *fac*-tricarbonyl and the dicarbonyl *cis,cis*-$[Mn(CO)_2(CNPh)_2$-$(bipy)]ClO_4$ (IIa). Longer reaction times led to a complex mixture in which the presence of more substituted species was observed, but which still contained starting material.

In view of the fact that this reaction led to a mixture of compounds we thought that the dicarbonyls might be prepared more easily, and in better yields, by promoting one CO substitution by the use of a decarbonylating agent such as $ONMe_3$. Thus, on stirring at room temperature a chloroform solution of *fac*-

$[Mn(CO)_3(CNR)(NN)]ClO_4$, I, the isocyanide and $ONMe_3$ (mol ratio 1 : 1 : 1) the dicarbonyls *cis,cis*-$[Mn(CO)_2(CNR)_2(NN)]ClO_4$ (IIa–d) were obtained as the only product in each case and each could easily be isolated in 70–80% yield as red-orange crystals.

The formation of the dicarbonyls IIa–d with a *cis,cis* geometry was not expected taking into account the *cis* labilizing character of bipy and phen, as mentioned earlier.

Moreover CO_2 was evolved during the reactions and dicarbonyl intermediates were detected. These intermediates, with two $\nu(CO)$ bands of similar intensity but at lower wavenumbers than those of the corresponding *cis,cis* derivatives II, and only one $\nu(CN)$ absorption, were the only carbonyl products obtained by treating

TABLE 1

MELTING POINTS, CONDUCTIVITY AND ANALYTICAL DATA FOR THE COMPLEXES I–V

Compound		m.p. (°C)	Λ_M [a]	Analysis (Found (calcd.) (%))		
				C	H	N
Ia	*fac*-$[Mn(CO)_3(CNPh)(bipy)]ClO_4$	165	95	48.44	2.59	8.50
				(48.26)	(2.63)	(8.44)
Ib	*fac*-$[Mn(CO)_3(CNPh)(phen)]ClO_4$	179	95	51.09	2.68	8.24
				(50.65)	(2.51)	(8.05)
Ic	*fac*-$[Mn(CO)_3(CNBu^t)(bipy)]ClO_4$	147	95	44.87	3.58	8.41
				(45.26)	(3.59)	(8.80)
Id	*fac*-$[Mn(CO)_3(CNBu^t)(phen)]ClO_4$	161	95	47.83	3.35	8.36
				(47.88)	(3.41)	(8.37)
IIa	*cis,cis*-$[Mn(CO)_2(CNPh)_2(bipy)]ClO_4$	143	90	54.27	3.19	9.67
				(54.52)	(3.17)	(9.78)
IIb	*cis,cis*-$[Mn(CO)_2(CNPh)_2(phen)]ClO_4$	158	90	56.23	2.96	9.35
				(56.35)	(3.04)	(9.39)
IIc	*cis,cis*-$[Mn(CO)_2(CNBu^t)_2(bipy)]ClO_4$	157	100	49.45	4.97	10.41)
				(49.59)	(4.92)	(10.51)
IId	*cis,cis*-$[Mn(CO)_2(CNBu^t)_2(phen)]ClO_4$	165	90	51.03	4.63	9.81
				(51.76)	(4.71)	(10.06)
IIe	*cis,cis*-$[Mn(CO)_2(CNPh)(CNBu^t)(phen)]ClO_4$	118	90	54.12	4.21	9.12
				(54.13)	(3.84)	(9.71)
IIf	*cis,cis*-$[Mn(CO)_2(CNBu^t)(CNPh)(phen)]ClO_4$	146	90	54.26	3.95	9.42
				(54.13)	(3.84)	(9.71)
IIIa	*mer*-$[Mn(CO)_3(CNBu^t)(bipy)]ClO_4$	110 [b]	100	45.29	3.63	8.67
				(45.26)	(3.59)	(8.79)
IIIb	*mer*-$[Mn(CO)_3(CNBu^t)(phen)]ClO_4$	122 [b]	95	47.52	3.51	8.22
				(47.88)	(3.41)	(8.37)
IVa	*fac*-$[Mn(CO)(CNBu^t)_3(bipy)]ClO_4$	163	90	53.15	6.08	11.78
				(53.11)	(6.00)	(11.91)
IVb	*fac*-$[Mn(CO)(CNBu^t)_3(phen)]ClO_4$	163	90	54.72	5.70	11.32
				(54.95)	(5.76)	(11.44)
Va	$[Mn(CNPh)_4(bipy)]ClO_4$	124 [c]	90	62.95	4.08	11.18
				(63.11)	(3.90)	(11.62)
Vb	$[Mn(CNPh)_4(phen)]ClO_4$	140 [c]	90	64.08	3.89	10.94
				(64.30)	(3.77)	(11.24)

[a] Molar conductivity, in S cm^2 mol^{-1}, of a 5×10^{-4} nitromethane solution at 25 °C. [b] When heated at this temperature it decomposed to give *fac*-$[Mn(CO)_3(CNBu^t)(NN)]ClO_4$. [c] They blacken before they melt.

fac-[$Mn(CO)_3(CNR)(NN)]ClO_4$ with excess of $ONMe_3$ in the absence of CNR in Cl_3CH at room temperature. For example, the reaction between *fac*-[$Mn(CO)_3(CNBu^t)(bipy)]ClO_4$ and $ONMe_3$ led to a *cis*-dicarbonyl complex with the following IR absorptions (in Cl_3CH): ν(CN) 2130 m, ν(CO) 1950s and 1880s, in the 2300–1800 cm^{-1} region. Attempts to isolate the complexes were unsuccesful, since they reacted with the water used to remove the excess of $ONMe_3$ from the chloroform solutions, to give new dicarbonyl complexes (IR (in Cl_3CH) when NN = bipy and CNR = $CNBu^t$: ν(CN) 2133m, ν(CO) 1960s and 1890s cm^{-1}) which also could not be isolated.

In accordance with the literature [7,8] it seems reasonable to assume that $ONMe_3$ "oxidizes" a carbonyl ligand to CO_2 thus creating a vacant site which can be occupied by the liberated NMe_3 or by $ONMe_3$ to give the intermediates *cis*-[$Mn(CO)_2(CNR)(L)(NN)]ClO_4$ (L = NMe_3 or $ONMe_3$); in the presence of CNR the ligand L would be replaced to give the *cis,cis*-dicarbonyls II, and probably in a similar way, L could be substituted by H_2O to give the second dicarbonyl, *cis*-[$Mn(CO)_2(CNR)(H_2O)(NN)]ClO_4$, when in contact with the water used to remove the excess of $ONMe_3$.

On the other hand, bubbling CO at atmospheric pressure through a chloroform solution of the mixture of the two dicarbonyls which result from treating *fac*-[$Mn(CO)_3(CNBu^t)(NN)]ClO_4$ with an excess of $ONMe_3$ and then washing the mixture with water (probably a mixture of *cis*-[$Mn(CO)_2(CNBu^t)(L)(NN)]ClO_4$, L = NMe_3 or $ONMe_3$, and *cis*-[$Mn(CO)_2(CNBu^t)(H_2O)(NN)]ClO_4$), leads to the formation of a new compound, which shows the characteristic CO pattern of a *mer*-tricarbonyl, which is independent of the relative proportions of the dicarbonyls in the starting mixture. Orange-yellow crystals were isolated from the solution, and their C,H,N analyses, IR spectrum and conductivity data correspond to the formation of *mer*-[$Mn(CO)_3(CNBu^t)(NN)]ClO_4$(IIIa–b), which are the first *mer*-tricarbonyl complexes of manganese(I) with *N*-donor chelate ligands. Attempts to prepare CNPh derivatives of the *mer*-tricarbonyl complexes III in the same way gave mixtures in which the expected *mer*-[$Mn(CO)_3(CNPh)(NN)]ClO_4$ complex could be identified by IR spectroscopy as the predominant species, but from which pure samples could not be isolated. (For instance, for NN = phen, in Cl_3CH, ν(CN) 2151m cm^{-1}, ν(CO) 2085w, 2020s and 1965m cm^{-1}).

During the measurement of the m.p. of the isolated *mer*-compounds, IIIa and IIIb, it was observed that they isomerized at 110–120°C, with decomposition, to give *fac*-[$Mn(CO)_3(CNBu^t)(NN)]ClO_4$ as shown by their IR spectra in the ν(CN) and ν(CO) regions. These isomerizations of *mer* → *fac* could be confirmed by heating the *mer*-derivatives under reflux in hexane to give the *fac*-isomers, together with the formation of small quantities of decomposition products. This suggests that the *fac*-isomers have greater thermal stability than their *mer*-isomers, in contrast with other cationic [9] and neutral [10] tricarbonyls.

When *mer*-[$Mn(CO)_3(CNBu^t)(bipy)]ClO_4$ was refluxed in THF a new *cis*-dicarbonyl was formed, with ν(CN) 2130m and ν(CO) 1962s, 1892s cm^{-1} in Cl_3CH. Although the attempts to isolate this complex led to its decomposition, the starting *mer*-tricarbonyl could be regenerated by bubbling CO through a chloroform solution which contained this *cis*-dicarbonyl, therefore it is thought that it was *cis*-[$Mn(CO)_2(CNBu^t)(THF)(bipy)]ClO_4$. The fact that this *cis*-dicarbonyl complex has similar ν(CN) and ν(CO) bands to those for the complex considered to be *cis*-

$[Mn(CO)_2(CNBu^t)(H_2O)(bipy)]ClO_4$ reinforces both assignments, since both H_2O and THF are *O*-donor ligands.

Assuming that the intermediate dicarbonyls are actually *cis*-$[Mn(CO)_2(CNR)(L)(NN)]ClO_4$ (L = NMe_3, $ONMe_3$, H_2O, or THF) and taking into account similar experiments cited in the literature [11] it seems reasonable to assume that CO replaces L to give the *mer*-derivatives without altering the relative positions of the other ligands. This would imply that in all the dicarbonyl intermediates *cis*-$[Mn(CO)_2(CNR)(L)(NN)]ClO_4$, L should occupy a position which is not only *cis* to both N atoms of bipy or phen but also to the isocyanide.

The lack of proper kinetic studies makes it difficult to know how $ONMe_3$ actually acts [7]. Nevertheless, it seems clear from literature [7] that only carbonyls with high CO force-constants can undergo nucleophilic attack by $ONMe_3$, e.g. at room temperature apparently only CO ligands with Cotton-Kraihanzel pseudo force constants (CKFC) higher than 1600 N m^{-1}, are attacked. In the *fac*-tricarbonyls I the CKFC for the CO *trans* to the isocyanide are in the range 1679–1693 N m^{-1}, while the corresponding values for CO *cis* to the isocyanide range between 1580–1593 N m^{-1}; therefore it would be expected that the CO ligand attacked by the $ONMe_3$ is the one *trans* to the CNR ligand. If we assume that this attack ends up with the formation of a 16-electron pentacoordinate intermediate, this should be stabilized with the NN ligand in the base of the square pyramid, (the most probably geometry) according to the "site preference model" [12]. Furthermore, the CNR ligand is a poorer π-acceptor than CO and therefore one CO should occupy the apex position in the 16-electron intermediate [13]. Although this rationale could explain why a *mer*-tricarbonyl III and a *cis,cis*-dicarbonyl are the observed products in the reactions being discussed, other commonly competing pathways [13] could also be followed.

It is unlikely that the first product in the formation of *cis,cis*-$[Mn(CO)_2(CNR)_2(NN)]ClO_4$, II, was *cis,trans*-$[Mn(CO)_2(CNR)_2(NN)]ClO_4$, and

TABLE 2

IR DATA [a] FOR THE COMPOUNDS I–V

Compound	ν(CO) (cm^{-1})			ν(CN) (cm^{-1})		
Ia	2060s	1992s	1959s	2183m		
Ib	2061s	1993s	1962s	2184m		
Ic	2058s	1982s	1954s	2197m		
Id	2064s	1988s	1957s	2201m		
IIa	1996s	1940s		2169m	2116s	
IIb	1995s	1939s		2169m	2117s	
IIc	1980s	1922s		2184m	2137s	
IId	1983s	1923s		2183m	2138s	
IIe	1986s	1932s		2188m	2117s	
IIf	1990s	1929s		2170m	2134s	
IIIa	2080w	2004s	1956m		2160m	
IIIb	2082w	2004s	1957m		2165m	
IVa		1924s		2166s	2112s	2046s
IVb		1924s		2163s	2112s	2055s
Va				2143w	2080s	1994m
Vb				2140w	2077s	1995m

[a] Spectra taken in Cl_3CH.

that this complex subsequently isomerized (for instance in the presence of NMe_3 or ONMe [7]) to the observed *cis,cis*-derivative, since the reaction of *fac*-$[Mn(CO)_3(CNPh)(phen)]ClO_4$, Ib, with $CNBu^t$ and $ONMe_3$ gave the *cis* dicarbonyl *cis,cis*-$[Mn(CO)_2(CNPh)(CNBu^t)(NN)]ClO_4$, IIe, whilst *cis,cis*-$[Mn(CO)_2(CNBu^t)(CNPh)(NN)]ClO_4$, IIf, was obtained from the reaction between *fac*-$[Mn(CO)_3(CNBu^t)(phen)]ClO_4$, Id, with CNPh and $ONMe_3$. Both of the compounds (IIe and IIf) occur as red-orange crystals, have the same elemental C,H,N analyses, and the same ν(CN) and ν(CO) patterns, although they differ in the positions of the ν(CN) and ν(CO) bands and in their m.p.'s. (see Tables 1 and 2). That the reactions give two different compounds (albeit isomers), excludes the possibility that the first step in the process was the formation of the *cis,trans*-$[Mn(CO)_2(CNR)(CNR')(NN)]ClO_4$, which would be identical for both reactions, because its isomerization should provide the same final product.

Further substitutions can be achieved treating the *cis,cis*-$[Mn(CO)_2(CNR)_2(NN)]ClO_4$, II, with CNR in refluxing Cl_2CH_2 in presence of $ONMe_3$. Thus, for CNR = $CNBu^t$ the reactions gave only the trisubstituted *fac*-$[Mn(CO)(CNBu^t)_3(NN)]ClO_4$ complexes (IVa–b), as dark red crystals, but when CNR = CNPh the reactions involved total replacement of the CO, giving the $[Mn(CNPh)_4(NN)]ClO_4$ complexes (Va–b), also as dark red crystals; none of the possible intermediates were observed.

Experimental

All reactions were carried out under nitrogen. The complexes *fac*-$[Mn(CO)_3(Me_2CO)(NN)]ClO_4$ (NN = bipy and phen) [3] and the ligands $CNBu^t$ and CNPh [14] were prepared by published methods. The IR spectra were recorded using Perkin-Elmer 599 spectrophotometer. Analyses were performed with a Perkin-Elmer 240 microanalyzer.

Preparation of fac-$[Mn(CO)_3(CNR)(NN)]ClO_4$, Ia–d

The complex *fac*-$[Mn(CO)_3(Me_2CO)(NN)]ClO_4$ (3.54 mmol) and the isocyanide (3.59 mmol) were stirred in 30 ml of acetone at room temperature for 1 h. The solution was evaporated to dryness and the residue was washed with hexane. Yield 90%. Recrystallization was from Cl_2CH_2/EtOH.

Preparation of cis,cis-$[Mn(CO)_2(CNR)(CNR')(NN)]ClO_4$ (CNR = CNR'), IIa–d

To a solution of *fac*-$[Mn(CO)_3(CNR)(NN)]ClO_4$ (0.6 mmol) in 30 ml of Cl_3CH, the ligand CNR (0.6 mmol) and freshly sublimed $ONMe_3$ (0.6 mmol) were added, and the mixture stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue washed with hexane. Yield 70–80%. The product may be crystallized from Cl_2CH_2/EtOH.

The same procedure was used to obtain the mixed dicarbonyls (CNR ≠ CNR', IIe–f), from the appropriate starting complex and ligand.

Preparation of mer-$[Mn(CO)_3(CNBu^t)(NN)]ClO_4$, IIIa–b

A mixture of *fac*-$[Mn(CO)_3(CNBu^t)(NN)]ClO_4$ (0.31 mmol) and freshly sublimed $ONMe_3$ (0.94 mmol) were stirred at room temperature in Cl_3CH for 5 min. The solution was washed three times with distilled water to remove the unreacted

$ONMe_3$ and then dried with anhydrous $MgSO_4$; CO was bubbled through this solution for 3 h. After adding 5 ml of EtOH, the solvent was evaporated until appears the desired crystals. Yield 40%.

Preparation of fac-[Mn(CO)(CNBu^t)$_3$(NN)]ClO$_4$, IVa–b

cis,cis-$[Mn(CO)_2(CNBu^t)_2(NN)]ClO_4$ (0.3 mmol), $ONMe_3$ (0.4 mmol) and $CNBu^t$ (0.36 mmol) were refluxed in 50 ml of Cl_2CH_2 for 4 h. The solvent was removed under reduced pressure and the residue was washed several times with hexane. Yield 90%. The products were recrystallized from Cl_2CH_2/EtOH.

Preparation of [Mn(CNPh)$_4$(NN)]ClO$_4$, Va–b

cis,cis-$[Mn(CO)_2(CNPh)_2(NN)]ClO_4$ (0.2 mmol), $ONMe_3$ (0.4 mmol) and CNPh (0.6 mmol) were refluxed in 30 ml of Cl_2CH_2 for 14 h. The solvent was evaporated and the residue was washed with hexane until free of CNPh. The compound was recrystallized from Cl_2CH_2/EtOH. Yield 40%.

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References

1 P.M. Treichel and D.W. Firsich, J. Organomet. Chem., 172 (1979) 223.
2 G.A. Carriedo and V. Riera, J. Organomet. Chem., 205 (1981) 371.
3 R. Usón, V. Riera, J. Gimeno and M. Laguna, Transition Met. Chem., 2 (1977) 123.
4 G.R. Dobson, K.I. Asali and N.S. Binzet, 183rd A.C.S. National Meeting, March/April, 1982, ref. 57.
5 T. Kruck and M. Noack, Chem. Ber., 97 (1969) 1693.
6 J.I. Moelwyn-Hughes, A.W. Garner and A.J. Howard, J. Chem. Soc. A, (1971) 2370.
7 D.J. Blumer, K.W. Barnett and T.L. Brown, J. Organomet. Chem., 173 (1979) 71.
8 P.O. Nubel, S.R. Wilson and T.L. Brown, Organometallics 2 (1983) 515.
9 R. Usón, V. Riera, J. Gimeno, M. Laguna and M.P. Gamasa, J. Chem. Soc., Dalton Trans., (1979) 996.
10 R.J. Angelici, F. Basolo and A.J. Poë, J. Am. Chem. Soc., 85 (1963) 2215.
11 G.R. Dobson, N.S. Binzet and J. Mansour, Inorg. Chim. Acta, 77 (1983) L19.
12 J.D. Atwood and T.L. Brown, J. Am. Chem. Soc., 98 (1976) 3160.
13 J.A.S. Howell and P.M. Burkinshaw, Chem. Rev., 83 (1983) 557.
14 W.P. Weber, G.W. Gobel and I.K. Ugi, Angew. Chem., Int. Ed. Engl., 11 (1972) 530.