O atom transfer reactions in some manganese and rhenium carbonyl compounds

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Abstract

The compounds $M(CO)_5Cl$ ($M = Mn$ (**1a**); $M = Re$ (**1b**)) undergo reaction with $(CH_3)_3NO$ in CH_2Cl_2 to produce the series of anionic derivatives $[M(CO)_4L_2]^{1-}$ ($M = Mn$ (**2a**); $M = Re$ (**2b**); $L = Cl$ or $N(CH_3)_3$), $[Mn(CO)_3Cl_3]^{2-}$ (**3a**) and $[Mn_2(CO)_6(\mu_2\text{-}Cl)_3]^-$ (**4a**). These products have been identified from a comparison of their IR spectroscopic properties with authentic samples prepared by the direct reaction of $Mn(CO)_5Cl$ with Et_4NCl. The PPN^+ salt of **4a** has been characterized by X-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/n$ with the following cell dimensions; $a = 9.5335(12)$, $b = 15.6246(19)$ and $c = 29.158(6)$ Å; $\beta = 92.369(16)°$. Further reactions of the intermediate manganese chloride complexes with $PPNNO_2$ in CH_2Cl_2 lead to the formation of the series of anionic derivatives $[Mn(CO)_3Cl_2(\mathit{N}O_2)]^{2-}$ (**5a**), $[Mn(CO)_3Cl(\mathit{N}O_2)_2]^{2-}$ (**6a**), $[M(CO)_3(\mathit{N}O_2)_2(\mathit{O}N(O))]^{2-}$ (**7a**) and upon crystallization the trimer $[Mn_3(CO)_6(\mu_2\text{-}\mathit{N}O(O))_4(\mu_2\text{-}O(NO))_2]^{2-}$ (**8a**). Reaction of $Re(CO)_5Cl$ with $PPNNO_2$ in CH_2Cl_2 in the absence of Me_3NO yields the anionic species $[Re(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]^{2-}$ (**7b**), whereas in tetrahydrofuran under the same conditions the dianion $[\mathit{fac}\text{-}Re(CO)_3(\mathit{O}NO)_3]^{2-}$ (**9b**) is formed. Both compounds have been characterized as their PPN^+ salts by X-ray structure analysis. Compound **7b** has been shown to exist in the monoclinic space group $P2_1/n$ with the following cell dimensions: $a = 10.728(5)$, $b = 13.231(3)$ and $c = 23.383(7)$ Å; $\beta = 100.58(3)°$. Complex **9b** crystallizes in the orthorhombic space group *Pbca*; the cell dimensions are $a = 16.931(12)$, $b = 19.593(9)$ and $c = 19.971(13)$ Å.

Key words: Manganese; Rhenium; Carbonyl

1. Introduction

We are currently undertaking an investigation into O atom transfer reactions in metal carbonyl complexes. In particular, we are keen to understand the reactions that coordinated $-NO_2$ and $-ONO$ groups undergo. As part of this study we have also explored the behaviour of Me_3NO, a reagent which is commonly used to activate carbonyl compounds. Despite its wide application the nature of its reactions is not well understood and certainly the adopted reaction pathway depends on the solvent employed. We have observed the formation of derivatives containing CH_3CN from interactions of carbonyls with $(CH_3)_3NO\text{-}CH_3CN$, as in the case of $Os_3(CO)_{12}$ to produce $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}(MeCN)_2$ [1]. Hydrides are detected in the reaction of $Os_6(CO)_{18}$ with $Me_3NO\text{-}CH_2Cl_2$, which amongst other products yields the anion $[HOs_6(CO)_{17}]^-$ [2] and higher polymeric structures have been obtained, for example when $Co_2(CO)_8$ is reacted with $Me_3NO\text{-}CH_2Cl_2$ to produce $Co_4(CO)_{12}$ [3]. In this work we have observed that in the reaction of $M(CO)_5Cl$ ($M = Mn$ or Re) with $Me_3NO\text{-}CH_2Cl_2$ chlorination occurs to produce the range of chloroanions $[M(CO)_4Cl_2]^-$ (**2a** and **2b**), $[M(CO)_3Cl_3]^{2-}$ (**3a** and **3b**) and $[Mn_2(CO)_6(\mu_2\text{-}Cl)_3]^-$ (**4a**) and the cation $[Me_3NCH_2Cl]^+$.

In addition, we have explored the reactions of the species **1–3** with $PPNNO_2$. Our objective has been to prepare materials containing both coordinated CO and NO_2 ligands (bonded either as nitro or nitrito groups) and hence to investigate the O atom transfer reactions that they might undergo. There has been some previous work in this area. The initial observation of Booth and Chatt [4], that the nickel(II) compounds $Ni(NO_2)_2(PR_3)_2$ react with CO to produce the nitrosyl species $Ni(NO_2)(NO)(PR_3)_2$, led others to examine the

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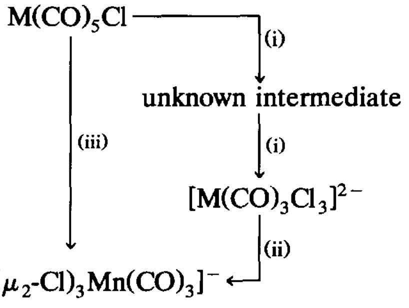


(i) Reaction with Me_3NO in CH_2Cl_2.
(ii) Crystallization from CH_2Cl_2 in the presence of $PPNNO_3$
(iii) Reaction with Et_4NCl in inert solvent at elevated temperatures.

Scheme 1. The reaction of $M(CO)_5Cl$ (M = Mn, Re) with $(CH_3)_3NO$ in CH_2Cl_2.

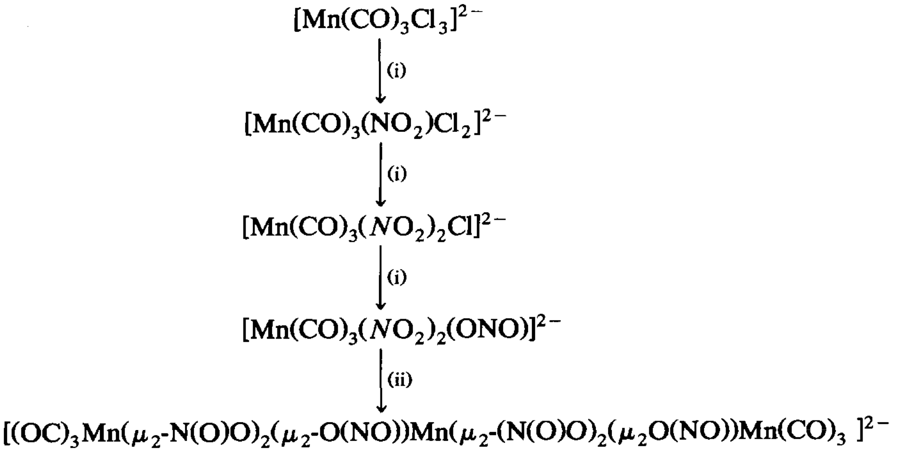
related chemistry of a wide range of complexes including mononuclear and polynuclear molecules as well as cluster compounds [5].

In this paper we present our studies of nitro–nitrito carbonyl complexes of both manganese and rhenium. Brief details of this work have been reported [6].

2. Results and discussion

The pentacarbonyl compounds $M(CO)_5Cl$ (M = Mn (**1a**); M = Re (**1b**)) undergo reactions with Me_3NO in CH_2Cl_2 according to Scheme 1. These reactions were initially monitored by following the change in the IR spectra (ν_{CO}) with time. They are dependent on the relative amount of the trimethylamine-*N*-oxide used (see Experimental section), but only in the extent to which the reaction proceeds. Thus, under all conditions the same reaction sequence **1** → (unknown complex) → **3** → **4** is observed. The IR spectrum recorded after **1** is treated with one equivalent of Me_3NO in CH_2Cl_2 shows clearly the presence of a compound of the geometry $[M(CO)_4\textit{cis}\text{-}L_2]^-$, but the wavenumbers recorded differ slightly from published ones (ν_{CO} = 2102w, 2023vs, 1995sh w, 1943ms, 1926sh w cm^{-1}, for comparison with the literature values see ref. 7). Attempts to crystallize this material have been unsuccessful so far. At the present stage we think that $N(CH_3)_3$ is involved and may be bonded to the metal. Further investigation is under way. In a separate experiment, **1** was treated with NEt_4Cl and the same sequence was observed; here the expected $[M(CO)_4Cl_2]^-$ (**2**) was prepared. Complexes **2**–**4** have been detected and fully characterized previously [7–9] and our IR data are in total agreement with those reported (Table 1).

The source of Cl^- in these reactions is clearly the dichloromethane and, consistent with this view, we succeeded in isolating a salt containing the $[Me_3NCH_2Cl]^+$ cation [6]. This species had earlier been prepared by the interaction of trimethylamine with CH_2Cl_2 and crystallographically characterized as the BF_4^- salt [10]. We have previously observed the formation of the hexaosmium cluster anion $[HOs_6(CO)_{17}]^-$ from the reaction with Me_3NO in CH_2Cl_2 (see above) and it is conceivable that the first product in the reactions reported here is a hydrido species. It is well known that compounds with terminally bonded hydrido ligands readily react with CH_2Cl_2 to form the corresponding chloro derivative. However, in the absence of any additional evidence we believe that the products are probably derived by direct Cl^- displacement from the CH_2Cl_2 by Me_3N produced during the oxidation of coordinated CO to CO_2.



(i) Reaction with $PPNNO_2$ in CH_2Cl_2 at RT/N_2.
(ii) Crystallization at −35°C in acetone/Et_2O mixture.

Scheme 2. The reaction of the halide intermediates, prepared by CO activation with Me_3NO/CH_2Cl_2, with $PPNNO_2$ in CH_2Cl_2.

It appears that the structure of the dimeric anion $[Mn_2(CO)_6(\mu_2\text{-}Cl)_3]^-$ has not been previously determined. We were able to separate good crystalline samples of this material and have carried out a full single-crystal X-ray analysis. Details regarding the determination of this structure can be found in Table 2. The two metal atoms are bonded to three carbonyl groups and to three bridging chlorides. The bond distances are as expected and the coordination geometry around the metal centers is almost ideally octahedral. Two different views of the molecule are given in Fig. 1. Several attempts to isolate $[Mn(CO)_3Cl_3]^{2-}$ in the solid state have failed, as dimerization to **4a** was observed in all experiments. However, on the basis of measurements of the electrical conductivity it is clear that in solution the dianionic monomer is present.

Our main interest has centred around the formation of nitro and nitrito derivatives of manganese and rhenium produced from the reaction of $PPNNO_2$ with the appropriate carbonyl precursor and the subsequent O transfer reactions that they undergo. We find that the chloropentacarbonyl compound $M(CO)_5Cl$ reacts with the $PPNNO_2$ in the presence of Me_3NO to produce a series of NO_2-containing anions **5**–**8** (Scheme 2). Initially all were observed by monitoring the reaction by IR spectroscopy. The IR spectra (ν_{CO}) of the species **5**–**8** are recorded in Table 1 and are consistent with the postulated structures.

TABLE 1. IR spectroscopic data; all spectra are recorded in CH_2Cl_2 at room temperature unless otherwise stated

Compound	$\nu(CO)$ (cm^{-1}) [a]
$Mn(CO)_5Cl$ (**1a**)	2142vw, 2055vs, 2009m
$Re(CO)_5Cl$ (**1b**)	2156vw, 2046vs, 1985m
$[Mn(CO)_4Cl_2]$ (**2a**)	2097vw, 2024vs, 1984w, 1936vs br
$[Mn(CO)_3Cl_3]^{2-}$ (**3a**)	2024vs, 1920vs br
$[(OC)_3Mn(\mu_2\text{-}Cl)_3Mn(CO)_3]^-$ (**4a**)	2024s, 1936vs br
$[Mn(CO)_3Cl_2(NO_2)]^{2-}$ [b] (**5a**)	2033w, 2022s, 1932vs br
$[Mn(CO)_3Cl(NO_2)_2]^{2-}$ [b] (**6a**)	
$[Mn(CO)_3(NO_2)_2(ONO)]^{2-}$ (**7a**)	2033vs, 2022w, 1942vs vbr
$[Re(CO)_3(NO_2)_2(ONO)]^{2-}$ (**7b**)	1990m, 1854s, 1844s [c]
$[Mn_3(CO)_6(\mu_2\text{-}N(O)O)_4\text{-}(\mu_2\text{-}O(NO))_2]^{2-}$ (**8a**)	2034s, 1954s, 1926vs [c] υ(nitro–nitrito), 1409, 1261, 1074 [d]
$[Re(CO)_3(ONO)_3]^{2-}$ (**9b**)	2012m, 1895s br [e]
$Mn(CO)_4(NO)$ (**10b**)	2100w, 2029vs, 1973s, υ(NO) 1757s [f]
$[Mn(CO)_2(NO)_2]^-$ (**11b**)	1978m, 1896s υ(NO) 1645s, 1607vs [f]

[a] The following abbreviations were used for the intensities: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; br, broad; vbr, very broad.

[b] At the present stage of our investigation it is impossible to distinguish between the two species on the basis of IR spectroscopy solely. Further studies are being undertaken.

[c] IR spectrum recorded in the solid state (Nujol mull).

[d] Owing to the Nujol mull and PPN^+ overlaps, not all the expected bands were observed.

[e] Spectrum recorded in acetone.

[f] Spectrum recorded in CH_3CN.

On standing at a low temperature, crystals of a new compound **10a** are slowly deposited from solutions of **9a** [6]. An X-ray analysis of this species revealed that it was the PPN^+ salt of the new trimeric anion $[Mn_3(CO)_6(\mu_2\text{-}NO(O))_4(\mu_2\text{-}O(NO))_2]^{2-}$. The trinuclear unit is centrosymmetric, with the central metal atom lying on an inversion centre. Its geometry is trigonally elongated from octahedral. The angles of the crystallographically unique O atoms have been reduced significantly to values as low as 80.62(14), 81.56(14) and 85.13(14)° respectively. The coordination geometry around Mn(2), which is bonded to three carbonyl groups, two nitrogen atoms from the NO(O) bridges and one oxygen atom from the O(NO) bridge, is only slightly distorted from octahedral.

Despite the apparent similarities between the anions **3a** and **8a** their polymerization to a dimer and trimer respectively clearly follows a different course. Whereas the dimer **4a** is a derivative of Mn^{II}, trimer **10a** contains both Mn^I and Mn^{II} ions. This species is clearly related to some derivatives of nickel, previously reported by Goodgame and co-workers [11]. Of special note are the two types of bridging NO_2 group observed. Two NO_2 moieties span an Mn^{II} and Mn^I ion in the more conventional Mn–N(O)–O–Mn coordination mode but the third adopts the less common nitrito bridge arrangement Mn–O(NO)–Mn. The reasons for this are not clear but it is apparent that the latter arrangement minimizes the steric strains that would be imposed on the system by three Mn–N(O)–O–Mn coordination modes. However, there is a further consideration. With three $\mu_2\text{-}NO_2$ it is impossible to derive a symmetrical bridging unit unless one adopts the nitrito arrangement. Adoption of this mode makes each Mn^I equivalent since it is coordinated to three CO, two NO_2 and one ONO ligands. Alternatively the change in bonding mode might be of electronic nature, but this should be reflected in differences in the bond lengths between the metal atom and the carbon of the CO ligand *trans* to the nitrogen and oxygen respectively. No such variations are observed. Thus, we are unable to understand fully this behaviour at the present stage of our investigations.

We also carried out direct reactions between $Re(CO)_5Cl$ and $PPNNO_2$. In an earlier publication, Stevens and Gladfelter [12], while working with related CO species and $PPNNO_2$, observed that in the reaction of $[Re(CO)_6]^+$ no nitrosyl species were generated and a spectrum very similar to $Re(CO)_5Cl$ was obtained. When reacting our starting material with the nitrite we were also unable to detect any nitrosyl absorptions in the IR spectrum. Crystals grown from reactions in tetrahydrofuran (THF) were shown to be (PPN)$_2$[Re(CO)$_3$(*O*NO)$_3$] (**9b**) and from CH_2Cl_2 solutions we were able to isolate and determine the structure of what appears to be a second isomeric form (PPN)$_2$[Re(CO)$_3$(*N*O$_2$)$_2$(*O*NO)] (**7b**). The two salts crystallize in different space groups, *Pbca* and $P2_1/n$ respectively.

In both cases the structures were solved to give a rhenium atom on a crystallographic inversion centre, and with two symmetry-related PPN$^+$ cations per rhenium. Therefore the rhenium must, in each case, be part of a dianion. Chemical considerations indicate that the only sensible species, which both satisfies charge neutrality and the 18-electron rule, is [Re(CO)$_3$(ONO)$_3$]$^{2-}$, and geometrical and linkage isomers thereof. However, such species cannot possess an inversion centre unless disordered and inevitably this is observed in **9b** and **7b**.

In **9b** this disorder consists of a complete scrambling of CO and *O*NO ligands over each site and was modelled with each site 50:50 CO:*O*NO. This gives a stoichiometry of [Re(CO)$_3$(*O*NO)$_3$] for the dianion, and chemical considerations would suggest that the *fac* isomer, in which each CO is *trans* to an *O*NO, should be preferred to the *mer* isomer (Fig. 1). Bond length constraints were applied to Re–C and Re–O bond lengths. The O $\cdots$ O contact within each ONO ligand was also restrained to be $\sqrt{3}$ times that of the O=N distances. These constraints allowed satisfactory refinement of the model structure, with sensible resulting bond lengths [Re–C distances, about 1.835(7)–1.882(7)

TABLE 2. Crystallographic data and details of measurements for (PPN)[(OC)$_3$Mn(μ_2-Cl)$_3$Mn(CO)$_3$] (**4a**), (PPN)$_2$[Re(CO)$_3$(NO$_2$)$_2$(ONO)] (**7b**) and (PPN)$_2$[Re(CO)$_3$(ONO)$_3$] (**9b**)

	7b	**9b**	**4a**
Crystal data			
Formula	$C_{75}H_{60}N_5O_9P_4Re$	$C_{75}H_{60}N_5O_9P_4Re$	$C_{43}H_{32}N_1O_6P_2Cl_5Mn_2$
Molecular weight	1484.9	1484.9	1007.5
Crystal system	Monoclinic	orthorthombic	Monoclinic
Space group	$P2_1/n$	*Pbca*	$P2_1/n$
a (Å)	10.728(5)	16.931(12)	9.5335(12)
b (Å)	13.231(3)	19.593(9)	15.6246(19)
c (Å)	23.383(7)	19.971(13)	29.158(6)
α (°)	90(–)	90(–)	90(–)
β (°)	100.58(3)	90(–)	92.369(16)
γ (°)	90(–)	90(–)	90(–)
V (Å^3)	3263	6625	4340
Temperature (K)	150	150	150
Z	2	4	4
μ (mm^{-1})	0.20	0.20	0.87
ρ (g cm^{-3})	1.51	1.49	1.48
Crystal size (mm)	0.56 × 0.45 × 0.14	0.51 × 0.51 × 0.43	0.39 × 0.39 × 0.19
Crystal colour	Pale brown	Pale yellow	yellow
Crystal shape	Plate	Block	Tablet
Data collection			
Diffractometer	Stoë Stadi-4	Stoë Stadi-4	Stoë Stadi-4
Radiation	Mo	Mo	Mo
λ (Å)	0.71073	0.71073	0.71073
Monochromator	Graphite	Graphite	Graphite
2θ scan range (°)	4–45	4–45	4–45
Scan mode	ω–2θ	ω	ω
Reflections collected	4205	4298	8029
Unique reflections with $F > 4\sigma(F)$	2402	2826	5885
Structure refinement			
R, R_w [19]	Refinement not completed		0.0628, 0.0906
$R1$, $wR2$ [a] [20]		0.0449, 0.1340	
S		1.011	1.155
$\Delta\rho_{max}$ (electrons Å^{-3})		1.14	1.39
$\Delta\rho_{min}$ (electrons Å^{-3})		−0.60	−0.61

[a] $R1$ calculated for reflections with $F_o > 4\sigma(F)$; $wR2$ is based on F^2 and is calculated for all data.

Å; Re–O distances, about 2.101(6)–2.169(7) Å] and normal bond angles. These bond lengths are comparable with, if slightly shorter than, those in the dianion $[\mathrm{Re(CO)_3}(N\mathrm{O_2})_2\mathrm{Cl}]^{2-}$, which is an ordered structure with Re–C bonds of about 1.91 Å, and Re–N bonds of 2.24 and 2.21 Å. The largest residual peak in the difference map is a little over 1e Å^{-3} and is associated with the disordered anion. No significant electron density was observed in positions consistent with the presence of any $N\mathrm{O_2}$ ligands in **9b**.

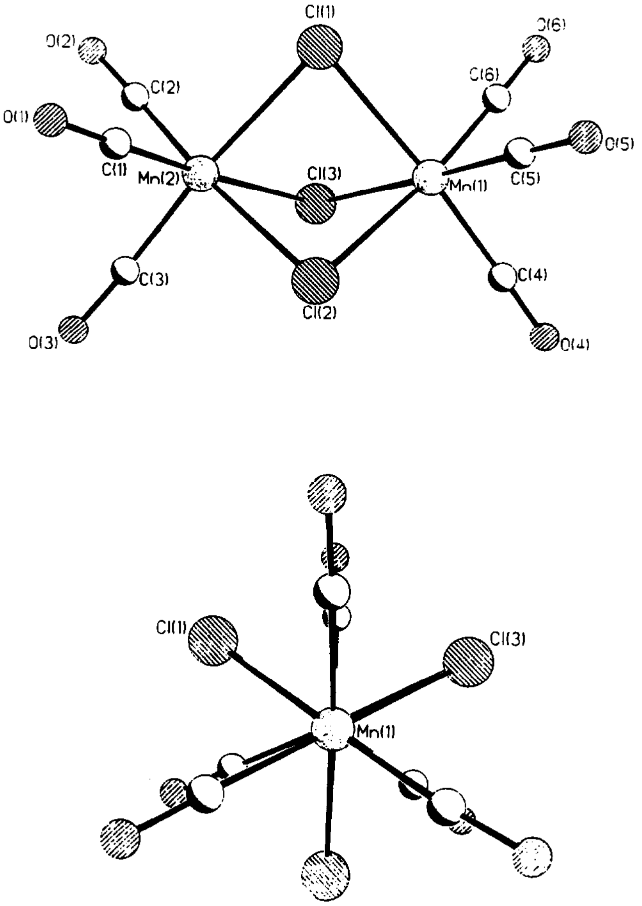


Fig. 1. The molecular and crystal structure of the PPN$^+$ salt of the dianion **4a**. The main bond distances are as follows: Mn(1)–Mn(2), 3.144(11); Mn(1)–C(4), 1.785(6); Mn(1)–C(5), 1.797(6); Mn(1)–C(6), 1.795(7); Mn(1)–Cl(1), 2.3751(15); Mn(1)–Cl(2), 2.4023(16); Mn(1)–Cl(3), 2.4281(20); Mn(2)–C(1), 1.799(6); Mn(2)–C(2), 1.808(7); Mn(2)–C(3), 1.792(7); Mn(2)–Cl(1), 2.3846(15); Mn(2)–Cl(2), 2.4007(16); Mn(2)–Cl(3), 2.4117(20) Å. The bond angles are the following: C(4)–Mn(1)–C(5), 90.9(3); C(4)–Mn(1)–C(6), 93.0(3); C(4)–Mn(1)–Cl(1), 174.24(20); C(4)–Mn(1)–Cl(2), 93.96(20); C(4)–Mn(1)–Cl(3), 93.83(20); C(5)–Mn(1)–C(6), 89.9(3); C(5)–Mn(1)–Cl(1), 94.11(21); C(5)–Mn(1)–Cl(2), 92.84(21); C(5)–Mn(1)–Cl(3), 172.55(21); C(6)–Mn(1)–Cl(1), 89.78(21); C(6)–Mn(1)–Cl(2), 172.45(22); C(6)–Mn(1)–Cl(3), 95.54(22); Cl(1)–Mn(1)–Cl(2), 83.01(5); Cl(1)–Mn(1)–Cl(3), 80.88(6); Cl(2)–Mn(1)–Cl(3), 81.14(6); C(1)–Mn(2)–C(2), 89.1(3); C(1)–Mn(2)–C(3), 89.7(3); C(1)–Mn(2)–Cl(1), 92.78(19); C(1)–Mn(2)–Cl(2), 93.81(20); C(1)–Mn(2)–Cl(3), 172.63(20); C(2)–Mn(2)–C(3), 90.8(3); C(2)–Mn(2)–Cl(1), 92.68(21); C(2)–Mn(2)–Cl(2), 174.74(21); C(2)–Mn(2)–Cl(3), 95.12(21); C(3)–Mn(2)–Cl(1), 175.79(23); C(3)–Mn(2)–Cl(2), 93.58(23); C(3)–Mn(2)–Cl(3), 96.27(23); Cl(1)–Mn(2)–Cl(2), 82.85(5); Cl(1)–Mn(2)–Cl(3), 81.03(6); Cl(2)–Mn(2)–Cl(3), 81.51(6); Mn(1)–Cl(1)–Mn(2), 82.69(5); Mn(1)–Cl(2)–Mn(2), 81.78(5); Mn(1)–Cl(3)–Mn(2) 81.03(6)°.

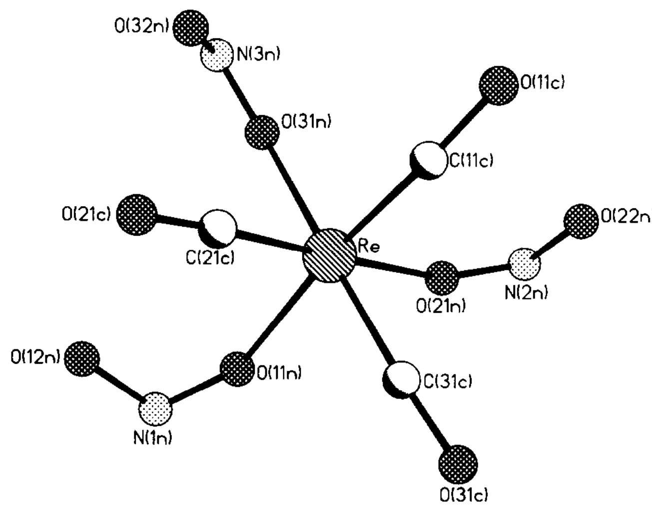
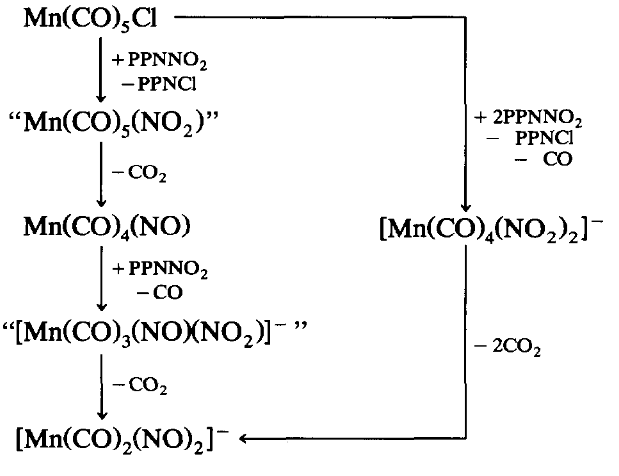


Fig. 2. The molecular and crystal structure of the PPN$^+$ salt of the dianion **9b**. The main bond distances are as follows: Re–C(21c), 1.835(7); Re–C(11c), 1.867(7); Re–C(31c), 1.882(7); Re–O(31n), 2.101(7); Re–O(11n), 2.164(6); Re–O(21n), 2.169(6) Å.

The dianion in **7b** is severely disordered, and refinement is concomitantly less satisfactory. What is clear so far is that the dianion must contain $N\mathrm{O_2}$ groups in addition to ONO groups as found in **9b**, as this is the only means by which the electron density observed can be explained. As each site can therefore contain CO, ONO and $N\mathrm{O_2}$ groups, even a system of restraints similar to those employed for **9b** does not allow refinement to proceed to an unambiguous conclusion. It does appear that there are more $N\mathrm{O_2}$ than ONO ligands within the species, which gives a probable formula of $[\mathrm{Re(CO)_3}(O\mathrm{NO})_2(N\mathrm{O_2})]^{2-}$ for the dianion. This is underlined by the solid state IR spectrum, which is very similar to the manganese trimer **7a**. The refinement of the structure is at the present not finished.

The separation of the anions **5**–**8** illustrates that it is possible for the oxidizing $\mathrm{NO_2}$ group and the reducing CO ligand to coexist in the coordination sphere of a metal ion. Similar examples have been reported previously but the compounds reported here appear to be amongst the first examples of stable systems containing multiple CO and $\mathrm{NO_2}$ bonded groups.

We have not been able to grow crystals of the corresponding mononuclear manganese $\mathrm{NO_2}$–CO species. The reaction mechanism is under study at the



Scheme 3. The reaction mechanism of the interaction of $Mn(CO)_5Cl$ with $PPNNO_2$ in CH_2Cl_2 or THF.

moment. Preliminary results show that the nature of the final product did not depend on the amount of Me_3NO added, as crystals obtained from the reaction of $Mn(CO)_5Cl$ with only one equivalent of the trimethylamine-*N*-oxide and subsequent addition of $PPNNO_2$ were shown to be identical with the above discussed structure. It seems so far that it is also possible to substitute NO_2^- for CO in Mn carbonyl complexes without the occurrence of oxygen transfer.

Conversion of the pre-formed nitro–nitrito complexes to the corresponding nitrosyl species has also been observed (Scheme 3). Treatment of $Mn(CO)_5Cl$ with $PPNNO_2$ in THF leads to the formation of the two nitrosyl compounds $Mn(CO)_4(NO)$ and $[Mn(CO)_2(NO)_2]^-$. It is clear that in these cases the precursor compounds $Mn(CO)_5(NO_2)$ and $[Mn(CO)_4(NO_2)_2]^-$ respectively are formed initially. In a separate experiment we have established that $Mn(CO)_4(NO)$ reacts with NO_2^- to form $[Mn(CO)_2(NO)_2]^-$ in quantitative amounts but we have been unable to find any evidence for the expected intermediate $[Mn(CO)_3(NO)(NO_2)]^-$. The addition of higher amounts of $PPNNO_2$ does not lead to further CO replacement and the preparation of new nitrosyl complexes. It would appear that the dianion $[Mn(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]^{2-}$ resists O atom transfer with the elimination of CO_2 to form the tricoordinated dianion $[Mn(NO)_3]^{2-}$. In these reactions it is clear that the compounds $Mn(CO)_5(NO_2)$ and probably **6a** are formed before conversion to the appropriate nitrosyl derivative occurs. It is thus indisputable that at least in the cases O transfer occurs from a coordinated NO_2 group rather than the nucleophilic addition of NO_2^- through one of its O atoms to a bonded CO ligand. In this respect the reactions differ from those reported for chromium [13] and other manganese [12,14] complexes. However, it is clear that, in the reaction of NO_2^- with $Cr(CO)_6$, prior coordination of the nitro ligand to give the anion $[Cr(CO)_5(NO_2)]^-$, in which the NO_2^- is bonded in the nitro fashion does not lead to O transfer and the formation of $[Cr(CO)_4(NO)]^-$.

3. Conclusions

In this work we have found that the carbonyl ligand, usually a strong reductant, and the NO_2 group, either in the nitro or nitrito form, may coexist in metal complexes. Oxygen transfer reactions do occur and are clearly solvent dependent. The formation of nitrosyl compounds by this process has been observed and would appear to proceed by an intramolecular pathway. Reoxidation of these nitrosyl species reveals a potential reduction–oxidation catalytic cycle.

4. Experimental details

4.1. General

All reactions were performed under an inert gas atmosphere (N_2) using standard Schlenk line techniques. $Mn_2(CO)_{10}$ and $Re(CO)_5Cl$ were purchased from Strem Chemicals Co. and used without further purification. $PPNNO_2$ was prepared as published [15]; $(CH_3)_3NO\ 2H_2O$ was dehydrated by azeotropic distillation with benzene followed by sublimation. $[Mn(CO)_4Cl_2]^-$ [7], $M_2(CO)_8(\mu_2\text{-}Cl)_2$ (M = Mn [16] and Re [16]), $[Mn(CO)_6(\mu_2\text{-}Cl)_3]^-$ [8] (as control experiment only) were prepared by literature procedures. All solvents were purified by known methods prior to use. IR measurements were carried out on a Perkin–Elmer Fourier Transform IR spectrometer, model 1605. IR data for all compounds are reported in Table 1.

4.2. Preparation of $Mn(CO)_5Cl$

In a typical experiment, 0.128 mmol (0.050 g) of $Mn_2(CO)_{10}$ was dissolved in 20 ml of chloroform. A water-cooled cold finger was immersed into the solution and strong magnetic stirring has to be provided. The solution was irradiated with a 600 W tungsten lamp. The reaction was followed by IR and terminated when no more CO absorptions due to $Mn_2(CO)_{10}$ were detected. Chloroform was removed under reduced pressure and the yellow $Mn(CO)_5Cl$ could then be redissolved in the solvent needed for further reactions.

4.3. Preparation of $[Mn_2(CO)_6(\mu_2\text{-}Cl)_3]^-$

0.256 mmol (0.060 g) of freshly prepared $Mn(CO)_5Cl$ was dissolved in 7 ml of dichloromethane and 0.513

mmol (0.038 g) of $(CH_3)_3NO$ was added at room temperature (RT). The yellow solution turned immediately orange and a heavy gas evolution (CO_2) was observed. The IR spectrum showed the presence of $[Mn(CO)_3Cl_3]^{2-}$ but, upon crystallization in CH_2Cl_2, dimerization occurred.

4.4. *Preparation of* $Mn(CO)_4(NO)$

0.256 mmol (0.060 g) of freshly prepared $Mn(CO)_5Cl$ was dissolved in 7 ml of either CH_2Cl_2 or THF at RT under N_2. To the yellow solution, 0.256 mmol (0.15 g) of $PPNNO_2$ were added directly. The solution turned dark red immediately and a strong gas evolution (CO_2) was observed. The product was identified by its characteristic IR absorptions in the CO and NO range. When the reaction was carried out in THF, it was impossible to obtain only $Mn(CO)_4(NO)$, as even addition of quantities of less than one equivalent of $PPNNO_2$ generated some $[Mn(CO)_2(NO)_2]^-$. We believe that this is caused by the different donor properties of the two solvents used.

4.5. *Preparation of* $[Mn(CO)_2(NO)_2]^-$

0.256 mmol (0.060 g) of freshly prepared $Mn(CO)_5Cl$ was dissolved in 7 ml of either CH_2Cl_2 or THF at RT under N_2^-. 0.512 mmol (0.30 g) of $PPNNO_2$ were added and an immediate change in colour from yellow to deep red-brown accompanied by a heavy gas evolution (CO_2) was detected. The IR spectrum, taken after the gas evolution had ceased, showed that a quantitative turn-over to the product had occurred.

4.6. *Preparation of* $[Mn(CO)_3(NO_2)_2(ONO)]^{2-}$

0.256 mmol (0.060 g) of freshly prepared $Mn(CO)_5Cl$ was dissolved in CH_2Cl_2. To the yellow solution, 0.512 mmol (0.038 g) of $(CH_3)_3NO$ was added. After the gas evolution had finished, the reaction mixture was stirred for another 1.5 h at RT. The IR spectrum showed that the only product present was $[Mn(CO)_3Cl_3]^{2-}$. 1.54 mmol (0.90 g) of $PPNNO_2$ was then immediately added to the orange solution and the mixture left to react for several hours. The reaction was followed by IR spectroscopy and terminated after the appearance of the final spectrum, characteristic for $[Mn(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]^{2-}$. For crystallization the CH_2Cl_2 was removed under reduced pressure at RT and the yellow-orange residue was redissolved in acetone. Several drops of Et_2O were added and crystallization occurred at −35°C.

The same final product could be prepared from the unknown intermediate observed after the addition of only one equivalent of $(CH_3)_3NO$ to a CH_2Cl_2 solution of $Mn(CO)_5Cl$. In this case the procedure was slightly changed; to a dichloromethane solution containing 0.512 mmol (0.060 g) $Mn(CO)_5Cl$ and 0.512 mmol (0.038 g) of Me_3NO were added directly. After gas evolution had ceased, the CO vibrations in the IR spectrum showed the presence of the unknown intermediate. To this yellow-orange solution, 1.54 mmol (0.90 g) of $PPNNO_2$ were added and the reaction mixture stirred for several hours. The addition of the $PPNNO_2$ provoked in this case a mild gas evolution, believed to be CO, as no IR absorptions characteristic of NO groups were observed. No measurements to determine exactly the nature and quantity of this gas have been carried out. The reaction was again stopped after the IR showed only the presence of **7a**. Crystallization procedures are as described above. The crystals observed were shown to be identical with **8a**.

4.7. *Preparation of* $[Re(CO)_3(NO_2)_2(ONO)]^{2-}$

0.083 mmol (0.030 g) of $Re(CO)_5Cl$ was dissolved in CH_2Cl_2 at RT. To the colourless solution, 0.257 mmol (0.150 g) of $PPNNO_2$ were added. No gas evolution or rapid colour change were observed. The reaction mixture went pale yellow, but this is due to dissolution of the PPN^+ cation. After stirring for 0.5 h at RT the IR spectrum revealed that a compound of the formula $[M(CO)_4\mathit{cis}\text{-}L_2]^-$ had been formed. The solution was then cooled to −35°C and the final product was crystallized by slow diffusion of Et_2O into the concentrated CH_2Cl_2 reaction mixture. It is assumed that the substitution of the third CO ligand occurs upon crystallization. Prolonged stirring of the reaction mixture at RT results in slow decomposition. No crystals of formula $[Re(CO)_4(NO_2)_2]^-$ were observed even when only two equivalents of $PPNNO_2$ were reacted. This unusual behaviour of the rhenium species is at the moment under investigation.

4.8. *Preparation of* $[Re(CO)_3(ONO)_3]^{2-}$

The reaction procedure is as described above for $[Re(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]^{2-}$; only the solvent in this case was THF. Upon addition of the $PPNNO_2$ a white precipitate was formed. This is partly due to the insolubility of the nitrite in THF but does not influence the reactivity. After stirring for 1 h at RT no starting material was left in the solution. The nature of the THF soluble product could not be determined yet. After filtration and several washings with THF the white precipitate was redissolved in acetone, to give a pale-yellow clear solution. The IR spectrum indicated that a product of formula $[Re(CO)_3(\mathit{N}O_2)_3]^{2-}$ had been formed. The bonding mode of the nitrite was established by X-ray crystallography to be nitrito, giving the molecular formula $(PPN)_2[Re(CO)_3(ONO)_3]$.

4.9. *Crystal structure determinations*

All X-ray measurements were made on a Stoë Stadi-4 four-circle diffractometer using graphite monochromated Mo Kα radiation. Data were collected at 150 K for all compounds, utilizing an Oxford Cryosystems low-temperature device [17]. Details of crystal data, data collection and structure refinement are summarized in Table 2.

The structures were solved by direct methods using SHELXS-86 [18] and refined with all full-occupancy non-hydrogen atoms anisotropic. Hydrogen atoms were included in the refinements in idealised positions (C–H, 1.08 Å) and with fixed isotropic thermal parameters ($U = 0.08$ Å^2) for **4a** and **7b**, but with the thermal parameters tied to a common free variable in **9b**. In **4a** a solvent fragment was located in the lattice; this was modelled as a half-occupancy diethyl ether. Refinement of **4a** was on F using SHELX76 [19].

In **7b** and **9b** the metal containing dianions were disordered. For **9b** this disorder is manifested as equal occupation of the metal coordination sites by carbonyl and nitrito groups. For each such site all five atomic positions, *i.e.* CO and ONO, could be resolved. Refinement against F^2 was possible by restraining chemically equivalent bonds and angles within the dianion to realistic values [20].

For **7b**, several possible model structures were refined, the most successful refinement involving similar constraints to those in **9b** for a model involving equal occupancy carbonyl and nitro groups in four coordination sites of the rhenium, and equal occupancy carbonyl and nitrito groups in the remaining two sites. It was not possible to resolve the position of the carbon of the carbonyls from the N of the nitro ligands, or from the bound oxygen of the nitrito groups, and refinement is not completed. Considerable electron density remains in the difference map, chiefly associated with the CO–ONO sites. Refinement was on F using SHELX76.

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