Rhenium Nitrosyl Complexes with Simple and with Sterically Demanding Aromatic Thiolate Ligands: *X*-Ray Crystal Structures of $[PPh_4][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]\cdot CH_2Cl_2$ and $[Re(SC_6H_3Pr^i_2\text{-}2,6)_4(NO)]$†

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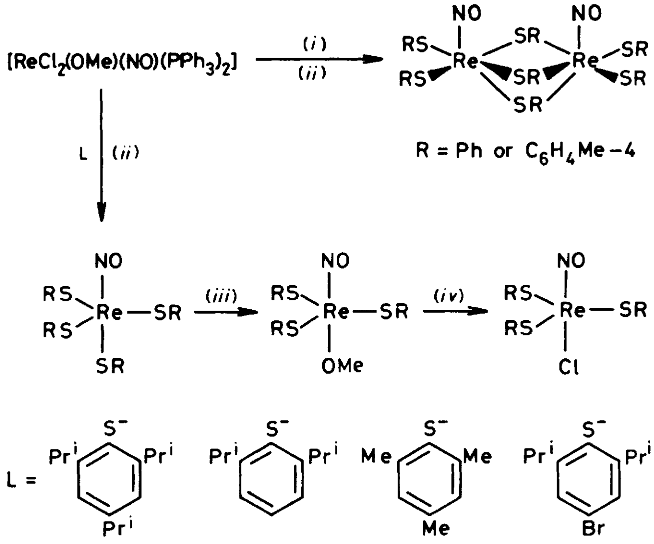
Reaction of $[ReCl_2(OMe)(NO)(PPh_3)_2]$ with a range of thiophenols under basic conditions gives one of two classes of products depending on the steric requirements of the thiols. A representative member of each class has been characterised by an *X*-ray crystal structure determination. Thiophenols with methyl or isopropyl groups in their *ortho* positions give the mononuclear complexes $[Re(SR)_4(NO)]$ ($SR = SC_6H_2Pr^i_3$-2,4,6, $SC_6H_3Pr^i_2$-2,6, $SC_6H_2Pr^i_2$-2,6-4-Br, or $SC_6H_2Me_3$-2,4,6) which are trigonal bipyramidal with an axial NO group. Thiophenols without *ortho*-substituents give the dinuclear anions $[Re_2(SR)_7(NO)_2]^-$ (SR = SPh or SC_6H_4Me-4) which contain a triple thiolate bridge between two equivalent rhenium atoms. These anions show a fluxionality involving intramolecular exchange of six thiolato-ligands.

The binding and activation of small molecules at transition metals (in particular molybdenum) ligated primarily by sulphur is of interest because of its relevance to the functioning of the enzyme nitrogenase, the active site of which is believed to be a Mo–Fe–S cluster. As part of our studies of the binding of small molecules to such sites we have prepared a series of nitrosylrhenium complexes with aromatic thiolato-co-ligands. The nitrosonium ion NO^+ is formally isoelectronic with N_2 and co-ordinated NO is analogous to the diazenido-ligand -NNH, the proposed primary intermediate in the biological reduction of N_2.

A large number of nitrosyl complexes of rhenium-(I), -(II), and -(III) is known. The majority of these contain some tertiary phosphines or other neutral donors, *e.g.* $[ReCl_3(NO)(PPh_3)_2]$[1] and $[ReF(CO)(NO)(PPh_3)_3]^+$.[2] Rhenium nitrosyl complexes with no neutral ligands include $[ReX_5(NO)]^{2-}$ (X = Cl[3] or Br[4]). There are no previously reported rhenium nitrosyl complexes with thiolato-ligands. However, there are a few rhenium thiolato-complexes of other types, including the oxo-complexes $[ReO(SCH_2CH_2S)_2]^-$ [5] and $[ReO(SPh)_4]^-$,[6] the neutral complex $[Re(SPh)_3(MeCN)(PPh_3)]$[7] and the tetrameric, cubane-like $[\{Re(SMe)(CO)_3\}_4]$, the *X*-ray crystal structure of which has been determined.[8]



Scheme 1. Preparation of complexes. (*i*) HSPh or HSC_6H_4Me-4; (*ii*) NEt_3–MeOH; (*iii*) MeOH; (*iv*) HCl

Results and Discussion

Preparation and Characterisation of the Complexes.—We have examined the reaction of $[ReCl_2(OMe)(NO)(PPh_3)_2]$‡ with thiophenol, 4-methylthiophenol, and a series of more sterically demending aromatic thiols, 2,4,6-tri-isopropylthiophenol, 2,6-di-isopropylthiophenol, 2,4,6-trimethylthiophenol, and 4-bromo-2,6-di-isopropylthiophenol, in the presence of triethylamine. The major NO-containing products fall into two categories depending on the steric properties of the thiol employed, *i.e.* whether it bears *ortho*-substituents. In addition, small amounts of side products are formed containing co-ordinated triphenylphosphine. These have not yet been fully characterised.

The reaction scheme is summarised in Scheme 1. The reactions with thiophenol and 4-methylthiophenol give the anionic, formally rhenium(II) complexes $[Re_2(SPh)_7(NO)_2]^-$ (**1**) and $[Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]^-$ (**2a**), (**2b**), isolated as a tetraphenylphosphonium salt [(**1**), (**2a**)] or as a triethylammonium salt [(**2b**)]. The empirical formulations for (**1**), (**2a**), and (**2b**) were based on microanalysis and integration of ^1H n.m.r. spectra. In addition, the diamagnetism of the complexes, as inferred from the sharp, unperturbed n.m.r. spectra, is consistent with their being dinuclear. The broadness of the NO

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† Tetraphenylphosphonium tri-μ-4-methylthiophenolato-bis[di(4-methylthiophenolato)nitrosylrhenate]–dichloromethane (1/1) and tetrakis(2,6-di-isopropylthiophenolato)nitrosylrhenium.

‡ This compound was originally prepared by Adams *et al.*[1] and formulated as $[ReCl_2(NO)(PPh_3)_2]$, but recently Cameron *et al.*[2] presented a convincing case for its reformulation as $[ReCl_2(OMe)(NO)(PPh_3)_2]$.

Supplementary data available (No. SUP 56230, 25 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Vibrational[a] and electronic spectra[b]

	Compound	$\tilde{\nu}$(NO)/cm^{-1}	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
(1)	$[PPh_4][Re_2(SPh)_7(NO)_2]$	1 738s, 1 718s	480	4 600
		(1 718s)	336	sh
(**2a**)	$[PPh_4][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]$	1 720s, 1 690m	473.5	4 290
		(1 720s)	340	sh
(3)	$[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_4(NO)]$	1 760s	516	4 450
		(1 760s)	390	sh
			355	28 900
			281	23 700
(4)	$[Re(SC_6H_3Pr^i_2\text{-}2,6)_4(NO)]$	1 758s	523	n.d.
		(1 758s)	388	sh
			347	n.d.
			281	n.d.
(5)	$[Re(SC_6H_2Me_3\text{-}2,4,6)_4(NO)]$	1 757s	498	4 600
		(1 763s)	365	sh
			346	27 600
			275	20 900
(6)	$[Re(SC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_4(NO)]$	1 755s	515	4 500
		(1 768s)	388	sh
			356	31 500
			282	25 500
(7)	$[Re(SC_6H_2Me_3\text{-}2,4,6)_3(OMe)(NO)]$[c]	1 747s	n.d.	n.d.
(8)	$[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(OMe)(NO)]$[d]	1 745s	n.d.	n.d.
(9)	$[Re(SC_6H_3Pr^i_2\text{-}2,6)_3(OEt)(NO)]$[e]	1 746s	n.d.	n.d.
			n.d.	n.d.
(10)	$[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3Cl(NO)]$	1 780s	n.d.	n.d.

[a] Nujol mulls; values in parentheses are for CH_2Cl_2 solutions. [b] Tetrahydrofuran (thf) solutions, range 250—600 nm; n.d. = not determined. [c] ν(CO) 1 086s cm^{-1}. [d] ν(CO) 1 087s cm^{-1}. [e] ν(CO) 1 060s, δ(OCH_2) 920 cm^{-1}.

stretching absorptions in the i.r. spectra, both in the solid state and in solution, is suggestive of weak vibrational coupling between two nitrosyl groups in a dinuclear complex. The formulation is confirmed in the case of (**2a**) by an *X*-ray crystal structure determination.

With thiols bearing *ortho*-substituents the products were the fourteen-electron, neutral, mononuclear rhenium(III) complexes $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_4(NO)]$ (3), $[Re(SC_6H_3Pr^i_2\text{-}2,6)_4(NO)]$ (4), $[Re(SC_6H_2Me_3\text{-}2,4,6)_4(NO)]$ (5), and $[Re(SC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_4(NO)]$ (6). Molecular-weight determinations on (3) and (5) are consistent with mononuclearity, as are the very narrow ν(NO) absorptions in their i.r. spectra. A conductivity measurement on a tetrahydrofuran solution of complex (5) showed no appreciable ionisation. The steric bulk of the thiols prohibits them from bridging between two metals, thus allowing formation of mononuclear species. Although the product type is markedly dependent on the *ortho*-substituents of the thiols, we do not rule out the possibility that the compounds $[Re(SR)_4(NO)]$ (R = aryl) when the thiol carries no large *ortho*-substituents can be formed *via* another synthetic route. The electrochemical behaviour (see below) of complexes (1) and (**2a**) suggests that $[Re(SPh)_4(NO)]$ and $[Re(SC_6H_4Me\text{-}4)_4(NO)]$ may be reasonably stable. It would appear that, under the reaction conditions employed, the anions $[Re(SR)_4(NO)]^-$ are unstable and their formation is avoided by formation of the bridged anions (1) and (**2a**), or where this is not possible because of the bulky *ortho*-substituents, by undergoing a one-electron oxidation to give ultimately $[Re(SR)_4(NO)]$. The fate of the electron in this oxidation is unknown. The isolated yields of the mononuclear compounds are low because of solubility problems imposed by the lipophilic substituents. All of these mononuclear compounds are highly soluble in hydrocarbons.

One of the thiolates, presumably that *trans* to NO, in each of the compounds (3)—(6) is labile, being slowly substituted by alkoxide (OR′) in an alcoholic solution in the absence of excess of thiol to give compounds of the type $[Re(OR')(SR)_3(NO)]$, *e.g.* (7)—(9). The alkoxide ligands in these compounds can be metathesised with chloride using HCl, to give, for example, (**10**). Compounds (7)—(**10**) have not been fully investigated and must be regarded as incompletely characterised.

I.r. data for all the complexes are given in Table 1. The NO stretching frequencies of (1) and (**2a**) are comparable to those of other formally rhenium(II) nitrosyl complexes, $[ReCl_5(NO)]^{2-}$ (1 720 cm^{-1}) and $[ReBr_5(NO)]^{2-}$ (1 715 cm^{-1}),[9] even though the latter two complexes carry a double negative charge per metal atom whereas (1) and (**2a**) carry only half a negative charge per metal atom. This probably reflects the strongly electron-releasing nature of the thiolato-ligands, and a certain degree of thiolate-to-metal π donation. It thus appears that the thiolato-ligands create a site of high 'electron-richness' available for donation to NO π* orbitals. The ν(NO) values for the mononuclear complexes (3)—(**10**) are *ca.* 100 cm^{-1} higher than those of the isoelectronic $[Mo(SPh)_4(NO)]^-$ anion (1 675 cm^{-1}),[10] consistent with the negative charge of the latter

Table 2. Electrochemical data[a]

Compound	Primary reduction potential (V)[b]	ΔE_p/V	Comments
(1)	−1.25		Reverse scan shows reversible wave at −0.65 V
(2a)	−1.44		Reverse scan shows reversible wave at −0.52 V
(3)	−0.83	0.09	*c*
(4)	−0.67	0.08	*c*
(5)	−0.64	0.08	*c*
(6)	−0.44	0.09	*c*

[a] *ca.* 1 mmol dm^{-3} solution in thf containing 0.2 mol dm^{-3} NBu_4BF_4 as supporting electrolyte, platinum-wire electrode, with $[Mo(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2]$ (−0.16 V *vs.* s.c.e. under these conditions) as internal reference, scan rates (v) 0.01—1.0 V s^{-1}. [b] Quoted *vs.* s.c.e. Compounds (3)—(6) show no oxidation in the range 0 to +1.8 V *vs.* s.c.e.; E_p^{red} is quoted for irreversible processes, $E_{\frac{1}{2}}$ for reversible processes. [c] $i_p^{ox}/i_p^{red} \approx 1$, $i_p^{red}/v^{\frac{1}{2}}$ = constant.

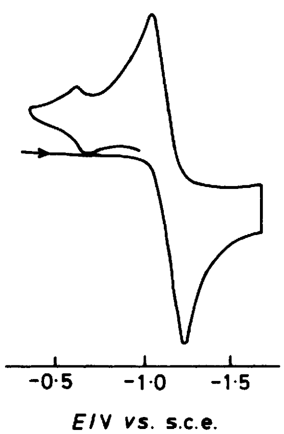


Figure 1. Cyclic voltammogram of $[PPh_4][Re_2(SPh)_7(NO)_2]$ (conditions as in Table 2), scan rate 0.3 V s^{-1}, held at negative switching potential for 10 s before reverse scan

complex, and comparable to that of $[ReCl_4(NO)(PMe_2Ph)_2]$ (1 750 cm^{-1}).[1]

The 90-MHz ^1H n.m.r. spectra of complexes (**2a**) and (**2b**) are consistent with their formulations as judged from the relative integrated intensities of the *p*-methyl and counter-ion resonances. In addition they show a temperature dependence which demonstrates a fluxional behaviour of the thiolato-ligands. This is discussed in detail below. The corresponding spectra of the mononuclear compounds (**3**)—(**6**) are complex, but in the 360-MHz n.m.r. spectra of (**4**) and (**6**) (in which the isopropyl splitting patterns are identical) at least seven magnetically distinct environments for the CH_3 groups are resolved. The methine protons in (**4**) and (**6**) give rise to two well separated heptets of integrated ratio 3 : 1. The 90-MHz spectrum of $[Re(SC_6H_2Me_3\text{-}2,4,6)_4(NO)]$ shows several methyl peaks which do not correspond to integral numbers of methyl groups. This may be the result of a conformational equilibrium in solution involving variation of the orientation of the aromatic groups, although solution i.r. studies give no support to this suggestion.

The electronic spectra of complexes (**1**) and (**2a**) are similar, as are those of (**3**)—(**6**) (see Table 1); all are dominated by intense charge-transfer bands. Detailed assignments are not made since for the dinuclear species insufficient data are available and for the mononuclear series there are no significant variations in $\nu_{max.}$ with the electron-releasing ability of the thiols. Corresponding absorptions are at similar wavelengths for all of the mononuclear tetrathiolato-complexes [even the strongly electron-withdrawing Br atoms in (**6**) have little effect] except (**5**), suggesting that the differences between (**5**) and the other mononuclear complexes are steric in origin, arising from the different distortions imposed by *ortho*-methyl and -isopropyl groups.

Table 3. Selected atomic co-ordinates (× 10^4) for $[PPh_4][Re_2(SC_6H_4\text{-}Me\text{-}4)_7(NO)_2]$ (**2a**)

Atom	*x*	*y*	*z*
Re(1)	9 144(1)	2 745(1)	7 639(1)
Re(2)	9 491(1)	1 003(1)	7 716(1)
S(1)	7 980(4)	1 713(4)	7 852(3)
S(2)	8 463(4)	1 555(3)	6 516(3)
S(3)	10 700(4)	2 065(3)	7 579(3)
S(4)	7 634(4)	3 623(4)	7 232(4)
S(5)	9 671(5)	3 878(4)	7 056(4)
S(6)	10 448(4)	−101(3)	7 253(3)
S(7)	8 719(4)	−253(4)	7 324(4)
N(1)	9 641(12)	3 306(11)	8 521(11)
O(1)	9 932(13)	3 688(13)	9 132(9)
N(2)	10 078(16)	911(11)	8 579(16)
O(2)	10 577(12)	931(13)	9 280(10)
C(1)	7 979(15)	1 805(15)	9 779(11)
C(8)	9 130(17)	1 681(13)	5 890(11)
C(15)	11 876(15)	2 412(12)	8 389(13)
C(22)	6 415(16)	3 013(15)	6 837(14)
C(29)	11 073(17)	4 063(12)	7 355(13)
C(36)	11 834(15)	196(12)	7 593(10)
C(43)	8 659(19)	−1 280(18)	7 570(17)

The electrochemistry of complexes (**1**)—(**6**) has been briefly studied using cyclic voltammetry (see Table 2). The mononuclear compounds (**3**)—(**6**) are reduced in a reversible one-electron process at potentials between −0.44 and −0.83 V *vs.* saturated calomel electrode (s.c.e.), at scan rates from 0.01 to 1.0 V s^{-1}. The reversible potentials show a qualitative correlation with the expected electron-withdrawing and -donating properties of the ring substituents, thus the electron-withdrawing nature of the bromine atoms in (**6**) enhances the relative stability of the reduced species. The reversible nature of the processes suggests that the fifteen-electron anions formed in the reduction, $[Re(SR)_4(NO)]^-$, are formed without any substantial structural change. Complexes (**1**) and (**2a**) are reduced irreversibly at more negative potentials. However on the reverse sweep (see Figure 1) secondary reversible waves appear at −0.65 and −0.52 V (*vs.* s.c.e.) for (**1**) and (**2a**) respectively. The similarity of these potentials with those of the reversible processes for (**3**)—(**6**) suggests that among the products of decomposition of the reduced species $[Re(SR)_7(NO)_2]^{2-}$ are $[Re(SR)_4(NO)]^-$ (SR = SPh or $SC_6H_4Me\text{-}4$) which are subsequently oxidised to $[Re(SR)_4(NO)]$ on the return sweep. The reversibility of the secondary wave suggests that $[Re(SPh)_4(NO)]$ and $[Re(SC_6\text{-}$

Table 4. Selected bond lengths (Å) and angles (°) for $[PPh_4][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]$ (**2a**)

Re(1)–Re(2)	2.783(1)	Re(2)–S(7)	2.445(2)	S(1)–Re(1)–S(2)	71.5(2)	S(6)–Re(2)–S(7)	79.0(2)
Re(1)–S(1)	2.383(1)	Re(2)–N(2)	1.638(27)	S(1)–Re(1)–S(3)	109.3(2)	Re(1)–Re(2)–N(2)	108.2(6)
Re(1)–S(2)	2.553(5)	S(1)–C(1)	1.807(24)	S(2)–Re(1)–S(3)	75.2(2)	S(1)–Re(2)–N(2)	97.4(9)
Re(1)–S(3)	2.408(5)	S(2)–C(8)	1.777(26)	S(1)–Re(1)–S(4)	87.8(2)	S(3)–Re(2)–N(2)	100.3(8)
Re(1)–S(4)	2.455(6)	S(3)–C(15)	1.825(18)	S(2)–Re(1)–S(4)	95.0(2)	S(6)–Re(2)–N(2)	94.8(8)
Re(1)–S(5)	2.441(7)	S(4)–C(22)	1.741(21)	S(2)–Re(1)–S(5)	98.1(2)	S(7)–Re(2)–N(2)	100.2(7)
Re(1)–N(1)	2.721(18)	S(5)–C(29)	1.778(23)	S(3)–Re(1)–S(5)	86.5(2)	Re(1)–S(1)–Re(2)	70.8(2)
Re(2)–S(1)	2.421(6)	S(6)–C(36)	1.777(19)	S(4)–Re(1)–S(5)	72.6(2)	Re(1)–S(1)–C(1)	116.3(7)
Re(2)–S(2)	2.575(5)	S(7)–C(43)	1.811(29)	Re(2)–Re(1)–N(1)	107.3(6)	Re(2)–S(1)–C(1)	111.8(7)
Re(2)–S(3)	2.388(5)	N(1)–O(1)	1.191(25)	S(1)–Re(1)–N(1)	96.9(7)	Re(1)–S(2)–Re(2)	65.7(1)
Re(2)–S(6)	2.439(6)	N(2)–O(2)	1.305(32)	S(3)–Re(1)–N(1)	99.7(6)	Re(1)–S(2)–C(8)	110.9(6)
				S(4)–Re(1)–N(1)	95.2(6)	Re(2)–S(2)–C(8)	118.1(7)
				S(5)–Re(1)–N(1)	96.3(7)	Re(1)–S(3)–Re(2)	70.9(2)
				S(1)–Re(2)–S(2)	70.6(2)	Re(1)–S(3)–C(15)	113.5(8)
				S(1)–Re(2)–S(3)	108.7(2)	Re(2)–S(3)–C(15)	115.2(8)
				S(2)–Re(2)–S(3)	75.1(2)	Re–$S_{terminal}$–C(av)	113.0(7)
				S(3)–Re(2)–S(6)	87.2(2)	Re(1)–N(1)–O(1)	176.5(18)
				S(1)–Re(2)–S(7)	80.5(2)	Re(2)–N(2)–O(2)	173.5(17)
				S(2)–Re(2)–S(7)	88.0(2)		

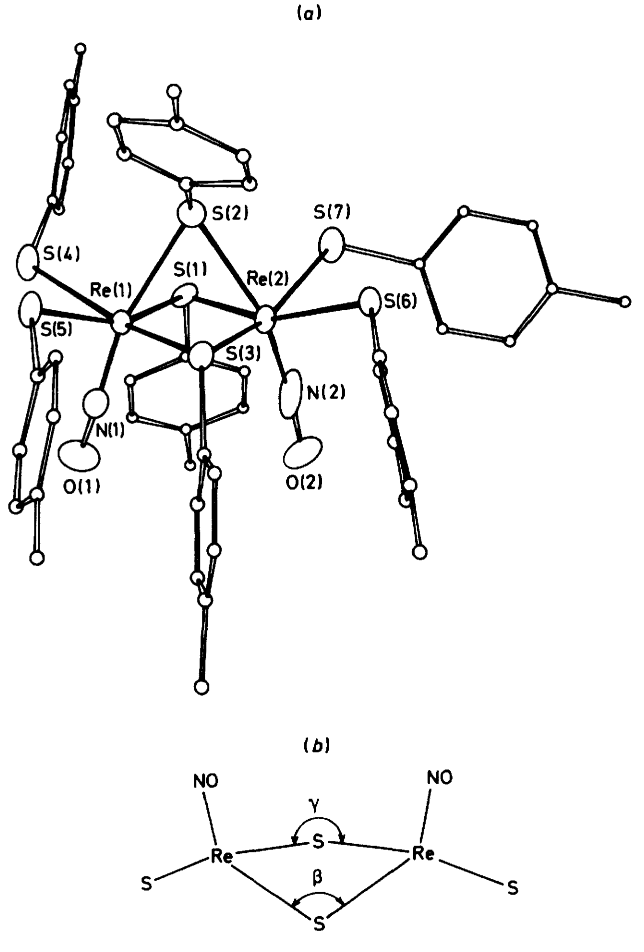


Figure 2. (*a*) Structure of $[Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]^-$, showing the atom labelling scheme; (*b*) diagram to show geometrical parameters discussed in the text

$H_4Me\text{-}4)_4(NO)]$ are stable on the time-scale used even though the thiolates are not bulky enough to prevent thiolato-bridge formation.

Structure of Complex (**2a**).—The *X*-ray crystal structures of a representative of each class of compound have been determined. Tables 3 and 4 give atomic co-ordinates and selected bond lengths and angles for (**2a**) and the structure is shown in Figure 2. Comparisons of Re–N and N–O bond lengths in (**2a**) with those in other structurally characterised rhenium nitrosyl complexes {$[ReCl_2(NO)(PMePh_2)_3]$, N–O 1.182(14), Re–N 1.775(10) Å;[1] $[ReF(CO)(NO)(PPh_3)_3]^+$, N–O 1.20(3), Re–N 1.76(2) Å[2]} show that in (**2a**) the Re–N distances are comparatively short and the N–O distances rather long, reinforcing the suggestion that π donation to NO is particularly strong.

The asymmetric structure of the triple thiolato-bridge implies the existence of a metal–metal bond. Evidence for this comes first from the short [2.783(1) Å] Re–Re distance and, further, from the observed diamagnetism of the complex, since a Re–Re bond would provide a suitable spin-pairing mechanism. A formal electron count reveals that each metal atom can attain an eighteen-electron configuration by formation of a Re–Re bond, all of the valence electrons occupying bonding orbitals according to the following scheme. If each NO contributes three electrons, each terminal thiolate one, each bridging thiolate three, and each rhenium seven, the overall uninegative charge brings the total electron count to 34. If a σ bond is allocated to each terminal ligand, two σ bonds to each bridging thiolate, and two π bonds to each Re–N group, there are 16 metal–ligand bonding orbitals occupied by 32 electrons, and a Re–Re bonding orbital occupied by two electrons. Considered in isolation, each Re had a singly occupied non-binding orbital of correct symmetry for mutual overlap.

The six thiolates *cis* to NO are bent away from the NO group so that N–Re–S angles are all greater than 90°, resulting in distortion of the bridge structure to C_{2v} symmetry. The bridge structure is also influenced by metal–metal bonding. Distortions of confacial bioctahedra due to metal–metal interactions have been quantified by Cotton and Ucko.[11] Of the geometric parameters they define, only ($\beta - 70.53°$) (where β = M–L–M angle for the bridging ligand) is meaningful in complex (**2a**) because of the lack of D_{3h} symmetry. The 'ideal' value for this parameter is 0°. In the absence of attractive M–M interactions this angle should deviate from the ideal so as to increase the M–M distance, because of strain at the ligand atom and an underlying repulsion between the metal atoms. A value close to 0° therefore suggests significant attraction between the metal atoms. The values for (**2a**), ($\beta - 70.53°$) = +0.3, −4.8, and +0.4° for S(1), S(2), and S(3) respectively, are thus indicative of a Re–Re bond. The only other structurally characterised example of a triple thiolato-bridge is the double-

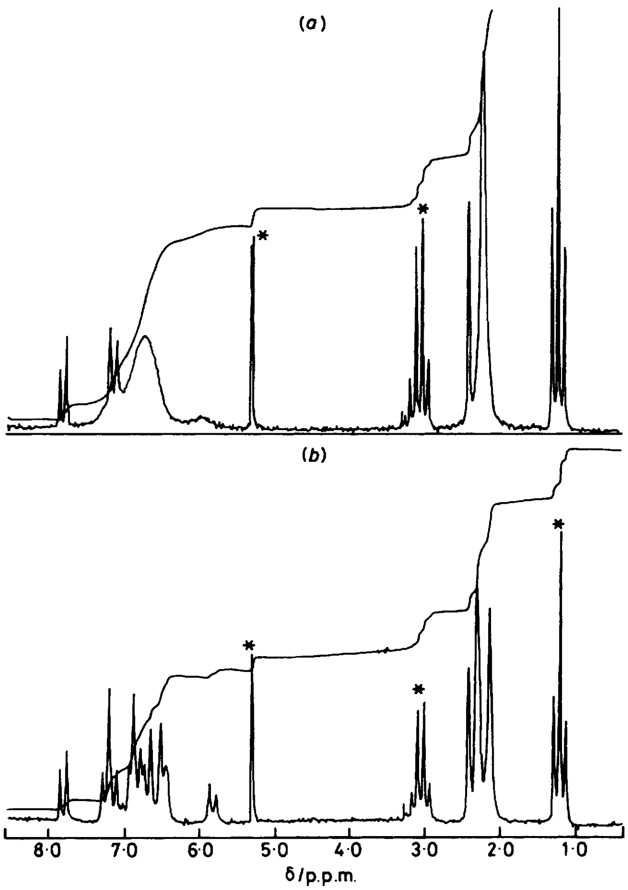
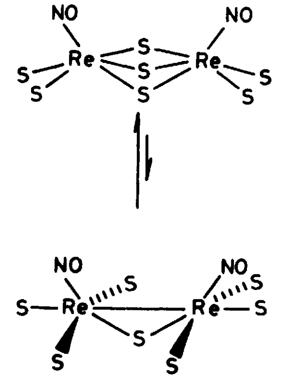


Figure 3. Proton n.m.r. spectra of $[NHEt_3][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]$ at 23.0 (*a*) and -6.5 °C (*b*) in CD_2Cl_2. Solvent and triethylammonium peaks are labelled (*)

cubane $[\{(EtS)_3MoFeS_4\}_2(\mu\text{-}SEt)_3]^{3-}$ reported by Holm and co-workers.[12] Here the Mo–Mo distance is 3.67 Å and the Cotton–Ucko criteria deviate from the 'ideal' in such a way as to suggest a lack of Mo–Mo bonding.

The observation of the nearly planar Re(1)–S(1)–Re(2)–S(3) unit (the dihedral angle $\gamma = 178.1°$, see Figure 2) suggests that there may be a special stability of this arrangement sufficient to contribute to the distortion of the bridging system away from D_{3h} symmetry. Metal–ligand distances for a given ligand are usually significantly longer for bridging than for terminal ligands. In complex (**2a**) this is true for the *trans* bridging thiolate but not for the *cis* bridging thiolates, for which the distances are smaller rather than larger than the terminal Re–S distances, although the difference of 0.04 Å (average) is small but significant.

Fluxional Behaviour of Complex (**2b**).—For the ^1H n.m.r. studies of the fluxional behaviour the triethylammonium salt (**2b**) was used to avoid complicating counter-ion peaks. The spectra in the fast- and slow-exchange limits are shown in Figure 3. The important features of the high-temperature spectrum are the signals due to the *p*-methyl groups and the *o*- and *m*-protons of the thiolates. The methyl signals consist of a sharp 3 H singlet ($\delta = 2.34$)[*] and a broad 18 H singlet (δ 2.18). Since the approximately C_{2v} symmetry of the anion permits only one unique methyl group, *i.e.* that of the bridging thiolate *trans* to NO, the 3 H singlet is unequivocally assigned to this ligand. The aromatic signals consist of a sharp 4 H 'AB' system (δ 7.42, *J* 8.2 and 60 Hz), similarly assigned to the *trans* bridging thiolate, and other very broad bands. Below 11 °C the broad signals split into a pattern of sharp lines. The 18 H methyl peak becomes a pair of sharp singlets (12 H, δ 2.36 and 6 H, δ 2.09) while the 3 H, δ 2.36 signal is unaffected. The 4 H AB quartet is also unchanged on lowering the temperature, while the broad aromatic signals split into a complex pattern. The entire low-temperature aromatic pattern is simulated as five overlapping AB quartets of integrated ratios 4 H:8 H:8 H:4 H:4 H, implying that, below 11 °C at least, rotation of aromatic rings about C–S or S–Re bonds is slow on the n.m.r. time-scale. The observed temperature dependence of the spectrum implies that the six 'equatorial' thiolates are interchanged by a fluxional mechanism, $T_c = 11$ °C, in which the *trans* thiolate is not involved.



Scheme 2.

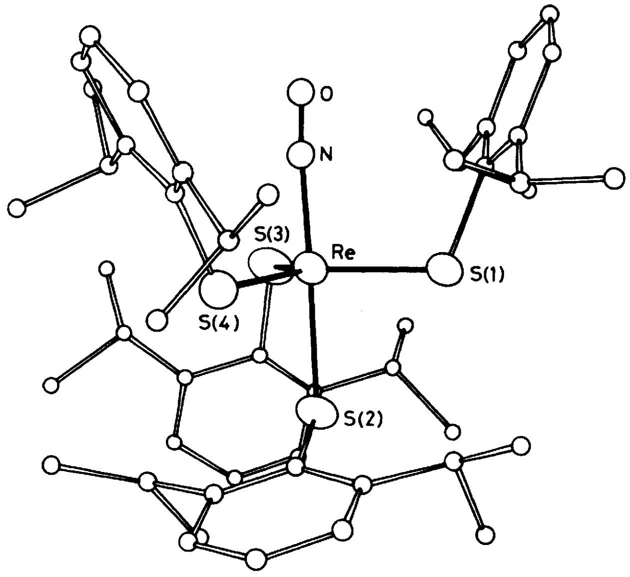


Figure 4. Structure of $[Re(SC_6H_3Pr^i{}_2\text{-}2,6)_4(NO)]$, showing the atom labelling scheme

The combined n.m.r. data suggest that above 11 °C the six equatorial ligands exchange rapidly about a rigid Re(1)–S(2)–Re(2) core. A plausible mechanism involving partial bridge cleavage is suggested in Scheme 2. A precedent for fluxional exchange of thiolato-ligands between bridging and terminal positions is the behaviour of the complex $[MoTl(SC_6F_5)_4(\eta\text{-}C_5H_5)]$[13] as observed by ^{19}F n.m.r. spectroscopy.

Structure of Complex (**4**).—Tables 5 and 6 give atomic co-ordinates and selected bond lengths and angles for (**4**). The

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[*] For $[NHEt_3][SC_6H_4Me\text{-}p]$ under these conditions $\delta(p\text{-}Me) = 2.25$.

Table 5. Selected atomic co-ordinates ($\times 10^4$) for [Re(SC$_6$H$_3$Pr$^i_2$-2,6)$_4$(NO)] (4)

Atom	*x*	*y*	*z*
Re	4 852(1)	6 967(1)	1 388(1)
S(1)	6 094(4)	6 197(3)	1 498(1)
S(2)	6 138(4)	7 676(3)	1 123(1)
S(3)	4 637(5)	7 741(3)	1 831(1)
S(4)	4 049(4)	7 082(3)	864(1)
O(1)	3 256(14)	6 098(9)	1 691(4)
N	3 889(12)	6 463(8)	1 588(4)
C(11)	5 632(18)	5 453(11)	1 736(6)
C(21)	6 179(17)	7 595(11)	648(5)
C(31)	5 404(17)	8 508(11)	1 786(5)
C(41)	2 886(16)	6 642(11)	833(5)

Table 6. Selected bond lengths (Å) and angles (°) for [Re(SC$_6$H$_2$Pr$^i_2$-2,6)$_4$(NO)] (4)

Re–S(1)	2.266(5)	S(1)–C(11)	1.820(23)
Re–S(2)	2.413(5)	S(2)–C(21)	1.818(21)
Re–S(3)	2.286(5)	S(3)–C(31)	1.817(22)
Re–S(4)	2.272(5)	S(4)–C(41)	1.765(22)
Re–N	1.781(16)	O–N	1.167(24)
S(1)–Re–S(2)	87.0(2)	S(3)–Re–N	87.7(5)
S(1)–Re–S(3)	113.1(2)	S(4)–Re–N	95.6(5)
S(2)–Re–S(3)	90.9(2)	Re–S(1)–C(11)	112.3(8)
S(1)–Re–S(4)	124.6(2)	Re–S(2)–C(21)	112.8(7)
S(2)–Re–S(4)	84.6(2)	Re–S(3)–C(31)	114.0(7)
S(3)–Re–S(4)	121.8(2)	Re–S(4)–C(41)	114.7(7)
S(1)–Re–N	94.1(5)	Re–N–O	173.6(14)
S(2)–Re–N	178.5(5)		

structure is shown in Figure 4. The molecule possesses a slightly distorted trigonal-bipyramidal structure similar to that of the isoelectronic [M(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_4$(MeCN)] (M = Ru or Os)[14] and it would appear since the recent preparation and characterisation of several different 14-electron complexes of the trigonal-bipyramidal geometry, with one or two π-acceptor ligands, that such structures have a particular stability with thiolate and alkoxide ligands. In such cases the π-acid ligands (CO,[15] MeCN,[16] NO,[10,17] or PR$_3$[7]) are always in axial sites. In the complex [Mo(SPh)$_4$(NO)]$^-$ the equatorial thiolates orient their aromatic groups towards the NO, forming a pocket which the NO occupies.[18] This arrangement may be adopted to minimise repulsion between the lone pairs of the equatorial sulphur atoms and the Mo–N–O π electrons. A similar arrangement occurs in the complexes [Re(SPh)$_3$(MeCN)(PPh$_3$)][7] and [W(OPr^i)$_3$(NO)(py)] (py = pyridine).[17] In contrast, two of the equatorial aromatic groups in complex (4) are directed towards (*endo*) the NO and one away (*exo*); presumably the steric interaction of the bulky substituents outweighs the effect of the sulphur–MNO repulsion. This arrangement is seen in other complexes of sterically hindered thiols, [MoL$_3$(CO)$_2$]$^-$ [15] and [RuL$_4$(MeCN)] (L = SC$_6$H$_2$Pr$^i_3$-2,4,6).[14] The axial aromatic group in (4) is oriented so as to occupy the space left between the equatorial aromatic groups. The Re–N–O group is slightly bent away from the *endo*-thiolates.

Consistent with the calculations of Rossi and Hoffmann,[19] the axial Re–S bond is longer (2.41 Å) than the average of the equatorial bond lengths (2.27 Å). Their calculation ignores the effect of π bonding in the equatorial bonds, but they further predict that weak π-donor ligands in d^4 systems will occupy equatorial positions and orient themselves so as to maximise π overlap in the *xy* plane (defining the Re–N bond as the *z* axis).

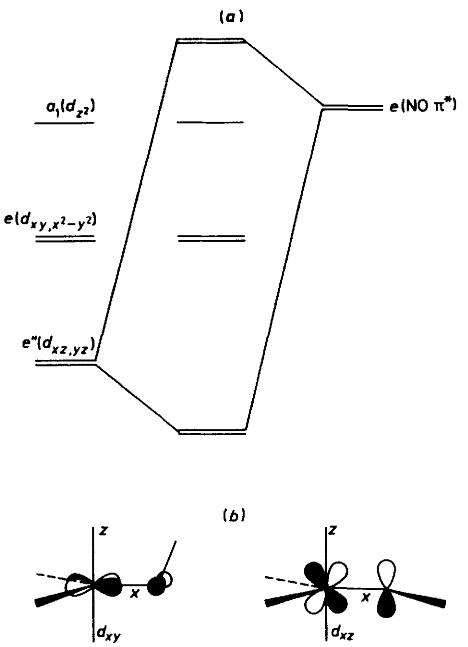

Figure 5. (*a*) Interaction of metal-based orbitals with NO π* orbitals in an idealised trigonal bipyramid[20]; (*b*) diagram showing interaction of the metal with the equatorial sulphur *p* orbital in ⊥ (left) and ∥ (right) planes

This is indeed the case in complex (4). π Donation by equatorial sulphurs (see Figure 5) would be weaker in a ∥ plane (*i.e.* one containing the *z* axis) since of the vacant orbitals available for π interaction with equatorial ligands the *e″* (which interacts in the ∥ plane) has much higher energy than the *e′* (which would interact in the ⊥ plane). Hence the S–C bonds of the equatorial thiolates are directed so as to maximise the weak S-to-Re π donation. Similarly there are no suitable metal orbitals available to accept π-electron density from the axial sulphur. Thus, π donation, although weak, probably accounts for the short equatorial Re–S bonds and explains why the equatorial thiolates do not adopt a 'propeller' arrangement with the S–C bonds in the *xy* plane, a situation which sterically would be more favourable particularly for [Mo(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(CO)$_2$]$^-$, where there are no bulky axial ligands.

Experimental

Crystal parameters and experimental details for the *X*-ray diffraction studies are given in Table 7. I.r. spectra were determined for Nujol mulls or CH$_2$Cl$_2$ solutions using a Pye-Unicam SP2000 spectrophotometer. Electronic spectra were determined for tetrahydrofuran solutions using a Perkin-Elmer Lambda 5 u.v.–visible spectrophotometer. N.m.r. spectra were recorded for CD$_2$Cl$_2$ solutions using JEOL FX-90Q (90 MHz) or Bruker WH360 (360 MHz) instruments. Cyclic voltammetric measurements were made using a Chemical-Electronics type RB1 waveform generator and type TR70/2A potentiostat and a Bryans 24000 A4 XY chart recorder. Molecular weights were measured cryoscopically in benzene solution. Carbon, H, and N analyses were performed by Mrs. G. Olney, University of Sussex, chlorine analyses by Butterworth Laboratories Ltd., Teddington, Middlesex.

All reactions were carried out in dry, deoxygenated solvents under a dinitrogen atmosphere unless indicated. The complex [ReCl$_2$(OMe)(NO)(PPh$_3$)$_2$] was prepared according to ref. 1. Thiophenol and 4-methylthiophenol were used as purchased. 2,4,6-Tri-isopropylthiophenol and 2,4,6-trimethylthiophenol

Table 7. Experimental details for *X*-ray diffraction study of $[PPh_4][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]$ (**2a**) and $[Re(SC_6H_2Pr^i_2\text{-}2,6)_4(NO)]$ (**4**)

(*a*) Crystal parameters at 23 °C[a]	(**2a**)·CH_2Cl_2	(**4**)
a/Å	13.465(3)	13.218(6)
b/Å	15.574(4)	19.534(9)
c/Å	19.630(5)	38.115(1)
α/°	98.00(2)	90.00
β/°	109.80(2)	90.00
γ/°	91.85(2)	90.00
U/Å^3	3 821.6(16)	9 841.30(6)
Space group	$P\bar{1}$	*Pbca*
Z	2	8
D_c/g cm^{-3}	1.49	1.35
D_m/g cm^{-3}	1.45—1.47[b]	1.33(2)
(*b*) Measurement of intensity data		
Crystal dimensions (mm)	0.10, 0.27, 0.33 (mounted in capillary)	0.20, 0.29, 0.24
Scan rate/° min^{-1}	Variable: 6—30	Variable: 10—30
Scan range/°	$3 < 2\theta < 45$	$0 < 2\theta < 45$
Background measurement	Stationary crystal and counter, at the beginning and end of each 2θ scan, each for one half the time taken for the 2θ scan	Stationary crystal and counter, at the beginning and end of each 2θ scan, each for the time taken for the 2θ scan
No. of reflections collected	8 347	7 240
No. of independent reflections used	6 371 for $F_o > 3\sigma\lvert F_o\rvert$	3 047 for $F_o > 3\sigma\lvert F_o\rvert$
(*c*) Reduction of intensity data and summary of structure solution and refinement[c]		
Absorption coefficient/cm^{-1}	35.8	28.0
Absorption correction	None (intensity ratio $T_{max.}/T_{min.} = 1.13$)	None ($T_{max.}/T_{min.} = 1.07$)
Final discrepancy factors[d] *R*	0.0792	0.0643
R′	0.0807	0.0634
Goodness of fit[e]	1.14	1.936

Details common to both complexes: diffractometer, Nicolet *R*3*m*; radiation, Mo-K_α ($\bar{\lambda}$ = 0.710 69 Å); scan mode, coupled θ(crystal)—2θ(counter); scan length, $[2\theta(\text{Mo-}K_{\alpha 1}) - 1.0]$ to $[2\theta(\text{Mo-}K_{\alpha 1}) + 1.0]$°; standards, 3 measured every 197 reflections, no significant deviations; neutral atomic scattering factors; anomalous dispersion correction applied to all non-hydrogen atoms ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3).

Structure solution: Re atoms located by Patterson synthesis; all other non-hydrogen atoms located on subsequent difference Fourier maps. All non-hydrogen and non-carbon atoms were refined anisotropically. Hydrogen atoms were included as fixed contributors in the final cycle of refinement. Three highly disordered CH_2Cl_2 molecules of crystallisation were located on the Fourier maps of (**2a**), each showing a population of *ca.* 0.33. No systematic attempt was made to resolve the disorder as this region of the structure was not of chemical interest.

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] Observed density varied with time as a consequence of the slow loss of CH_2Cl_2 of crystallisation. Over a period of a week crystals of (**2a**) became opaque and analysis revealed loss of CH_2Cl_2. [c] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described by G. M. Sheldrick, Nicolet SHELTX Operations Manual, Nicolet XRD Corp., Cupertino, 1979. Data corrected for background attenuators, Lorentz and polarisation effects in the usual manner. [d] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$; g = 0.001 for (**4**), 0.005 for (**2a**). [e] $[\Sigma w(|F_o|-|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o is the number of observations and N_v the number of variables.

were prepared from 2,4,6-tri-isopropylbenzenesulphonyl chloride and 2,4,6-trimethylbenzenesulphonyl chloride (each used as purchased from Aldrich Chemicals Ltd.) respectively. 2,6-Di-isopropylthiophenol and 4-bromo-2,6-di-isopropylthiophenol were prepared from 2,6-di-isopropylphenol (used in 90% purity as purchased from Aldrich Chemicals Ltd.) by an adaptation of the Newman–Kwart rearrangement.[20]

2,4,6-*Tri-isopropylthiophenol.*—Lithium aluminium hydride (27 g, 0.71 mol) was suspended in diethyl ether (200 cm^3) in a flask equipped with an efficient condenser and cooled to 0 °C in an ice-bath. While this suspension was magnetically stirred, a solution of 2,4,6-tri-isopropylbenzenesulphonyl chloride (100 g, 0.33 mol) in diethyl ether (300 cm^3) was added dropwise. When this addition was complete and the initial vigorous reaction had subsided, a further 13 g (0.34 mol) of lithium aluminium hydride powder was added and the solution refluxed for 5 h. The large excess of hydride was destroyed by dropwise addition of excess of methanol under N_2. The solution was then poured into 1 l of iced water. Finally this mixture was acidified with 2 mol dm^{-3} H_2SO_4 and extracted with diethyl ether (3 × 200 cm^3). The combined ether extracts were dried over $MgSO_4$, and the solvent stripped on a rotary evaporator. The liquid residue was distilled (b.p. 117—120 °C, 0.3 mmHg) to yield 67.4 g (87%) of 2,4,6-tri-isopropylthiophenol as a colourless liquid.

2,4,6-*Trimethylthiophenol* was prepared exactly analogously from 2,4,6-trimethylbenzenesulphonyl chloride, using similar molar ratios of $LiAlH_4$, in similar yield (b.p. 69—72 °C, 0.3 mmHg).

2,6-*Di-isopropylthiophenol.*—Crude 2,6-di-isopropylphenol (100 g, containing 0.51 mol) was dissolved in *N,N*-dimethylformamide. To the magnetically stirred solution, sodium hydride (15.3 g of an 80% dispersion in mineral oil, 0.15 mol) was added slowly. When gas evolution was complete, dimethylthiocarbamoyl chloride[21] (63 g, 0.51 mol) was added slowly. On completion of the addition the stirred solution was heated at 100 °C for 16 h, then cooled to room temperature and poured into 1.5 l of 2% aqueous KOH. The resulting precipitate was collected and recrystallised from hot ethanol, to give off-white O-2,6-*di-isopropylphenyl* N,N-*dimethylthiocarbamate*, 50 g (34%). This material was heated at 230 °C for 48 h under dinitrogen; on melting it was continuously stirred. On cooling to room temperature, the solid product (crude S-2,6-*di-isopropylphenyl* N,N-*dimethylthiocarbamate*) was used without purification for the next step. The crude material (50 g, 0.19 mol) was dissolved in 1,2-dimethoxyethane (200 $\mathrm{cm^3}$) and the solution added dropwise to a stirred suspension of lithium aluminium hydride (22 g, 0.58 mol) in 1,2-dimethoxyethane (150 $\mathrm{cm^3}$) cooled in an ice-bath. When the initial reaction had subsided the solution was refluxed for 6 h. The excess of hydride was destroyed as described above. Acidification, ether extraction, drying, and solvent removal were carried out as for $\mathrm{HSC_6H_2Pr^i_3}$-2,4,6. The final yellow liquid residue was distilled (b.p. 82—88 °C, 0.3 mmHg) to yield 2,6-di-isopropylthiophenol as a colourless liquid, 20 g (20% based on 2,6-di-isopropylphenol).

4-*Bromo*-2,6-*di-isopropylthiophenol*.—Crude 2,6-di-isopropylphenol (100 g, containing 0.51 mol) was dissolved in glacial acetic acid (200 $\mathrm{cm^3}$). Dibromine (81.6 g, 0.51 mol) was added dropwise to the stirred solution. On completion of the addition the mixture was poured into water (500 $\mathrm{cm^3}$), forming a separable brown oil, which was washed repeatedly with water and dried over $\mathrm{MgSO_4}$, to give crude 4-bromo-2,6-di-isopropylphenol, 118 g (91%). This material, without purification and assuming 100% purity, was used to make 4-bromo-2,6-di-isopropylthiophenol in a manner exactly analogous to that for $\mathrm{HSC_6H_3Pr^i_2}$-2,6 and in overall yield based on 2,6-di-isopropylphenol of 15% (b.p. 140—141 °C, 0.3 mmHg).

Tetraphenylphosphonium Tri-μ-*thiophenolato-bis*[*nitrosyldi*(*thiophenolato*)*rhenate*], $\mathrm{[PPh_4][Re_2(SPh)_7(NO)_2]}$ (**1**).—To a suspension of $\mathrm{[ReCl_2(OMe)(NO)(PPh_3)_2]}$ (0.3 g, 0.36 mmol) in methanol (30 $\mathrm{cm^3}$) were added thiophenol (0.24 $\mathrm{cm^3}$, 2.2 mmol) and triethylamine (0.21 $\mathrm{cm^3}$, 1.5 mmol). The system was heated under reflux for 1 h. The cooled orange-brown solution was filtered to remove insoluble side products, and treated with tetraphenylphosphonium bromide (0.3 g) yielding microcrystalline (**1**). After washing with $\mathrm{Pr^iOH}$ and diethyl ether, the product was recrystallised from dichloromethane–diethyl ether as orange-brown needles, 49% (Found: C, 51.4; H, 3.75; N, 1.90. $\mathrm{C_{66}H_{55}N_2O_2PRe_2S_7}$ requires C, 51.6; H, 3.60; N, 1.80%).

Tetraphenylphosphonium Tri-μ-4-*methylthiophenolato-bis*[*di*(4-*methylthiophenolato*)*nitrosylrhenate*], $\mathrm{[PPh_4][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]}$ (**2a**), was prepared analogously to (**1**) using 4-methylthiophenol, yield 59% of orange prisms (Found: C, 53.7; H, 4.45; N, 1.75. $\mathrm{C_{73}H_{69}N_2O_2PRe_2S_7}$ requires C, 53.6; H, 4.25, N, 1.70%). Crystals suitable for *X*-ray crystallography were grown by diffusion of diethyl ether into a dichloromethane solution of (**2a**).

Triethylammonium Tri-μ-4-*methylthiophenolato-bis*[*di*(4-*methylphenolato*)*nitrosylrhenate*], $\mathrm{[NHEt_3][Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]}$ (**2b**).—The reaction was carried out as for complex (**2a**) but instead of adding tetraphenylphosphonium bromide the filtered reaction solution was evaporated under reduced pressure to *ca.* 10 $\mathrm{cm^3}$, yielding an orange, microcrystalline precipitate which was washed with $\mathrm{Pr^iOH}$ and diethyl ether to give pure (**2b**) (Found: C, 47.35, H, 4.90; N, 2.95. $\mathrm{C_{55}H_{65}N_3O_2Re_2S_7}$ requires C, 47.3; H, 4.65; N, 3.00%).

Nitrosyltetrakis(2,4,6-*tri-isopropylthiophenolato*)*rhenium*, $\mathrm{[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_4(NO)]}$ (**3**).—To a stirred suspension of $\mathrm{[ReCl_2(OMe)(NO)(PPh_3)_2]}$ (1.0 g, 1.2 mmol) in methanol (30 $\mathrm{cm^3}$) were added $\mathrm{HSC_6H_2Pr^i_3}$-2,4,6 (1.87 $\mathrm{cm^3}$, 7.13 mmol) and triethylamine (0.82 $\mathrm{cm^3}$, 5.93 mmol). The system was heated under reflux for 0.5 h then the solution was filtered quickly while hot. On cooling the filtrate, brown microcrystals formed which were collected and washed with methanol, yielding 0.61 g (44%) of dark brown, hydrocarbon-soluble (**3**) (Found: C, 62.15; H, 7.70; N, 1.20. $\mathrm{C_{60}H_{92}NOReS_4}$ requires C, 62.25; H, 7.95; N, 1.20%).

Tetrakis(2,6-*di-isopropylthiophenolato*)*nitrosylrhenium*, $\mathrm{[Re(SC_6H_3Pr^i_2\text{-}2,6)_4(NO)]}$ (**4**).—To a stirred suspension of $\mathrm{[ReCl_2(OMe)(NO)(PPh_3)_2]}$ (0.2 g, 0.24 mmol) in methanol (30 $\mathrm{cm^3}$) were added $\mathrm{HSC_6H_3Pr^i_2}$-2,6 (0.23 $\mathrm{cm^3}$, 1.18 mmol) and triethylamine (0.16 $\mathrm{cm^3}$, 1.16 mmol). The system was heated under reflux for 0.5 h then the solution was filtered while hot. On cooling, brown crystals of (**4**) were formed in the filtrate. Extraction of the insoluble residue with diethyl ether gave a brown solution which was filtered and evaporated to dryness. The residue was recrystallised from hot methanol to give a further crop of complex (**4**). The total yield was 0.16 g (66%) (Found: C, 58.45; H, 7.15; N, 1.35. $\mathrm{C_{48}H_{68}NOReS_4}$ requires C, 58.3; H, 6.90; N, 1.40%). Crystals suitable for *X*-ray analysis were obtained by recrystallising from dichloromethane–methanol.

Nitrosyltetrakis(2,4,6-*trimethylthiophenolato*)*rhenium*, $\mathrm{[Re(SC_6H_2Me_3\text{-}2,4,6)_4(NO)]}$ (**5**), was prepared in an exactly analogous manner to (**4**), using $\mathrm{HSC_6H_2Me_3}$-2,4,6 (0.17 $\mathrm{cm^3}$, 1.18 mmol) in place of $\mathrm{HSC_6H_3Pr^i_2}$-2,6 to yield brown crystals of (**5**), 0.11 g (55%) (Found: C, 52.5; H, 5.40; N, 1.70. $\mathrm{C_{36}H_{44}NOReS_4}$ requires C, 52.4; H, 5.50; N, 1.65%).

Tetrakis(4-*bromo*-2,6-*di-isopropylthiophenolato*)*nitrosylrhenium*, $\mathrm{[Re(SC_6H_2Pr^i_2\text{-}2,6\text{-}Br\text{-}4)_4(NO)]}$ (**6**).—To a stirred suspension of $\mathrm{[ReCl_2(OMe)(NO)(PPh_3)_2]}$ (0.31 g, 0.37 mmol) in methanol (30 $\mathrm{cm^3}$) were added $\mathrm{HSC_6H_2Pr^i_2}$-2,6-Br-4 (0.38 $\mathrm{cm^3}$, 1.81 mmol) and triethylamine (0.21 $\mathrm{cm^3}$, 1.52 mmol). The system was heated under reflux for 0.75 h, giving a brown suspension. The solid was collected by filtration while hot and washed with methanol, yielding a crude sample of (**6**). The filtered reaction solution, on cooling to room temperature, gave a second crop of complex (**6**). The combined crops were recrystallised from hot hexane, yield 0.31 g (65%) (Found: C, 44.65; H, 5.20; N, 1.10. $\mathrm{C_{48}H_{64}NOReS_4}$ requires C, 44.5; H, 4.90; N, 1.05%).

Methoxonitrosyltris(2,4,6-*trimethylthiophenolato*)*rhenium*, $\mathrm{[Re(SC_6H_2Me_3\text{-}2,4,6)_3(OMe)(NO)]}$ (**7**), was obtained as brown crystals by partial evaporation of a $\mathrm{CH_2Cl_2}$–MeOH solution of (**5**) which had been standing at room temperature for several days (Found: C, 47.5; H, 5.25; N, 1.95. $\mathrm{C_{28}H_{36}NO_2ReS_3}$ requires C, 48.0; H, 5.15; N, 2.00%).

Methoxonitrosyltris(2,4,6-*tri-isopropylthiophenolato*)*rhenium*, $\mathrm{[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(OMe)(NO)]}$ (**8**), was obtained as red-brown crystals in a similar manner to (**7**). No microanalytical data available; the formulation was on the basis of similarity of the i.r. spectrum with that of complex (**7**).

Tris(2,6-*di-isopropylthiophenolato*)*ethoxonitrosylrhenium*, $\mathrm{[Re(SC_6H_3Pr^i_2\text{-}2,6)_3(OEt)(NO)]}$ (**9**), was obtained as brown crystals by partial evaporation of an ethanolic solution of (**4**) which had been standing for several days (Found: C, 54.2; H, 6.30; N, 1.65; $\mathrm{C_{38}H_{56}NO_2ReS_3}$ requires C, 54.25; H, 6.65; N, 1.65%).

Chloronitrosyltris(2,4,6-*tri-isopropylthiophenolato*)*rhenium*, (**10**).—To a solution of complex (**8**) in dichloromethane-methanol (50:50) was added excess of chlorotrimethylsilane. The solution turned green immediately but on standing the orange-brown colour returned. Partial evaporation under reduced pressure yielded orange-brown crystals of (**10**), which were collected and washed with methanol (Found: C, 56.5; H, 7.30; Cl, 3.35; N, 1.40. $\mathrm{C_{45}H_{69}ClNOReS_3}$ requires C, 56.45; H, 7.20; Cl, 3.70; N, 1.45%).

References

1 R. W. Adams, J. Chatt, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1974, 1075.

2 T. S. Cameron, K. R. Grundy, and K. N. Robertson, *Inorg. Chem.*, 1982, **21**, 4149.

3 B. K. Sen, P. Bandyopadhyay, and P. B. Sarkar, *J. Indian Chem. Soc.*, 1967, **44**, 227.

4 S. Rakshit and P. Bandyopadhyay, *J. Indian Chem. Soc.*, 1970, **47**, 1205.

5 A. Davidson, C. Orvig, H. S. Trop, M. Sohn, B. V. DePamphilis, and A. G. Jones, *Inorg. Chem.*, 1980, **19**, 1988.

6 A. C. McDonell, T. W. Hambley, M. R. Snow, and A. G. Wedd, *Aust. J. Chem.*, 1983, **36**, 253.

7 J. R. Dilworth, B. D. Neaves, J. P. Hutchinson, and J. A. Zubieta, *Inorg. Chim. Acta*, 1982, **65**, L223.

8 E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *Chem. Commun.*, 1970, 1531.

9 D. Giusto and G. Cova, *Gazz. Chim. Ital.*, 1972, **102**, 265.

10 J. R. Dilworth, P. T. Bishop, and J. A. Zubieta, unpublished work.

11 F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, 1972, **6**, 161.

12 T. W. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, 1979, **101**, 4140.

13 J. L. Davidson, K. Davidson, and W. E. Lindsell, *J. Chem. Soc., Chem. Commun.*, 1983, 452.

14 S. A. Koch and M. Miller, *J. Am. Chem. Soc.*, 1983, **105**, 3362.

15 J. R. Dilworth, J. Hutchinson, and J. A. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1983, 1034.

16 P. J. Blower, unpublished work.

17 M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *Inorg. Chem.*, 1979, **18**, 116.

18 J. A. Zubieta, personal communication.

19 A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.

20 M. S. Newman and H. A. Karnes, *J. Org. Chem.*, 1966, **31**, 3980.

21 M. S. Newman and F. W. Hetzel, *Org. Synth.*, 1971, **51**, 139.

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