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New mixed carbonyl–nitro and –nitrito complexes of manganese and rhenium

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Treatment of $[Mn(CO)_5Cl]$ with Me_3NO in CH_2Cl_2 in the presence of $[N(PPh_3)_2][NO_2]$ gave the anion *cis*-$[Mn(CO)_4(NO_2)_2]^-$ which, on further reaction, yielded the new dianionic trimer $[Mn_3(CO)_6(\mu\text{-}NO_2)_4(\mu\text{-}ONO)_2]^{2-}$ containing both bridging nitro- and nitrito-groups. Reactions of $[Mn_2(CO)_8(\mu\text{-}Cl)_2]$, *cis*-$[Mn(CO)_4Cl_2]^-$, $[Mn_2(CO)_6(\mu\text{-}Cl)_3]^-$ or $[Mn(CO)_3Cl_3]^{2-}$ with $[N(PPh_3)_2][NO_2]$ also produce the same final product. The crystal and molecular structure of the $[N(PPh_3)_2]^+$ salt has been established by X-ray diffraction analysis. The molecule $[N(PPh_3)_2]_2[Mn_3(CO)_6(\mu\text{-}NO_2)_4(\mu\text{-}ONO)_2]$ crystallises in the triclinic space group $P\bar{1}$. Addition of $[N(PPh_3)_2][NO_2]$ to $[Re(CO)_5Cl]$ in CH_2Cl_2 yielded a series of mixed carbonyl–nitro/nitrito isomers, which have been characterised in solution. The unusual complex salt $[NMe_3(CH_2Cl)]_3[$*fac*$\text{-}Re(CO)_3(NO_2)_2Cl]Cl$ has been characterised in the solid state by single-crystal X-ray diffraction methods. The molecule crystallises in the monoclinic space group $P2_1/a$.

Oxygen-atom-transfer reactions involving NO_x (x = 1–3) and CO_x (x = 1 or 2) species are of fundamental importance particularly to those interested in the effect of these species on the environment. The ability of co-ordinated NO_2 and NO_3 groups to undergo oxygen-atom-transfer reactions to CO, presumably also co-ordinated to the same metal ion, was originally discovered by Booth and Chatt[1] in 1961, and has since been the subject of considerable study.[2–5] Although intensive studies into the mechanism of these intriguing reactions have been undertaken,[4,6,7] so far no data which may be taken to indicate unambiguously either an intra- or intermolecular pathway have been put forward.

The discovery of the high reactivity of the salt $[N(PPh_3)_2][NO_2]$ in the presence of neutral or positively charged carbonyl compounds has led to the preparation and characterisation of a wide variety of mixed CO–NO complexes.[8–10] However, as far as we are aware, neither the nature of the intermediates nor the reaction mechanism has been fully established in any case. During our investigation into oxygen-atom-transfer reactions of the early transition metals we have synthesised a series of mixed carbonyl–nitro/nitrito compounds in order to undertake studies of their ability to undergo O-atom transfer. Particular attention has been given to the solid-state structures of such species because the bonding mode of the NO_2^- moiety (nitro or nitrito) is regarded as an important factor in any understanding of oxygen-atom-transfer reactions and should provide information about the nature of the mechanism involved.

The mechanism of oxygen-atom transfer may be of one or two separate types. In the first, the prior co-ordination of the NO_2^- ligand either as nitro or nitrito may be thought to occur, followed by O-atom transfer to a bonded carbonyl ligand. In the second the bonded CO group is considered to undergo nucleophilic attack by the incoming NO_2^- ligand leading to an ONOCO bonded moiety followed by elimination of CO_2 and transfer of the NO ligand to the metal site in what is presumably a concerted process. In this work the primary objective has been to ensure prior co-ordination of the NO_2^- ligand to the metal centre by direct replacement of Cl^- and hence direct the reaction pathway towards the first mechanism. Some aspects of this work have been communicated previously.[11,12]

Results and Discussion

As all reactions between metal carbonyl compounds and $[N(PPh_3)_2][NO_2]$ carried out so far have led only to the isolation of products of oxygen-atom transfer, *viz.* the mixed carbonyl–nitrosyl species, we considered that the substitution of one or more carbonyl groups by a chloride ligand prior to the reaction with the NO_2^- anion might provide a specific point of substitution by the incoming nitrite ion. In our view the exchange of a Cl^- ligand by NO_2^- is expected to be favoured because of the differing solubilities of $[N(PPh_3)_2][NO_2]$ and $[N(PPh_3)_2]Cl$ and we concluded that the nitrite anion would preferentially co-ordinate to the metal. Our intention was to isolate and characterise these possible carbonyl–nitro/nitrito 'intermediate species' in the oxygen-atom-transfer process.

During these investigations we have been able to develop a new preparative route to mixed carbonyl–halide complexes of manganese and rhenium,[12] which were subsequently treated with either $[N(PPh_3)_2][NO_2]$ or $[PPh_4][NO_2]$. Of special interest to us were the anticipated changes in the reactivity, mechanism and products as a consequence of a gradual increase in the halide/carbonyl ratio. Some unsubstituted carbonyl species were also examined, either directly with nitrite or after activation with Me_3NO. Related reactions have also been carried out with several Group VIA complexes and found to yield mixed CO–NO_2 species.[13]

Reaction of $[Mn(CO)_5Cl]$ 1 with $[R][NO_2]$ $[R = N(PPh_3)_2^+$ or $PPh_4^+]$

The direct reaction of $[Mn(CO)_5Cl]$ **1** with $[N(PPh_3)_2][NO_2]$ led solely to the isolation of the oxygen-atom-transfer product $[Mn(CO)_4(NO)]$ which was readily identified on the basis of its IR spectrum. No reliable kinetic data could be collected and, because of the high reaction rate, no intermediate species, such as $[Mn(CO)_5(NO_2)]$, were detected, even at temperatures as low as −40 °C. It seems logical to assume that substitution of the halide by NO_2^- is followed by rapid intramolecular oxygen-atom transfer. Addition of 2 equivalents of $[N(PPh_3)_2][NO_2]$ to complex **1** results in the formation of the dinitrosyl salt $[N(PPh_3)_2][Mn(CO)_2(NO)_2]$.

Reaction of $[NEt_4][$*cis*$\text{-}Mn(CO)_4Cl_2]$ 2 and $[(OC)_4Mn(\mu\text{-}Cl)_2\text{-}Mn(CO)_4]$ 3 with $[N(PPh_3)_2][NO_2]$

Addition of 2 equivalents of $[N(PPh_3)_2][NO_2]$ to a solution of complex **2** in dichloromethane did not result in oxygen-atom

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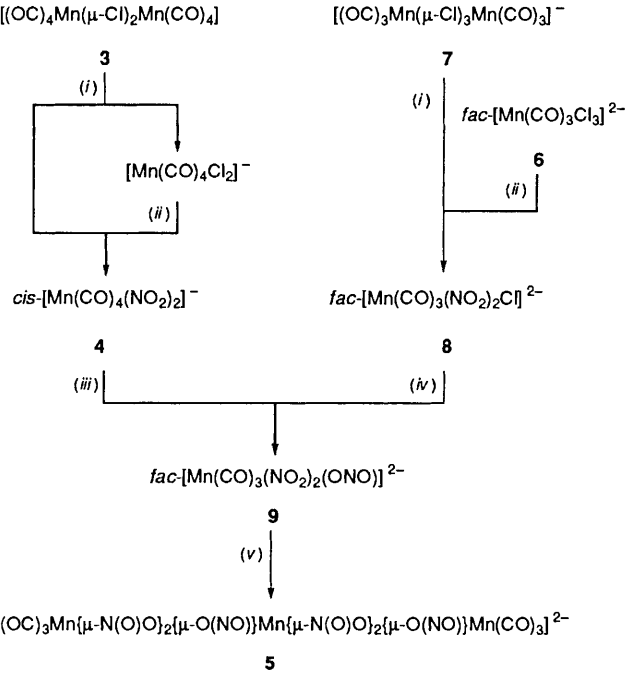
Table 1 Infrared data for compounds

Compound	$\tilde{\nu}(CO)/cm^{-1}$
1 $[Mn(CO)_5Cl]$	2142w, 2055vs, 2009ms $(CH_2Cl_2)^a$
2 $[NEt_4][\textit{cis}\text{-}Mn(CO)_4Cl_2]$	2097vw, 2024vs, 1984w, 1936vs (br) $(CH_2Cl_2)^a$
3 $[(OC)_4Mn(\mu\text{-}Cl)_2Mn(CO)_4]$	2107w, 2048s, 2012m, 1975ms $(CH_2Cl_2)^a$
4 $\textit{cis}\text{-}[Mn(CO)_4(\textit{N}O_2)_2]^-$	2101w, 2027vs, 1995w, 1940vs (br) (CH_2Cl_2)
5 $[N(PPh_3)_2]_2[(OC)_3Mn\{\mu\text{-}\textit{N}(O)\textit{O}\}_2\{\mu\text{-}\textit{O}(NO)\}\text{-}Mn\{\mu\text{-}\textit{N}(O)\textit{O}\}_2\{\mu\text{-}\textit{O}(NO)\}Mn(CO)_3]$	2034s, 1954s, 1926s (Nujol mull)^b ν(nitro/nitrito) 1409, 1261, 1074^c
6 $\textit{fac}\text{-}[Mn(CO)_3Cl_3]^{2-}$	2024s, 1924vs (br) (CH_2Cl_2)
7 $[(OC)_3Mn(\mu\text{-}Cl)_3Mn(CO)_3]^-$	2024s, 1936vs (br) $(CH_2Cl_2)^a$
8 $\textit{fac}\text{-}[Mn(CO)_3(\textit{N}O_2)_2Cl]^{2-}$	2033w, 2022s, 1932vs (br) (CH_2Cl_2)
9 $\textit{fac}\text{-}[Mn(CO)_3(\textit{N}O_2)_2(\textit{O}NO)]^{2-}$	2033vs, 2022w, 1942vs (br) (CH_2Cl_2)
10 $[Re_2(CO)_{10}]$	2070ms, 2009vs (br), 1966ms (thf)^a
11 $[N(PPh_3)_2]\,[Re_2(CO)_9(NO_2)]$	2093w, 2033m, 1982vs (br), 1941m, 1895m (thf); 2100w, 2039m, 1983vs (br), 1943m, 1906m (CH_2Cl_2)
12 $[NMe_3(CH_2Cl)][\textit{fac}\text{-}Re(CO)_3(\textit{N}O_2)_2Cl]Cl$	2011s, 1982s, 1891vs (br) (CH_2Cl_2)
13 $\textit{fac}\text{-}[Re(CO)_3(\textit{N}O_2)_3]^{2-}$	2012s, 1895vs (br) (acetone)
15 $[N(PPh_3)_2][\textit{cis}\text{-}Re(CO)_4(NO_2)_2]$	2106vw, 2003vs, 1967m, 1911s (CH_2Cl_2)
16 $\textit{fac}\text{-}[Re(CO)_3(\textit{O}NO)_3]^{2-}$	2006s, 1884vs (CH_2Cl_2)
17 $\textit{fac}\text{-}[Re(CO)_3(\textit{N}O_2)_2(\textit{O}NO)]^{2-}$	2025s, 2015s, 1903vs (br) (CH_2Cl_2)
18 $\textit{fac}\text{-}[Re(CO)_3Cl_3]^{2-}$	2002s, 1866vs (br) (CH_2Cl_2)

^{a} In accordance with literature values.[14–16] ^{b} Compound decomposes upon dissolution in CH_2Cl_2. ^{c} Owing to overlap with the Nujol mull and $[N(PPh_3)_2]^+$ not all expected $\nu(NO_2)$ bands are observed.



Scheme 1 (*i*) 2 equivalents $[N(PPh_3)_2][NO_2]$ in CH_2Cl_2; (*ii*) substitution of Cl^- ligands by NO_2^- (nitro) ligands; (*iii*) substitution of CO ligand by ONO^- (nitrito) ligand; (*iv*) substitution of Cl^- ligand by ONO^- (nitrito) ligand; (*v*) crystallisation in acetone–Et_2O at −25 °C

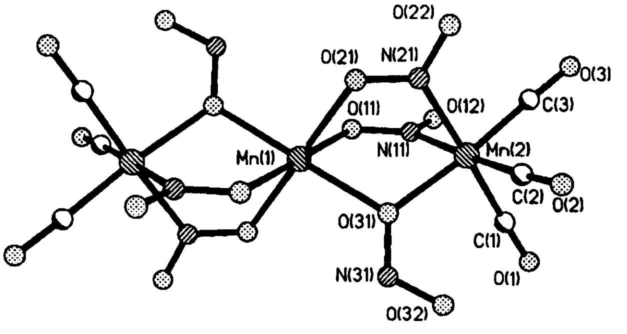


Fig. 1 Molecular structure of the dianion of complex **5**

transfer. A shift to higher wavenumbers for the ν(CO) absorptions was observed in the IR spectrum, indicating that replacement of both Cl^- ligands by incoming nitrite ions to yield the anion $\textit{cis}\text{-}[Mn(CO)_4(NO_2)_2]^-$ **4** had occurred (Table 1). No IR evidence for the monosubstituted product $[Mn(CO)_4Cl(NO_2)]^-$ was found during the reaction. Attempts to crystallise the *cis*-dinitro-species $\textit{cis}\text{-}[Mn(CO)_4(NO_2)_2]^-$ were unsuccessful, and this monoanion was found to react further either with any excess of $[N(PPh_3)_2][NO_2]$ present (or sacrificially to scavenge NO_2^- ligands from **4**) to yield the species $[N(PPh_3)_2]_2[(OC)_3Mn\{\mu\text{-}\textit{N}(O)\textit{O}\}_2\{\mu\text{-}\textit{O}(NO)\}Mn\{\mu\text{-}\textit{N}(O)\textit{O}\}_2\{\mu\text{-}\textit{O}(NO)\}Mn(CO)_3]$ **5** (see Scheme 1).

We found that the reaction proceeds similarly in the case of the neutral dimer **3**. Thus, on addition of 4 equivalents of $[N(PPh_3)_2][NO_2]$ to a solution of **3** in CH_2Cl_2 two distinct compounds are formed, as evidenced by changes in the IR spectrum. One set of ν(CO) absorptions may be matched to the known anionic species **2** and the other to the monoanion **4** (see Scheme 1). Eventually the complex anion **2** undergoes complete conversion into **4**. Again, **5** was the only crystalline product isolated from the reaction mixture.

Reaction of $\textit{fac}\text{-}[Mn(CO)_3Cl_3]^{2-}$ 6 and $[(OC)_3Mn(\mu\text{-}Cl)_3Mn(CO)_3]^-$ 7 with $[N(PPh_3)_2][NO_2]$

Addition of 3 equivalents of $[N(PPh_3)_2][NO_2]$ to a freshly prepared solution of complex **6**[12] in dichloromethane results in a change from yellow to orange. The ν(CO) IR absorptions show a shift to higher wavenumbers as expected upon substitution of the π-donating Cl^- ions by nitrite ligands. Two steps are observed, which, on the basis of the ν(CO) absorptions and the observed final product **5** may be regarded first as the rapid replacement of two Cl^- ions by incoming nitro groups, forming $\textit{fac}\text{-}[Mn(CO)_3(\textit{N}O_2)_2Cl]^{2-}$ **8** and then replacement of the third halide by NO_2^- to yield the dianion $\textit{fac}\text{-}[Mn(CO)_3(\textit{N}O_2)_2(\textit{O}NO)]^{2-}$ **9** (see Scheme 1). Upon crystallisation **5** is again isolated: the appearance of this trinuclear species from all reactions, independent of the starting material, points to its high stability in comparison to its mono- and di-nuclear precursors. Complex **9** could not be isolated as a solid, and unlike its rhenium analogue did not undergo conversion to $\textit{fac}\text{-}[Re(CO)_3(ONO)_3]^{2-}$

Molecular and crystal structure of complex 5

The molecular structure of complex **5** in the solid state has been established by single-crystal X-ray diffraction. Relevant structural parameters are reported in Table 2. From Fig. 1 it can

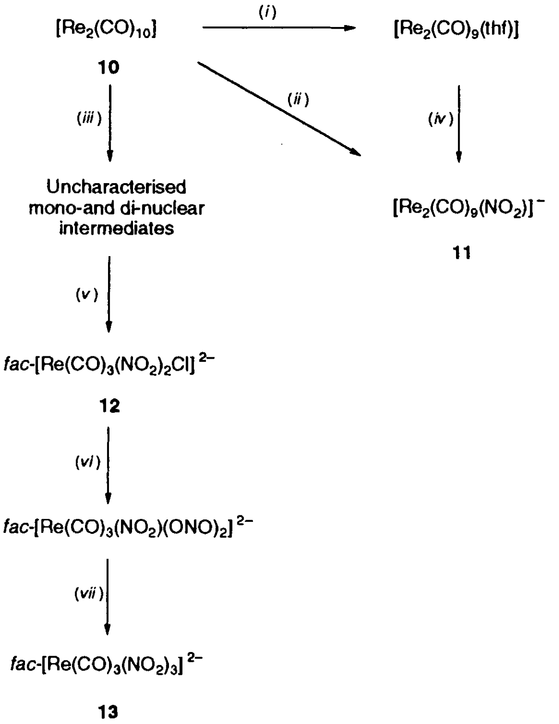
Table 2 Selected bond distances (Å) and angles (°) for compound **5**

Mn(1)–O(11)	2.180(4)	Mn(2)–C(3)	1.798(6)
Mn(1)–O(21)	2.159(4)	N(11)–O(11)	1.273(6)
Mn(1)–O(31)	2.129(4)	N(11)–O(12)	1.238(6)
Mn(2)–N(11)	2.044(4)	N(21)–O(21)	1.279(6)
Mn(2)–N(21)	2.040(4)	N(21)–O(22)	1.225(6)
Mn(2)–O(31)	2.032(4)	N(31)–O(31)	1.280(6)
Mn(2)–C(1)	1.832(6)	N(31)–O(32)	1.223(7)
Mn(2)–C(2)	1.809(6)		
O(11)–Mn(1)–O(21)	85.13(14)	C(1)–Mn(2)–C(2)	90.3(3)
O(11)–Mn(1)–O(31)	81.56(14)	C(1)–Mn(2)–C(3)	90.6(3)
O(21)–Mn(1)–O(31)	80.62(14)	C(2)–Mn(2)–C(3)	89.9(3)
N(11)–Mn(2)–N(21)	86.47(17)	Mn(2)–N(11)–O(11)	121.5(3)
N(11)–Mn(2)–O(31)	84.77(16)	Mn(2)–N(11)–O(12)	122.0(3)
N(11)–Mn(2)–C(1)	92.79(22)	O(11)–N(11)–O(12)	116.5(4)
N(11)–Mn(2)–C(2)	176.92(22)	Mn(1)–O(11)–N(11)	119.3(3)
N(11)–Mn(2)–C(3)	89.74(22)	Mn(2)–N(21)–O(21)	122.5(3)
N(21)–Mn(2)–O(31)	85.33(16)	Mn(2)–N(21)–O(22)	121.8(3)
N(21)–Mn(2)–C(1)	177.70(22)	O(21)–N(21)–O(22)	115.7(4)
N(21)–Mn(2)–C(2)	90.48(22)	Mn(1)–O(21)–N(21)	118.4(3)
N(21)–Mn(2)–C(3)	91.569(22)	O(31)–N(31)–O(32)	117.0(5)
O(31)–Mn(2)–C(1)	92.43(21)	Mn(1)–O(31)–Mn(2)	110.50(17)
O(31)–Mn(2)–C(2)	95.43(21)	Mn(1)–O(31)–N(31)	121.4(3)
O(31)–Mn(2)–C(3)	173.84(21)	Mn(2)–O(31)–N(31)	127.9(3)

be seen that a centrosymmetric array of three Mn atoms, charge balance requires that two oxidation states, Mn^{I} and Mn^{II}, are present. The central metal atom lies on an inversion centre and is bonded to six oxygen donors from two sets of symmetry-related bridging NO_2^- ligands. The co-ordination geometry around Mn(1) is trigonally elongated from the ideal octahedral arrangement, with the angles between the three crystallographically unique oxygen atoms being 80.62(14), 81.56(14) and 85.13(14)° respectively. As this metal site is unique, and the metal is bound to six oxygen donors, we assign this as the manganese(II) site. The Mn–O distances of *ca.* 2.16 Å are not unusual for this oxidation state.

The second metal atom Mn(2) is bonded to three carbonyl groups and two nitrogen donors from the nitro-bridges as well as the oxygen atom from the nitrite bridging ligand. In this case, the geometry is only slightly distorted from octahedral, typical for a low-spin d^6 metal atom. These factors, together with charge-balance considerations, lead us to assign this site to the manganese(I) oxidation state. The occurrence of more than one bonding mode for the nitrite ligand is rare but not unknown: Goodgame *et al.*[17] have previously isolated a trinuclear nickel complex which was not only bridged by nitro- and nitrito-moieties, but also contained a chelating NO_2^- species. Packing plots of complex **5** show that there appear to be no obvious steric reasons for this configuration. If electronic factors were influential, differences in the bond distances between Mn(2) and the C atoms *trans* to the nitro- and nitrito-bridges respectively might have been expected. This is not observed; the Mn–C bond *trans* to the O-donor is shortest [at 1.798(6) Å], but not in a statistically significant way. The Mn–N distances of *ca.* 2.042 Å are normal.

The mechanism of formation of the trinuclear species during crystallisation seems to be complex. We might speculate that the dianion $[Mn(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]^{2-}$ is able to function as a tridentate ligand co-ordinating to the oxyphilic manganese(II) ion through three oxygen atoms from each co-ordinated NO_2^- ligand. The presence of a mixed-valence species was unexpected; the pale yellow colour of the crystals leads us to believe there are no intervalence electronic transitions.



Scheme 2 (*i*) 1 Me_3NO in thf, 25 °C; (*ii*) 1 Me_3NO + 1 $[N(PPh_3)_2][NO_2]$ in CH_2Cl_2, 25 °C; (*iii*) 3–4 Me_3NO in CH_2Cl_2, 25 °C; (*iv*) 2 $[N(PPh_3)_2][NO_2]$ in thf, 25 °C; (*v*) 3 $[N(PPh_3)_2][NO_2]$ in CH_2Cl_2, 25 °C, 72 h; (*vi*) reflux in CH_2Cl_2, 1–2 h; (*vii*) reflux in CH_2Cl_2, 4–5 h

Reaction of $[Re_2(CO)_{10}]$ 10 with $[N(PPh_3)_2][NO_2]$

The direct reaction between $[Mn_2(CO)_{10}]$ and $[N(PPh_3)_2][NO_2]$, yielding $[N(PPh_3)_2][Mn(CO)_2(NO)_2]$ and $[N(PPh_3)_2][Mn(CO)_5]$ was investigated by Gladfelter and co-workers.[8] No analogous studies were undertaken for rhenium at that time. In this work we have observed that the addition of 1 equivalent of $[N(PPh_3)_2][NO_2]$ to a solution containing complex **10** in tetrahydrofuran (thf) results in the quantitative substitution of one equatorial carbonyl group for a nitrite ion (see Scheme 2) to give $[N(PPh_3)_2][Re_2(CO)_9(NO_2)]$ **11**. This species, which was identified on the basis of its spectroscopic properties, was found to resist oxygen-atom transfer in the absence of thermal or photochemical activation. Despite this stability we were unable to isolate **11** as a pure material. The co-ordination mode of the NO_2^- ligand has not been fully established but, by comparison with other related rhenium compounds, and the observation that in all other cases we have examined the first substitution results in a nitro-co-ordination, it seems probable that this is also the case here. In general, the well defined and characteristic N–O stretches for $\mathit{N}O_2^-$ and $\mathit{O}NO^-$ in the IR spectrum allow a satisfactory differentiation of the bonding modes.[18] However, in this system the nitrite peaks were not well resolved because of the peaks arising from the presence of $[N(PPh_3)_2]^+$ or $[PPh_4]^+$ (see below) and solvent.

Complex **11** could alternatively be synthesised *via* Me_3NO activation in the non-co-ordinating solvent CH_2Cl_2 in the presence of $[R][NO_2]$ [R = $N(PPh_3)_2^+$ or PPh_4^+].

Reaction of complex 10 with $[N(PPh_3)_2][NO_2]$ in the presence of Me_3NO in CH_2Cl_2

When the dinuclear precursor **10** was treated with 3–4 equivalents of Me_3NO in CH_2Cl_2 at room temperature and in the absence of any co-ordinating ligand (*e.g.* MeCN or NO_2^-), the metal–metal bond was cleaved and several air-sensitive mononuclear species were detected. No attempts were made to isolate these materials which are believed to be anionic and contain, besides carbonyl groups, chloride or hydride ligands. However, if the reaction is carried out in the presence of 3 equivalents of $[N(PPh_3)_2][NO_2]$ the pale brown cloudy solution slowly darkens to brown. The reaction was stirred, in the absence of direct sunlight, for up to 72 h, after which no further changes in the IR spectrum were observed. The

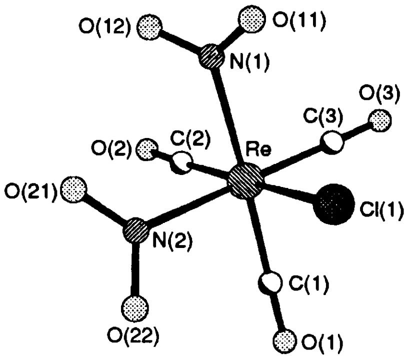


Fig. 2 Molecular structure of the dianion of complex **12**

appearance of the ν(CO) absorptions pointed to a mononuclear dianionic species with a *fac*-$[\mathrm{M(CO)_3L^1{}_2L^2}]$ structure and on crystallisation from CH_2Cl_2–Et_2O at 5 °C the salt $[\mathrm{NMe_3(CH_2Cl)}][fac\text{-}\mathrm{Re(CO)_3(}N\mathrm{O_2)_2Cl}]\mathrm{Cl}$ **12** was isolated and structurally characterised.

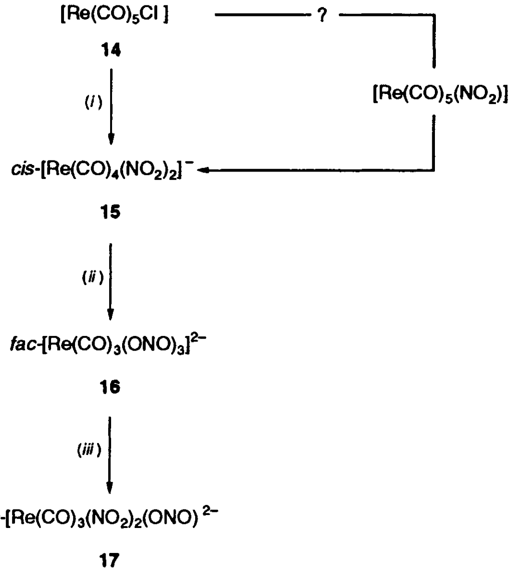
The reasons for the presence of the chloride ligand instead of a nitrite group are not clear, as 3 equivalents of NO_2^- per rhenium atom were initially added to the mixture. Substitution of the Cl^- ion in complex **12** could be achieved in CH_2Cl_2 under reflux in the presence of an excess of $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$. The solution turns dark brown over the period of 1–2 h. The halide ion is replaced by an NO_2^- ligand which adopts the nitrito bonding mode: evidence for this comes from the observation that the shifted carbonyl bands in the IR spectrum retain the pattern of three absorptions characteristic for a *fac*-$[\mathrm{M(CO)_3L^1{}_2L^2}]$ complex. However, it was noted that the substitution reaction was followed by a rearrangement of the nitrite ligands on further reflux in CH_2Cl_2. The IR spectrum changed slowly over 4–5 h at the end of which the appearance of two ν(CO) bands pointed to the complex dianion *fac*-$[\mathrm{Re(CO)_3(}N\mathrm{O_2)_3}]^{2-}$ **13**. The assignment of the bonding mode as nitro was made on the basis of the shift of the carbonyl absorptions. Although crystals could be grown in CH_2Cl_2–Et_2O mixtures at −35 °C these were not of adequate quality for diffraction studies.

Crystal and molecular structure of complex 12

The structure of the dianion is shown in Fig. 2: both NO_2^- ligands are bonded *via* their nitrogen atoms to form a dinitro arrangement and lie *trans* to carbonyl groups. There is only one other known example of a rhenium complex containing both carbonyl and NO_2^- ligands, *viz.* the species of formula $[\mathrm{Re_3(CO)_{14}(NO_2)}]$[19] but in that case the typical nitro/nitrito co-ordination is not observed, instead a bonding mode involving all three atoms of the NO_2^- moiety is seen. Relevant structural parameters for compound **12** are reported in Table 3.

Differences in π-electron donor/acceptor properties of the nitro and the halide ligands might be expected to influence the bond distances between the metal and carbonyl carbon atom in the respective *trans* position in complex **12**. However, this is not observed and all three Re–C bond lengths are identical within the estimated error.

The isolation of the unusual cation $[\mathrm{NMe_3(CH_2Cl)}]^+$ suggests that the chloride ions present in the structure have been scavenged from the solvent. It also shows that in the presence of smaller counter ions ordered structures are found, whereas the direct reactions between rhenium carbonyl complexes and $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$ result in disordered anions in the crystal (see below). The cation $[\mathrm{NMe_3(CH_2Cl)}]^+$ had previously been observed by Ebsworth and co-workers[20] as its BF_4^- salt. The weakly co-ordinated NMe_3 is, at least partly, responsible for the air-sensitivity of complex **12**: on exposure to air a smell of trimethylamine is immediately detected.



Scheme 3 (*i*) 2 $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$ in CH_2Cl_2, 25 °C; (*ii*) 1 $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$ in CH_2Cl_2, reflux, 1 h; (*iii*) reflux in CH_2Cl_2, 4–5 h

Table 3 Selected bond distances (Å) and angles (°) for the dianion **12**

Re–Cl(1)	2.488(5)	C(2)–O(2)	1.153(15)
Re–C(1)	1.921(13)	C(3)–O(3)	1.156(14)
Re–C(2)	1.908(12)	N(1)–O(11)	1.099(17)
Re–C(3)	1.906(12)	N(1)–O(12)	1.208(19)
Re–N(1)	2.243(11)	N(2)–O(21)	1.187(16)
Re–N(2)	2.208(11)	N(2)–O(22)	1.234(17)
C(1)–O(1)	1.151(16)		
Cl(1)–Re–C(1)	92.4(4)	C(2)–Re–N(1)	90.9(5)
Cl(1)–Re–C(2)	175.0(4)	C(2)–Re–N(2)	92.3(5)
Cl(1)–Re–C(3)	94.9(4)	C(3)–Re–N(1)	94.7(4)
Cl(1)–Re–N(1)	85.7(3)	C(3)–Re–N(2)	178.6(5)
Cl(1)–Re–N(2)	83.8(3)	N(1)–Re–N(2)	85.5(4)
C(1)–Re–N(1)	176.5(5)	O(11)–N(1)–O(12)	121.7(14)
C(1)–Re–N(2)	91.4(5)	O(21)–N(2)–O(22)	117.9(12)

Reaction of $[\mathrm{Re(CO)_5Cl}]$ 14 with $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$

Addition of 1 equivalent of $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$ to a CH_2Cl_2 solution of complex **14** at 0 °C did not result in any evolution of gas or an immediate colour change. The observation of a new set of ν(CO) bands in addition to those of the starting material indicated that a rapid reaction had taken place. The pattern of these new absorptions is characteristic for complexes of the formula *cis*-$[\mathrm{M(CO)_4L_2}]^-$. The complex present should therefore be formulated as $[\mathrm{N(PPh_3)_2}][cis\text{-}\mathrm{Re(CO)_4(NO_2)_2}]$ **15** (Scheme 3). Addition of a second equivalent of $[\mathrm{N(PPh_3)_2}][\mathrm{NO_2}]$ resulted in the complete conversion of the precursor into **15**. Attempts to detect the monosubstituted species $[\mathrm{Re(CO)_5(NO_2)}]$ were unsuccessful, implying that its stability is low or that it reacts with any excess of nitrite faster than does the parent compound **14**. Although the species has been postulated as one of the products of the reaction of $[\mathrm{Re_2(CO)_{10}}]$ with N_2O_4,[21] no supporting evidence has yet been published.

Isolation and full characterisation of the disubstituted anion **15** was unsuccessful: again, further substitution of a third carbonyl group for an NO_2^- ligand occurred upon crystallisation in CH_2Cl_2–Et_2O at −35 °C. A crystal structure solution revealed the presence of two cations per rhenium species, which therefore must have undergone further replacement reactions to give a dianionic compound. The crystal structure could not be refined satisfactorily, as the central rhenium atom lies on an inversion centre, which is incompatible with *fac*-$[\mathrm{Re(CO)_3(NO_2)_3}]^{2-}$. Owing to similar bond distances expected for Re–C (carbonyl), Re–N (nitro) or Re–O (nitrito) no satisfactory refinement models involving partial occupancies could be derived. The utilisation of a smaller counter ion, because the large $N(PPh_3)_2^+$ is believed to cause the observed serious disorder, did not produce crystals of diffraction quality.

The disubstituted complex **15** could readily be converted into the dianion *fac*-$[Re(CO)_3(NO_2)_3]^{2-}$ in refluxing CH_2Cl_2 in the presence of an excess of $[N(PPh_3)_2][NO_2]$. The substitution of the carbonyl group is accompanied by linkage isomerisation of all three NO_2^- ligands to form initially *fac*-$[Re(CO)_3(ONO)_3]^{2-}$ **16** (see Scheme 3). This species then converts slowly, over a period of 4–5 h at temperatures of ≈40 °C, into *fac*-$[Re(CO)_3(NO_2)_2(ONO)]^{2-}$ **17**.

The analogous reaction was also carried out in thf, as it was assumed that the solvent had a strong influence on the reaction rate and possibly the mechanism. The solubility of both $[N(PPh_3)_2][NO_2]$ and $[PPh_4][NO_2]$ is lower in thf than in CH_2Cl_2. It was found that the reactivity of $[PPh_4][NO_2]$ decreased strongly but for $[N(PPh_3)_2][NO_2]$ a rapid reaction was observed despite the presence of undissolved nitrite in the reaction solution. Addition of 2–3 equivalents of the $[N(PPh_3)_2][NO_2]$ to a thf solution containing $[Re(CO)_5Cl]$ resulted in the immediate appearance of a white precipitate. No colour change or evolution of gas was observed. The reaction was terminated after 1 h and the product in solution was found to be **15**. Examination of the precipitate revealed the presence of a second reaction product. The off-white powder was dried and redissolved in acetone. The IR spectrum indicated the complex dianion **13**. It seems therefore that this species is formed more rapidly in thf, a donor solvent, than in CH_2Cl_2. Recrystallisation of this powder by diffusion of Et_2O into a solution of the compound in acetone led to the isolation of **16**, the crystal structure of which has been described in an earlier publication.[12] It seems that the complete rearrangement of all three NO_2^- ligands during crystallisation is a consequence of attempts by the dianion to minimise steric differences between cation and anion in the crystal lattice. Linkage-isomerisation reactions of nitrite complexes have been investigated by several researchers[22,23] and it was shown that an increase in the volume occurs on exchange from a nitro to a nitrito ligand. For the complex $[Co(NH_3)_5(NO_2)]^{2+}$ a 'swelling' of the cation by 19% was calculated.[24]

Reaction of mixed chloride–carbonyl complexes of rhenium with [R][NO$_2$]

Addition of 1.2 equivalents of Me_3NO to a CH_2Cl_2 solution of complex **14** did not cause a colour change, but a weak evolution of gas was detected. The reaction was monitored by IR spectroscopy and within 20 min at room temperature complete conversion of the precursor $[Re(CO)_5Cl]$ into *cis*-$[Re(CO)_4Cl_2]^-$ was observed. A small amount of disubstituted material was also present in the reaction mixture. Addition of $[N(PPh_3)_2][NO_2]$ to this solution did not, however, result in any further changes in the IR spectrum.

The substitution of two carbonyl ligands *via* activation with Me_3NO was attempted. It was expected that the removal of two CO ligands and the subsequent co-ordination of two chloride ions would generate *fac*-$[Re(CO)_3Cl_3]^{2-}$ **18**. For this dianion two absorptions in the carbonyl region of the IR spectrum should be observed. The detection of three bands, pointing to the presence of two different ligands, shows that incorporation of either hydrides or NMe_3 has occurred. This species was not further characterised, but on reaction with 3 equivalents of $[N(PPh_3)_2][NO_2]$ a new ν(CO) pattern was observed in the IR spectrum. The two new peaks indicate the formation of the trinitrito species **13**.

The complex dianion **18** has been prepared by Hawkes and Ginsberg[25] by thermal activation. They presented only an IR spectrum, consisting of three carbonyl bands in both solution (MeCN) and Fluorolobe mull. It seems that these two media are inappropriate choices for this complex: in acetonitrile, replacement of one halide ion by MeCN should occur readily, whereas in a Fluorolobe mull exchange between F^- and Cl^- is expected. To avoid these problems we synthesised the trisubstituted dianion *fac*-$[Re(CO)_3Cl_3]^{2-}$ and recorded its spectrum in CH_2Cl_2. Our observation of only two ν(CO) absorptions at 2002s and 1866vs (br) cm^{-1} clarifies the expected co-ordination. If the species is dissolved in MeCN the spectrum is identical to that recorded by Hawkes and Ginsberg.[25]

The addition of 3 equivalents of either $[N(PPh_3)_2][NO_2]$ or $[PPh_4][NO_2]$ to the air- and moisture-sensitive complex **18** results in changes in the IR spectrum, but it was impossible to interpret the new bands. No crystalline material was obtained and it is therefore assumed that more than one product is formed. As all mixed carbonyl–nitro/nitrito complexes within this project display ν(CO) absorption bands in a fairly narrow range, overlap can be a problem.

Conclusion

In this work we have established that both nitro- and nitrito-ligands will bond to either manganese or rhenium carbonyl units to produce stable carbonyl–nitro/nitrito complexes. In certain cases these complexes undergo O-atom transfer to produce nitrosyl derivatives with the liberation of CO_2. These observations may be taken reliably to indicate that the oxygen-atom transfer may occur between bonded NO_2 and CO. The precise role of the nitro- and nitrito-bonding modes is difficult to ascertain but it is clear that they readily undergo interconversion and the barrier for this process is low. As might be expected the rhenium derivatives are more reluctant to undergo O-atom transfer.

Experimental

Unless otherwise stated all reactions were performed in an inert atmosphere of dry nitrogen gas using standard Schlenk-line techniques. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1605 spectrometer in 0.1 mm thick NaCl solution cells or as Nujol mulls between NaCl plates. The following materials were used without further purification: $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$ and $[Re(CO)_5Cl]$ (Strem Chemicals Co.); $NaNO_2$, $[N(PPh_3)_2]Cl$, $[PPh_4]Cl$ (Aldrich Chemicals Co.). All solvents were purified prior to use by distillation over sodium–benzophenone or CaH_2. Trimethylamine *N*-oxide hydrate was obtained from the Aldrich Chemicals Company and dehydrated by azeotropic distillation with benzene followed by sublimation prior to all reactions. The following complexes were synthesised by literature methods: $[(OC)_4M(\mu\text{-}Cl)_2M(CO)_4]$ (M = Mn or Re),[15] $[NEt_4][(OC)_3Mn(\mu\text{-}Cl)_3Mn(CO)_3]$,[16] $[NEt_4][Mn(CO)_4Cl_2]$,[26] $[NEt_4]_2[$*fac*-$Mn(CO)_3Cl_3]$,[12] $[NEt_4]_2[$*fac*-$Re(CO)_3Cl_3]$[24] and $[N(PPh_3)_2][NO_2]$.[27] All manganese complexes synthesised in this work were yellow-orange both in solution and the solid state. Rhenium compounds were pale yellow; the low concentration generally made accurate colour determination impossible.

Preparation of [PPh$_4$][NO$_2$]

The salts $[PPh_4]Cl$ (0.18 g, 8.75 mmol) and $NaNO_2$ (30 g) were separately dissolved in hot water (150 and 60 cm^3). The two solutions were mixed immediately and slow cooling to room temperature caused the precipitation of $[PPh_4][NO_2]$. The solution was kept at 0 °C for 30 min and then filtered. The white microcrystalline salt was washed with Et_2O (10 cm^3) and dried at room temperature. It was stored at ambient temperatures under dry conditions and used without recrystallisation (yield 95%) (Found: C, 74.6; H, 5.6; N, 3.7. Calc.: C, 74.8; H, 5.2; N, 3.6%).

Preparation of $[Mn(CO)_5Cl]$

The compound $[Mn_2(CO)_{10}]$ (0.050 g, 0.128 mmol) was dissolved in chloroform (20 cm^3). A water-cooled cold-finger was immersed into the solution, which was stirred rapidly. The solution was irradiated with a 600 W tungsten lamp. The reaction was followed by IR spectroscopy and terminated when no CO absorptions due to $[Mn_2(CO)_{10}]$ were detected. Chloroform was removed under reduced pressure and complex **1** was collected and used without further purification (yield 91%).

Reaction of $[Mn_2(CO)_{10}]$ with Me_3NO and $[N(PPh_3)_2][NO_2]$

To a CH_2Cl_2 solution (7 cm^3) containing $[Mn_2(CO)_{10}]$ (0.1 g, 0.256 mmol) was added freshly dehydrated Me_3NO (0.050 g, 0.640 mmol) with vigorous stirring. Evolution of gas and changes in the IR spectrum were observed immediately. After the production of CO_2 had ceased, $[N(PPh_3)_2][NO_2]$ (0.375 g, 0.640 mmol) was introduced, but no changes to the IR spectrum were noted within 1 h. The mixture was stirred at room temperature with exclusion of direct sunlight for up to 76 h. The final CO absorptions in the IR spectrum pointed to a mononuclear, dianionic species, which contained three carbonyl and three nitrite ligands. Owing to the high instability of this compound no further data other than the solution IR spectrum were gained. The solution decomposed even at temperatures of −35 °C under a nitrogen atmosphere.

Reaction of $[Mn(CO)_5Cl]$ 1 with $[N(PPh_3)_2][NO_2]$

The salt $[N(PPh_3)_2][NO_2]$ (0.375 g, 0.640 mmol) was added directly to a solution (CH_2Cl_2, MeCN or thf) (7 cm^3) containing $[Mn(CO)_5Cl]$ (0.060 g, 0.260 mmol) with strong stirring. An immediate evolution of CO_2 was observed and the initially pale yellow mixture became dark red. Within 5 min at room temperature no IR absorptions belonging to the precursor were detected: instead the spectrum showed quantitative conversion into $[Mn(CO)_4(NO)]$. No significant decrease in the reaction rate was achieved by lowering the temperature to values as low as −45 °C (for MeCN, 0 °C).

Preparation of $[N(PPh_3)_2]_2[Mn(CO)_3(\mathit{N}O_2)_2(\mathit{O}NO)]$ 9 and $[N(PPh_3)_2]_2[(OC)_3Mn\{\mu\text{-}NO(O)\}_2\{\mu\text{-}O(NO)\}Mn\{\mu\text{-}NO(O)\}_2\text{-}\{\mu\text{-}O(NO)\}Mn(CO)_3]$ 5

Freshly prepared $[Mn(CO)_5Cl]$ (0.060 g, 0.256 mmol) was dissolved in CH_2Cl_2 (7 cm^3). To the yellow solution freshly dehydrated Me_3NO (0.038 g, 0.512 mmol) was added. After the CO_2 evolution had ceased, the reaction mixture was stirred for 1.5 h at room temperature. The IR spectrum showed that the only product present was $[Mn(CO)_3Cl_3]^{2-}$. The salt $[N(PPh_3)_2][NO_2]$ (0.90 g, 1.54 mmol) was added to the orange solution and the mixture left to react for several hours. (Direct sunlight should be avoided.) The reaction was monitored by IR spectroscopy and terminated after the appearance of the final spectrum, characteristic for **9**. Yellow, tablet-shaped crystals were grown from an acetone–Et_2O mixture at −35 °C. Upon X-ray analysis it was shown that compound **9** had been converted into **5** during crystallisation. Elemental analysis of crystalline product: C, 55.6; H, 3.7; N, 6.5 (Calc. for **5**: C, 55.5; H, 3.6; N, 6.6%).

Reaction of $[NEt_4][(OC)_3Mn(\mu\text{-}Cl)_3Mn(CO)_3]$ 7 with $[N(PPh_3)_2][NO_2]$

To a CH_2Cl_2 solution (7 cm^3) containing $[NEt_4][(OC)_3Mn(\mu\text{-}Cl)_3Mn(CO)_3]$ (0.02 g, 0.040 mmol) were added directly 6 equivalents of $[N(PPh_3)_2][NO_2]$ (0.14 g, 0.24 mmol) at room temperature. No gas evolution or strong colour change was observed. The reaction was monitored by IR spectroscopy and was found to occur analogously to that with $[Mn(CO)_3Cl_3]^{2-}$. After 16–18 h of stirring at room temperature the spectrum showed absorptions due to **9**. Upon crystallisation from acetone–Et_2O the trinuclear complex **5** was again formed.

Reaction of $[(OC)_4Mn(\mu\text{-}Cl)_2Mn(CO)_4]$ 3 with $[N(PPh_3)_2][NO_2]$

To a CH_2Cl_2 solution (7 cm^3) containing $[(OC)_4Mn(\mu\text{-}Cl)_2Mn(CO)_4]$ (0.020 g, 0.050 mmol) were added 4 equivalents of $[N(PPh_3)_2][NO_2]$, (0.115 g, 0.200 mmol) at room temperature with vigorous stirring. No immediate colour change or gas evolution was observed, but IR spectroscopy indicated that a reaction took place within 5 min to give $[N(PPh_3)_2][Mn(CO)_4(NO_2)_2]$. Attempts to crystallise this material led to further reaction giving first complex **9** and then the trinuclear species **5**, even at temperatures as low as −35 °C. The exchange of a CO for an NO_2^- ligand could be achieved quantitatively by addition of a further equivalent of $[N(PPh_3)_2][NO_2]$ (0.060 g, 0.1 mmol) at room temperature and prolonged stirring (18–24 h).

Reaction of $[NEt_4][Mn(CO)_4Cl_2]$ 2 with $[N(PPh_3)_2][NO_2]$

To a CH_2Cl_2 solution (7 cm^3) containing $[NEt_4][Mn(CO)_4Cl_2]$ (0.02 g, 0.054 mmol) were added 2 equivalents of $[N(PPh_3)_2][NO_2]$ (0.064 g, 0.108 mmol) at room temperature and with stirring. The reaction occurred in the same fashion as described for the neutral dimer $[(OC)_4Mn(\mu\text{-}Cl)_2Mn(CO)_4]$ and the final complex isolated was again the trimer **5**.

Preparation of $[N(PPh_3)][Re_2(CO)_9(NO_2)]$ 11

***(a) via* Substitution in thf.** To a thf solution (7 cm^3), containing $[Re_2(CO)_{10}]$ (0.05 g, 0.077 mmol) was added directly $[N(PPh_3)_2][NO_2]$ (0.045 g, 0.077 mmol) with vigorous stirring. As the nitrite dissolved over a period of 5 min the solution became bright yellow and IR absorptions characteristic of the monosubstituted anion were obvious. The mixture was stirred for 1–2 h at ambient temperature, after which all starting material had been converted into complex **11**.

***(b) via* Chemical activation with Me_3NO in CH_2Cl_2–$[N(PPh_3)_2][NO_2]$.** To a CH_2Cl_2 solution (7 cm^3) containing $[Re_2(CO)_{10}]$ (0.05 g, 0.077 mmol) and $[N(PPh_3)_2][NO_2]$ (0.045 g, 0.077 mmol) was added directly freshly dehydrated Me_3NO (0.006 g, 0.077 mmol) with vigorous stirring. The solution turned yellow and CO_2 was evolved. The reaction was monitored by IR spectroscopy and, after the gas evolution had ceased, absorptions for the monoanion **11** were detected. The mixture was stirred for 1 h after which only peaks attributable to **11** were observed. Crystallisation attempts were also unsuccessful in this case.

Preparation of $[NMe_3(CH_2Cl)][\mathit{fac}\text{-}Re(CO)_3(NO_2)_2Cl]Cl$ 12

To a CH_2Cl_2 solution (7 cm^3) containing $[Re_2(CO)_{10}]$ (0.05 g, 0.077 mmol) were added 3 equivalents of freshly dehydrated Me_3NO (0.018 g, 0.231 mmol) with vigorous stirring. Evolution of CO_2 and a change from colourless to dark yellow were observed. The solution IR spectrum, recorded after CO_2 evolution had ceased, showed a mixture of several, so far unidentified species. To this mixture 3 equivalents of $[N(PPh_3)_2][NO_2]$ (0.134 g, 0.231 mmol) were added and the resulting solution was stirred for a minimum of 18 h. The reaction was monitored by IR spectroscopy throughout this period, and several intermediate complexes, not fully identified, were observed. The final spectrum was characteristic of a dianionic and mononuclear complex, which could be either *mer*-$[Re(CO)_3L_3]^{2-}$ or *fac*-$[Re(CO)_3L_2L']^{2-}$ (L, L′ = one-electron-donor ligands). Crystallisation was carried out in CH_2Cl_2 under a nitrogen atmosphere at temperatures between 5 and 7 °C: failure to exclude air or oxygen causes immediate decomposition. Pale brown crystals were grown over a period of several weeks, during which time the IR spectrum did not change further. The highly air-sensitive nature of the crystals prevented an accurate elemental analysis being obtained.

Table 4 Experimental data for the X-ray diffraction studies of compounds **5** and **12**

	5	**12**
Formula	$C_{76}H_{60}Mn_3N_8O_{18}P_4$	$C_{15}H_{33}Cl_5N_5O_7Re$
M	1686	758.9
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/a$
a/Å	10.705(7)	12.2591(15)
b/Å	12.886(7)	23.712(4)
c/Å	15.924(8)	9.8119(13)
α/°	71.22(5)	
β/°	79.24(3)	90.055(13)
γ/°	83.67(3)	
U/Å^3	2040	2852
Z	1[a]	4
D_c/g cm^{-3}	1.37	1.77
F(000)	863	1496
Crystal size/mm	0.54 × 0.31 × 0.16	0.31 × 0.43 × 0.43
μ/mm^{-1}	0.58	4.83
Unique data	4934	3385
Observed data [$I > 2\sigma(I)$]	4078	2886
No. parameters	518	299
Maximum Δ/σ ratio	0.008	0.003
R, *R'*[b]	0.0603, 0.0820	0.0482, 0.0643
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.003F^2$	$\sigma^2(F) + 0.003F^2$
Goodness of fit	1.315	1.092
Largest residuals/e Å^{-3}	0.93, −0.73	1.48, −0.96

[a] The anion lies on an inversion centre. [b] Ref. 28.

Reaction of complex 12 with an excess of $[N(PPh_3)_2][NO_2]$

To a CH_2Cl_2 (7 cm^3) solution containing complex **12** (0.02 g, 0.026 mmol) were added 2 equivalents of $[N(PPh_3)_2][NO_2]$ (0.03 g, 0.052 mmol). As stirring this solution at room temperature did not have any effect on the IR spectrum, the reaction was heated to 40–50 °C, whereupon the pale brown, cloudy solution darkened and cleared. The now dark brown solution was refluxed gently for 4–5 h during which time a series of IR changes, associated with substitution of the Cl^- ligand for an NO_2^- group followed by linkage isomerisations, was observed.

Reaction of $[Re(CO)_5Cl]$ with $[N(PPh_3)_2][NO_2]$

To CH_2Cl_2 solution (7 cm^3) containing $[Re(CO)_5Cl]$ (0.01 g, 0.028 mmol) was added directly 1 equivalent of $[N(PPh_3)_2][NO_2]$ (0.016 g, 0.028 mmol) at 0 °C. No colour change or gas evolution was observed. (The concentration of the solution was, however, very low which decreased the possibility of detection.) The complex observed at this early stage was formulated as **13** on the basis of the IR absorptions. The conversion of the starting material into this species was not quantitative, and the addition of 2 equivalents of $[N(PPh_3)_2][NO_2]$ (0.032 g, 0.056 mmol) became necessary. A crystal-structure determination on the pale brown crystals implied the presence of a dianion with two $N(PPh_3)_2^+$ species in the crystallographic asymmetric unit. Refinement of the structure revealed complete scrambling of all ligands in the anion. No model for satisfactory refinement could be devised and although the presence of three CO and three NO_2^- ligands (*N*O_2^- and *O*NO^-) was inferred no confirmation could be obtained {Found: C, 61.2; H, 4.3; N, 4.9. Calc. for $[N(PPh_3)_2]_2[Re(CO)_3(NO_2)_3]\cdot 2CH_2Cl_2$: C, 60.7; H, 4.0; N, 4.7%}.

Incorporation of a third NO_2^- group can also be achieved quantitatively by gently refluxing complex **13** in the presence of an excess of $[N(PPh_3)_2][NO_2]$ in CH_2Cl_2 at 50 °C. During a reaction period of 5–6 h several linkage isomers, after the substitution of a second CO for NO_2^- has taken place, can be identified.

Preparation of $[Re(CO)_3(ONO)_3]^{2-}$ 16

Upon addition of $[N(PPh_3)_2][NO_2]$ (0.032 g, 0.056 mmol) to a thf solution (7 cm^3) containing $[Re(CO)_5Cl]$ (0.01 g, 0.028 mmol) a white precipitate was formed. This is partly due to the insolubility of the nitrite in tetrahydrofuran, but does not influence the reactivity. After 1 h of stirring at room temperature no starting material was left in the solution (IR spectroscopy). The thf-soluble product was identified as complex **15** *via* IR spectroscopy. After filtration and washings with thf (3 × 2 cm^3) the white precipitate was redissolved in acetone, to give a pale yellow clear solution. The IR spectrum indicated that a product of formula $[Re(CO)_3(ONO)_3]^{2-}$ had been formed.

Reaction of $[Re(CO)_5Cl]$ with Me_3NO in non-co-ordinating solvents

Addition of 1 equivalent of Me_3NO (0.003 g, 0.028 mmol) to a CH_2Cl_2 solution (7 cm^3) containing $[Re(CO)_5Cl]$ (0.01 g, 0.028 mmol) resulted in the observation of *cis*-$[Re(CO)_4Cl_2]^-$ and some disubstituted *fac*-$[Re(CO)_3Cl_3]^{2-}$ *via* IR spectroscopy. Addition of 2 equivalents of Me_3NO (0.005 g, 0.056 mmol) to a colourless CH_2Cl_2 solution (7 cm^3) containing $[Re(CO)_5Cl]$ (0.01 g, 0.028 mmol) did not prompt a colour change or CO_2 evolution. (The concentration of the solution was, however, very low which decreased the possibility of detection.) Infrared spectroscopy indicated the formation of at least two new species, *cis*-$[Re(CO)_4Cl_2]^-$ and *fac*-$[Re(CO)_3Cl_3]^{2-}$. An increase in the $Me_3NO/[Re(CO)_5Cl]$ ratio did not produce the dianion quantitatively, as *cis*-$[Re(CO)_4Cl_2]^-$ was always observed in the solution.

Reaction of $[NEt_4]_2$[*fac*-$Re(CO)_3Cl_3$] 18 with $[N(PPh_3)_2][NO_2]$

To a CH_2Cl_2 solution (4 cm^3) containing $[NEt_4]_2$[*fac*-$Re(CO)_3Cl_3$] (0.01 g, 0.016 mmol) were added 3 equivalents of $[N(PPh_3)_2][NO_2]$ (0.028 g, 0.047 mmol) at room temperature. No distinctive colour change or gas evolution was observed. After 2 h of stirring at room temperature several new bands were detected in the ν(CO) region, but the number of absorptions pointed to a mixture of several complexes, which could not be separated and fully identified.

Crystallography

Crystal data and data collection and refinement parameters for compounds **5** and **12** are given in Table 4, final atomic coordinates in Tables 5 and 6.

Data collection and processing. Data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystem low-temperature device[29] operating at 150.0(2) K using graphite-monochromated Mo-Kα radiation and ω–2θ scans using the learnt-profile method.[30] Data were corrected for Lorentz and polarisation factors for both structures. For complex **12** a semiempirical absorption correction based on azimuthal measurements was applied with minimum and maximum transmission coefficients of 0.063 and 0.111 respectively. No absorption correction was applied to the data for **5**.

Table 5 Fractional atom coordinates with standard deviations for compound **5**

Atom	*x*	*y*	*z*
Mn(1)	0.0	0.0	0.0
Mn(2)	−0.048 32(7)	−0.038 06(6)	−0.194 14(5)
N(11)	−0.016 10(4)	−0.172 3(3)	−0.088 1(3)
O(11)	−0.004 4(3)	−0.163 0(3)	−0.012 74(24)
O(12)	−0.011 1(3)	−0.266 8(3)	−0.092 6(3)
N(21)	−0.199 0(4)	0.002 8(3)	−0.109 2(3)
O(21)	−0.185 2(3)	0.028 8(3)	−0.041 06(25)
O(22)	−0.309 0(3)	0.004 9(3)	−0.121 45(25)
N(31)	0.151 3(5)	0.099 9(4)	−0.182 2(3)
O(31)	0.057 1(3)	0.040 0(3)	−0.141 55(23)
O(32)	0.180 4(4)	0.115 4(4)	−0.263 1(3)
C(1)	0.091 3(5)	−0.073 3(4)	−0.267 9(4)
O(1)	0.176 3(4)	−0.094 3(3)	−0.315 8(3)
C(2)	−0.084 9(5)	0.082 3(5)	−0.284 4(4)
O(2)	−0.113 9(4)	0.157 3(3)	−0.341 5(3)
C(3)	−0.146 1(5)	−0.116 8(4)	−0.228 6(3)
O(3)	−0.207 4(4)	−0.166 4(3)	−0.253 5(3)
N(1)	0.456 3(3)	0.389 4(3)	−0.707 5(3)
P(1)	0.351 01(11)	0.481 18(10)	−0.690 71(8)
C(11)	0.415 2(4)	0.605 3(4)	−0.694 3(3)
C(12)	0.410 3(5)	0.703 0(4)	−0.763 8(4)
C(13)	0.472 3(5)	0.792 2(5)	−0.764 2(5)
C(14)	0.537 9(5)	0.785 3(5)	−0.696 0(5)
C(15)	0.542 9(5)	0.689 1(5)	−0.626 8(4)
C(16)	0.483 0(5)	0.599 5(5)	−0.625 0(4)
C(21)	0.262 3(4)	0.423 4(4)	−0.580 5(3)
C(22)	0.199 5(5)	0.491 1(5)	−0.529 7(4)
C(23)	0.131 2(5)	0.444 6(5)	−0.445 3(4)
C(24)	0.123 5(5)	0.333 4(5)	−0.412 0(4)
C(25)	0.182 8(5)	0.265 1(5)	−0.461 7(4)
C(26)	0.251 7(5)	0.311 9(4)	−0.546 4(3)
C(31)	0.241 6(4)	0.514 6(4)	−0.768 8(3)
C(32)	0.147 6(5)	0.600 9(4)	−0.770 8(4)
C(33)	0.063 1(5)	0.624 4(5)	−0.831 3(4)
C(34)	0.069 1(5)	0.564 9(4)	−0.889 1(4)
C(35)	0.157 2(5)	0.476 9(5)	−0.886 2(3)
C(36)	0.245 2(5)	0.452 7(4)	−0.827 6(3)
P(2)	0.594 75(11)	0.390 38(10)	−0.763 97(8)
C(41)	0.604 4(4)	0.287 4(4)	−0.820 1(3)
C(42)	0.696 6(4)	0.289 1(4)	−0.894 8(3)
C(43)	0.701 3(5)	0.207 5(5)	−0.935 0(4)
C(44)	0.615 9(5)	0.124 0(4)	−0.899 7(4)
C(45)	0.522 55(5)	0.122 4(4)	−0.825 0(4)
C(46)	0.519 3(5)	0.204 1(4)	−0.785 1(3)
C(51)	0.633 1(4)	0.520 2(4)	−0.847 8(3)
C(52)	0.571 5(5)	0.552 2(4)	−0.922 2(3)
C(53)	0.587 3(5)	0.654 8(4)	−0.984 0(3)
C(54)	0.664 6(5)	0.726 0(4)	−0.971 8(4)
C(55)	0.726 4(5)	0.695 3(4)	−0.899 2(4)
C(56)	0.711 5(5)	0.591 5(4)	−0.835 7(4)
C(61)	0.712 7(4)	0.352 3(4)	−0.690 4(3)
C(62)	0.843 0(5)	0.354 2(4)	−0.726 0(4)
C(63)	0.931 4(5)	0.320 0(4)	−0.669 1(4)
C(64)	0.891 7(6)	0.282 8(5)	−0.576 8(4)
C(65)	0.763 7(5)	0.280 0(5)	−0.541 3(4)
C(66)	0.673 8(5)	0.315 3(4)	−0.598 0(3)
C(1S)	0.382 5(19)	0.060 8(16)	0.456 3(13)
C(2S)	0.491(3)	0.013 2(22)	0.463 8(15)
C(3S)	0.317 8(23)	−0.009 8(19)	0.453 3(16)
C(4S)	0.161 0(25)	0.028 9(21)	0.461 5(18)

Table 6 Fractional atom coordinates with standard deviations for compound **12**

Atom	*x*	*y*	*z*
Re	0.084 33(4)	0.116 53(2)	0.450 56(4)
Cl(1)	−0.043 4(4)	0.197 80(21)	0.466 6(5)
C(1)	0.012 4(10)	0.077 1(6)	0.595 9(13)
O(1)	−0.028 5(8)	0.053 6(4)	0.684 9(10)
C(2)	0.179 8(10)	0.054 1(5)	0.421 5(12)
O(2)	0.240 9(7)	0.018 2(4)	0.401 1(9)
C(3)	0.184 8(9)	0.145 5(5)	0.581 4(12)
O(3)	0.246 2(8)	0.163 3(4)	0.659 7(9)
N(1)	0.1585(8)	0.162 9(5)	0.274 1(11)
O(11)	0.150 8(10)	0.208 8(7)	0.262 7(13)
O(12)	0.210 2(14)	0.134 8(6)	0.194 4(14)
N(2)	−0.034 9(9)	0.084 6(5)	0.300 4(11)
O(21)	−0.015 4(9)	0.079 5(5)	0.182 6(10)
O(22)	−0.125 8(8)	0.069 8(7)	0.341 0(12)
Cl(2)	−0.553 8(4)	0.099 33(23)	0.458 3(5)
C(21)	−0.490 8(11)	0.152 2(7)	0.557 3(14)
N(21)	−0.369 3(9)	0.153 0(5)	0.529 0(11)
C(22)	−0.327 8(12)	0.201 0(7)	0.613 8(17)
C(23)	−0.346 4(11)	0.165 4(7)	0.383 8(16)
C(24)	−0.314 8(11)	0.101 4(6)	0.567 0(16)
Cl(3)	−0.617 5(3)	0.006 00(24)	0.750 5(4)
C(31)	−0.702 5(10)	−0.027 8(6)	0.869 5(12)
N(31)	−0.745 0(8)	0.011 4(4)	0.978 1(9)
C(32)	−0.651 9(10)	0.034 8(7)	1.061 3(13)
C(33)	−0.817 3(10)	−0.021 7(6)	1.065 6(13)
C(34)	−0.810 3(13)	0.058 6(7)	0.916 0(15)
Cl(4)	−0.022 1(6)	0.182 1(3)	−0.163 0(7)
C(41)	−0.002 4(13)	0.222 7(8)	−0.023 3(15)
N(41)	−0.104 0(8)	0.245 6(5)	0.036 1(11)
C(42)	−0.188 1(17)	0.196 2(9)	0.069 3(23)
C(43)	−0.072 1(14)	0.282 7(8)	0.151 5(15)
C(44)	−0.162 1(12)	0.282 3(7)	−0.066 0(15)
Cl(5)	0.080 3(4)	0.371 35(20)	0.916 1(5)

Structure analysis and refinement. Both structures were solved by direct methods using SHELXS 86.[31] All remaining non-hydrogen atoms were located from subsequent ΔF maps and refined anisotropically, except for a disordered solvent fragment in complex **5** which contains four atoms each of which was refined as a half-occupancy carbon and with isotropic thermal parameters. Hydrogen atoms were included in the refinements in calculated positions and with fixed, isotropic thermal parameters [$U(\mathrm{H}) = 0.06$ Å^3 for **5** and 0.08 Å^3 for **12**]. Details of refinement which used SHELX 76[28] are given in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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