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The Effects of Steric Hindrance on the Chemistry of Rhenium and Molybdenum Nitrosyl Thiolato-complexes. The Structures of [Mo($SC_6H_2Pr_3^i$)$_3$(NH_3)(NO)] and [Re($SC_6H_3Pr_2^i$)$_4$(NO)]

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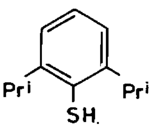
Abstract

The Re(II) nitrosyl complex [$ReCl_2$(OMe)(NO)(PPh_3)$_2$] reacts with excess 2,6-$Pr_2^iC_6H_3S^-$($DIPT^-$) in methanol to give the Re(III) complex [Re(DIPT)$_4$(NO)] (I) whereas thiophenolate gives a thiolato-bridged Re(II) dimer. Crystal data for (I): crystallizes in the orthorhombic space group *Pbca*, a = 13.218(6) Å, b = 19.534(9) Å, c = 38.115(13) Å, V = 9841.3(6) Å^3 to give D_{calc} = 1.35 g cm^{-3} for Z = 8. Structure solution and refinement are based on 3047 reflections with $I_o > 3\sigma|I_o|$ and yielded a final R value of 0.064. The overall geometry about Re is trigonal bipyramidal with an apical NO group with a nearly linear Re–N–O system (Re–N–O, 173.6(14)°).

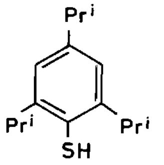
The polymeric species '{Mo(NO)(NH_2O)}$_n$' reacts with excess 2,4,6-$Pr_3^iC_6H_2S^-$($TIPT^-$) to give [Mo(TIPT)$_3$(NH_3)(NO)]·C_5H_{12} (II) (C_5H_{12} = n-pentane) whereas thiophenolate anion gives [Mo(SPh)$_4$(NO)]$^-$. Crystal data for (II): space group $P2_1/n$ with a = 10.477(3) Å, b = 26.359(5) Å, c = 20.124(4) Å, β = 87.21(1)°, with V = 5550.9(12) Å^3 to give D_{calc} = 1.05 g cm^{-3} for Z = 4. Structure refinement was based on 1040 reflections with $I_o > 3\sigma|I_o|$ and yielded a final R value of 0.079. The geometry about Mo is again trigonal bipyramidal with apical NO and NH_3 groups and again an essentially linear Mo–N–O system (Mo–N–O = 174.2(3)°).

The current interest in metal sulphur complexes, particularly those of molybdenum, derives principally from their relevance to the active sites of metalloenzymes [1–3]. Despite numerous systematic investigations there have been few examples of metal thiolato-complexes interacting with or indeed containing small molecules. This is mainly due to the formation of sulphur-bridged oligomers which lack available binding sites for small molecules. Sterically hindered thiols such as 2,6,-diisopropylthiophenol** [4] (HDIPT) (III) and 2,4,6-triisopropylthiophenol† (HTIPT) (IV) inhibit bridge formation [5] and sulphide formation by C–S bond cleavage.



HDIPT

III



HTIPT

IV

Nitrosyl complexes are of interest as NO^+ is isoelectronic with N_2, and co-ordinated NO is formally analogous to N_2H, the presumed primary intermediate in the protonation of N_2. We here compare and contrast the syntheses and structures of molybdenum and rhenium nitrosyl complexes with both simple aromatic and sterically demanding thiols.

The rhenium(II) precursor [$ReCl_2$(OMe)(NO)(PPh_3)$_2$] [6a]§ reacts with excess HDIPT in methanol in the presence of triethylamine to give the Re(III) nitrosyl [Re(DIPT)$_4$(NO)] (I). Under similar conditions thiophenolate ion forms the triply-thiolato-bridged dimer [Re_2(NO)$_2$(SPh)$_7$]$^-$ [7]. Since the sterically hindered thiol prevents thiolate bridging, the fifteen electron species [Re-

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**Prepared by a modified version of the Newman-Kwart rearrangement form 2,6-diisopropylphenol [4].

†Prepared in ~80% yield by the $LiAlH_4$ reduction of 2,4,6-triisopropylbenzenesulphonyl chloride in diethylether.

§The complex was originally formulated as [$ReCl_2$(NO)(PPh_3)$_2$] [6b].

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$(DIPT)_4(NO)]^-$ might be expected to be formed. However, under the reaction conditions this species is apparently unstable and is oxidized[§§] to the observed five co-ordinate fourteen electron species.

The X-ray crystal structure[≠] of $[Re(DIPT)_4(NO)]$ is shown in Fig. 1 together with selected bond lengths and angles. The geometry about the rhenium is trigonal bipyramidal with the NO group occupying an axial site. The Re–N–O angle of 173.6(4)° and the Re–N distance of 1.781(16) Å are both consistent with the NO ligand functioning as a three electron donor giving an overall formal electron count of fourteen. The steric constraints exerted by the aryl substituents prevent the aryl groups of the equatorial thiolates all being directed *endo* with respect to the NO group to minimize repulsions from the sulphur non-bonding electrons. Such orientations are found in $[Re(SPh)_3(MeCN)(PPh_3)]$ [8], $[Mo(SPh)_4(NO)]^-$ [12], and $[WCl(SPh)_3(NO)]^-$ [9]. In complex (I) two of the equatorial thiolate aryl groups lie *endo* with respect to the NO group whereas the other is directed towards the axial thiolate. A similar arrangement was observed for the complex $[Mo(CO)_2(TIPT)_3]^-$ [10].

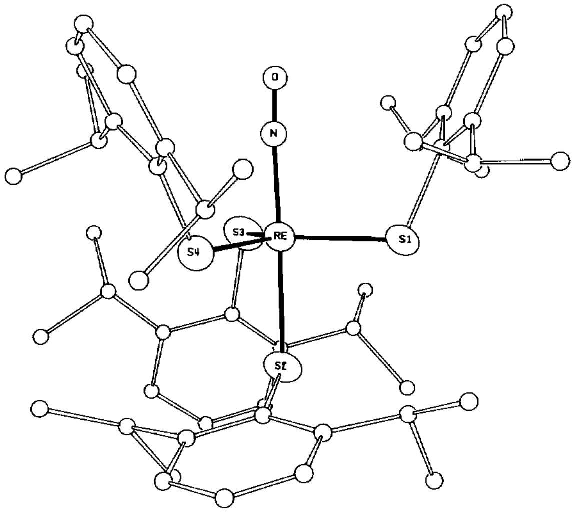

Fig. 1. ORTEP representation of the molecular geometry of $[Re(DIPT)_4(NO)]$, (I), omitting hydrogen atoms. Relevant bond lengths (Å) and angles (°): Re–S1, 2.266(5); Re–S2, 2.413(5); Re–S3, 2.286(5); Re–S4, 2.272(5); Re–N, 1.78(1); S1–Re–S2, 87.0(2); S1–Re–S3, 113.1(2); S1–Re–S4, 124.6(2); S1–Re–N, 94.1(S);S2–Re–S3, 90.9(2); S2–Re–S4, 84.6(2); S2–Re–N, 178.5(5); S3–Re–S4, 121.8(2); S3–Re–N, 87.7(5); S4–Re–N, 95.6(5); Re–N–O, 173.6(14).

The polymeric nitrosyl hydroxylamido-complex '$\{Mo(NO)(NH_2O)\}_n$' [11] reacts with excess thiophenolate anion to give $[Mo(SPh)_4(NO)]^-$ [9] and the hydroxylamido-ligand is reduced to ammonia[††]. This unusual[*] reduction occurs at the metal, since thiophenolate anion does not reduce free hydroxylamine. With the sterically demanding HTIPT the polymeric precursor gives neutral $[Mo(TIPT)_3(NH_3)(NO)]\cdot C_5H_{12}$ (**II**) (C_5H_{12} = n-pentane) even after protracted reaction times with a large excess of $TIPT^-$. Substitution of the ammonia ligand is prevented by the steric shielding afforded by the three equatorial TIPT molecules. However the smaller thiol 2,4,6-trimethylthiophenol gives $[Mo(SC_6H_2Me_3)_4(NO)]^-$ with no evidence for an ammonia complex. The closely related complex $[W(OBu^t)_3(NH_3)(NO)]$ has been prepared from $[W(OBu^t)_3(NO)_2]$ and ammonia [12] and presumably has a similar structure to that of the molybdenum complex (**II**) reported below.

The X-ray crystal structure of $[Mo(TIPT)_3(NH_3)(NO)]$ was determined[**] and is shown in Fig. 2 together with selected bond lengths and angles. The geometry about the molybdenum is again trigonal bipyramidal with axial NO and NH_3 groups. The molybdenum–ammonia N(2) distance of 2.20 Å is consistent with the axial occupancy of the NH_3 group and the relatively weak *trans*-influence of the NO group. The bond lengths and angles within the Mo–N–O system indicate that the NO is behaving as a three electron donor conferring an overall formal electron count of fourteen.

Both nitrosyl complexes are members of a series of five co-ordinate complexes of general formula $[M(SAr)_3(X)(Y)]^n$ (n = 0, −1; Ar = aryl) with fourteen valence electrons. Such complexes all have trigonal bipyramidal geometries which is favoured by π-acceptor ligands such as NO in an axial site and weak π-donors such as thiolate in the equatorial sites. The ligand geometry will stabilize the occupied d_{xz} and d_{yz} metal orbitals and relatively destabilize

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[§§] The species reduced has not been identified, but the high yields suggest it is not a rhenium complex and may be solvent.

[≠] Crystal data for $C_{48}H_{68}NOS_4Re$: space group *Pbca*, a = 13.218(6) Å, b = 19.534(9) Å, c = 38.115(13) Å, $\alpha = \beta = \gamma$ = 90°, V = 9841.3(6) Å^3, to give D_{calc} = 1.35 g cm^{-3} for Z = 8. Structure solution and refinement based on 3047 reflections with $F_o > 3\sigma(F_o)$ yielded a final R value of 0.064.

[††] The ammonia was removed from the reaction mixture with a stream of nitrogen and identified colorimetrically using the indophenol reagent.

[*] The only reported related reaction occurs during the electrochemical reduction of $[Ru(trpy)(bipy)(NO)]^{3+}$ to $[Ru(trpy)(bipy)(NH_3)]^{2+}$ which may involve intermediates such as $[Ru(trpy)(bipy)(NHO)]^{2+}$ [12].

[**] Crystal data for $C_{50}H_{84}N_2OS_3Mo$: space group $P2_1/c$ with a = 10.477(3) Å, b = 26.359(5) Å, c = 20.124(4) Å, β = 87.21(1)°, with V = 5550.9(12) Å^3 to give D_{calc} = 1.05 g cm^{-3} for Z = 4. Structure solution and refinement based on 1040 reflections with $I_o > 3\sigma(I_o)$ to give final R value of 0.075.

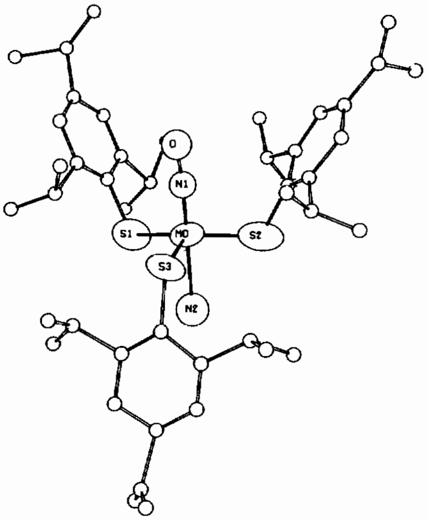

Fig. 2. ORTEP representation of the molecular geometry of [Mo(TIPT)$_3$(NO)(NH$_3$)] (II), omitting hydrogen atoms. Relevant bonds lengths and angles: Mo–S1, 2.319(10); Mo–S2, 2.302(11); Mo–S3, 2.316(11); Mo–N1, 1.78(3); Mo–N2, 2.22(2); S1–Mo–S2, 119.9(4); S1–Mo–S3, 117.9(4); S1–Mo–N1, 87.8(10); S1–Mo–N2, 90.2(6); S2–Mo–S3, 121.0(4); S2–Mo–N1, 96.3(11); S2–Mo–N2, 84.3(6); S3–Mo–N1, 96.7(10); S3–Mo–N2, 84.7(6); N1–Mo–N2, 177.9(10); Mo–N1–O, 176.1(30).

the LUMO $d_{x^2-y^2}$ and d_{xy} orbitals. The relatively high energy of the LUMO would explain the apparent instability of [Re(TIPT)$_4$(NO)]$^-$ which would be expected to be a strong reducing agent, readily oxidized to the Re(III) species***.

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***Cyclic voltammetry of (I) (1 mmolar solution in THF with [Bu$_4^n$N][BF$_4$] support electrolyte, Pt electrode and [Mo(N$_2$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] as internal reference) showed a reversible reduction step at E = –0.67 V *vs.* S.C.E. due to formation of [Re(TIPT)$_4$(NO)]$^-$. A species formed at this potential could be capable of reducing adventitious water in the solvent.