A Novel Co-ordination Mode of Nitric Oxide. Synthesis and Crystal Structure of the $[\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$ Anion

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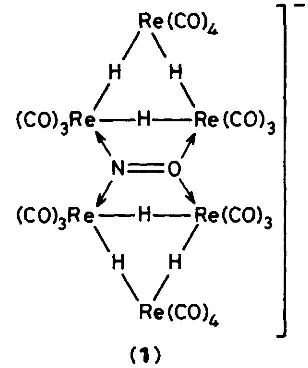
Reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with $NOBF_4$ in CH_2Cl_2 gives the $[\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$ anion, containing a nitrosyl group which holds together two triangular cluster moieties by bridging one edge of each triangle through both the N and O atoms.

Nitric oxide shows a variety of co-ordination modes to transition metals[1] including terminal (linear or bent), double bridging {even on two non-bonded metals, as in $[Os_4H_3(CO)_{12}(\mu\text{-}NO)]^2$}, and triple bridging, as in $[Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)(C_5H_5)_3]$.[3] Here we report the synthesis and characterization of a rhenium carbonyl cluster anion which contains a nitric oxide molecule bound, for the first time, through both N and O, and acting as a μ_4-ligand [(**1**)].

Our previous studies on the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (ref. 4) have shown its peculiar reactivity toward electrophiles.[5] We have therefore attempted the reaction with $NOBF_4$ in order to obtain a nitrosyl derivative, as a possible intermediate to nitrido species.[2,6]


(**1**)

The salt $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ was dissolved under nitrogen in carefully dried CH_2Cl_2 and a stoicheiometric amount of freshly sublimed $NOBF_4$ was added as a solid at room temperature. In a few minutes the colour of the solution turned from yellow to dark violet. Evolution of H_2, together with some CO, was observed. Flash chromatography on silica gel under nitrogen allowed the separation of neutral products {the dominant one being $[Re_3(\mu\text{-}H)_3(CO)_{12}]$}, followed by the violet $[NEt_4][\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]$ (**1**) (yield *ca.* 25%), and then by some of the unreacted parent compound.

The formation of compound (**1**) probably involves the addition of NO^+ to the parent anion, giving an unstable neutral $[Re_3H_4(CO)_{10}(NO)]$ or $[Re_3H_3(CO)_{10}(HNO)]$ species, which then condenses with a second $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ anion, with H_2 evolution.

The novel anion has ν(CO) 2100mw, 2055w, 2025s, 2015sh, 2000sh, 1960m, 1940mw, and 1910w cm^{-1}, in CH_2Cl_2. The ^1H n.m.r. spectrum in CD_2Cl_2 exhibits three sharp singlets in the hydridic region, at δ −9.13, −11.18, and −13.37, of equal intensity and in the expected ratio with respect to the cationic signals. The electronic spectrum, in CH_2Cl_2, shows a strong absorption band in the visible region (λ_{max} 560 nm). Crystallization from CH_2Cl_2–n-C_7H_{16} at −20 °C afforded crystals suitable for *X*-ray investigation.†‡

The anions (A) and (B)† have similar dimensions so the structure of one is shown in Figure 1. It consists of two centrosymmetrically related triangular cluster units $[Re_3(\mu\text{-}H)_3(CO)_{10}]$, joined by an NO^- ligand (disordered about an inversion centre), which bridges four rhenium atoms. The idealized anion symmetry is C_2 (with the two-fold axis passing through the nitrosyl atoms), but this becomes C_{2h} in the crystal structure, because of the NO disorder.

The ligand stereochemistry of each triangular cluster moiety resembles that of the anions $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$, being intermediate between the cases where X is a single atom (*e.g.* Cl)[7] or a chelating group such as a carboxylate.[8] The hydrides have not been directly located, but are presumed to be bridging on all the triangular edges, as indicated by the values of the metal–metal bonds and by the carbonyl geometry. They give rise to three high-field n.m.r. signals, in accordance with a C_2 symmetry in solution.

The NO^- ligand lies fairly well in the plane of four Re atoms [Re(2), Re(3), and their centrosymmetric partners]. The dihedral angle between this plane and the plane of each of the two Re_3 triangles is 105.4°. The Re–N and Re–O bond distances [range 2.106(9)—2.149(9) Å] have a mean value, 2.133 Å, comparable with the Re–N bonds in $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ (mean 2.13 Å)[5b] and with the Re–N [2.14(2) Å] and Re–O [2.13(2) Å] bonds in $[Re_3(\mu\text{-}H)_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}OC(Ph)NH\}]^-$.[9] The nitrosyl co-ordination indicates an sp^2 hybridization of the N and O atoms (Re–N–O and Re–O–N mean 114.4° and Re–N–Re and Re–O–Re mean 131.1°) with the ligand formally acting as an eight-electron σ-donor [(**1**)]. However the N–O bond lengths [1.32(2) Å in (A) and 1.35(2) Å in (B)] are rather long, longer than the N–O bond of the triple bridging nitrosyl in $[Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)(C_5H_5)_3]$ [1.247(5) Å].[3] The values are approximately intermediate between those of a double (*ca.* 1.20 Å) and of a single (*ca.* 1.45 Å) N–O bond, suggesting that some additional π interaction between the ligand and the metal atoms occurs.§

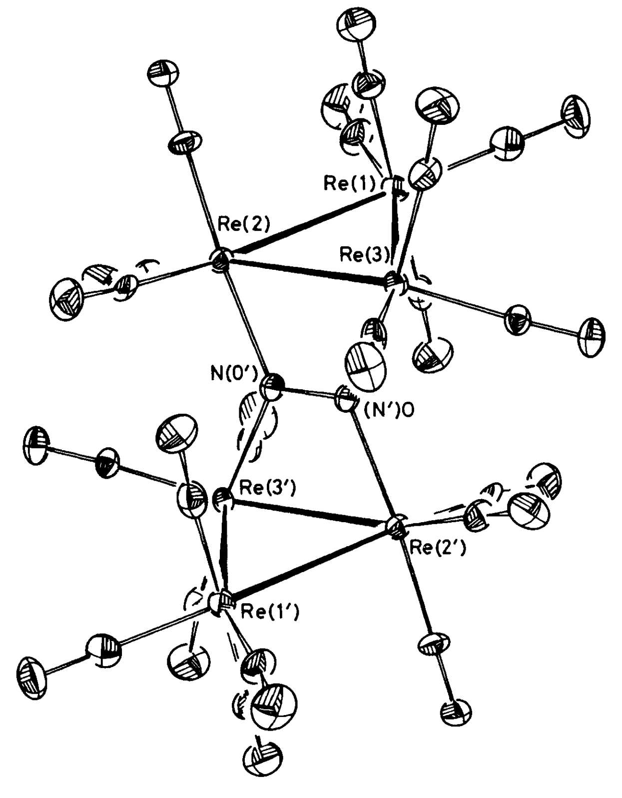


Figure 1. A view of the $[\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$ anion [(A)] (primed atoms are centrosymmetrically related to unprimed ones and the disordered orientations of NO^- are indicated). Metal–metal bond lengths are as follows for (A) [in square brackets for (B)]: Re(1)–Re(2) 3.207(1) [3.192(1)], Re(1)–Re(3) 3.212(1) [3.193(1)], Re(2)–Re(3) 3.093(1) [3.101(1)] Å. The overall mean values of the Re–C and C–O interactions in the $Re(CO)_4$ and $Re(CO)_3$ units are 1.96, 1.14 and 1.93, 1.15 Å, respectively.

This novel co-ordination mode of a nitrosyl ligand is reminiscent of that of nitroso ligands in species such as $[Fe_4(CO)_{11}(\mu_4\text{-}NEt)(\mu_4\text{-}\eta^2\text{-}ONEt)]$,[11] $[Pd_3(\mu\text{-}\eta^2\text{-}ONPh)_3(PBu^t{}_3)_3]$,[10] $[Fe_2(CO)_6(\mu\text{-}\eta^2\text{-}3\text{-}Cl\text{-}2\text{-}MeC_6H_3NO)_2]$,[12] and others, though the hybridization of N in these compounds significantly deviates from sp^2. Carbon monoxide shows a completely different type of μ_4-η^2-bonding in the anion $[Fe_4H(CO)_{13}]^-$.[13]

We think that η^2-co-ordination of nitric oxide is possible in the present case because of the particular disposition of the surrounding metal atoms and that it is stabilized by the four metal–ligand bonds. Nevertheless this finding suggests the possibility that similar η^2-interactions could play some role in the absorption of nitric oxide on metallic surfaces in heterogeneous catalysis; moreover, it should enlighten knowledge of the process of N–O cleavage in the formation of nitrido–carbonyl from carbonyl clusters by reaction with $NOBF_4$.[2,6]

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† *Crystal data:* $C_{28}H_{26}N_2O_{21}Re_6$, M = 1843.7, triclinic, space group $P\bar{1}$(No. 2), a = 13.928(2), b = 14.959(3), c = 12.583(2) Å, α = 109.67(2), β = 116.10(2), γ = 70.13(2)°, U = 2159.2 Å^3, D_c = 2.836 g cm^{-3} for Z = 2. The intensity data were collected on a CAD4 Enraf-Nonius diffractometer within the limits $3 < \theta < 25°$. An empirical absorption correction was applied (relative transmission factors in the range 0.70—1.0). The structure was solved by Patterson and Fourier methods, on the basis of 4124 significant [$I > 3\sigma(I)$] reflections. Refinement by full-matrix least-squares led to current values of the conventional R and R_w factors of 0.029 and 0.034, respectively. In the unit cell there are two symmetry-related NEt_4^+ cations and two independent anions [(A) and (B)] each of which lies on a centre of symmmetry so that the asymmetric unit consists of one cation and one half of each anion. The centres of symmetry give rise to disorder with equal probability of NO or ON orientations of the nitric oxide; the site was treated as occupied by (½N + ½O).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The presence of the cationic signals in the i.r. spectrum prevents the unambiguous assignment of the ν(NO) mode; a band at 1060m cm^{-1}, not attributable to the cation, might be tentatively ascribed to this stretching, in accord with values found in η^2-nitroso species (ref. 10).

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