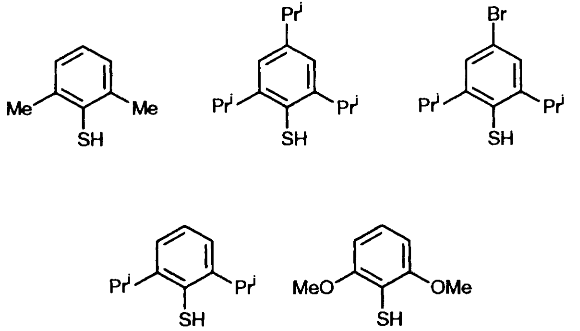
Syntheses and Structures of $[Re(SC_6H_3Me_2\text{-}2,6)_3(PPh_3)]$, $[Re(SC_6H_3Me_2\text{-}2,6)_3(Bu^tNC)_2]$, $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3L(PPh_3)]$ ($L = N_2$ or CO) and $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$†

Jonathan R. Dilworth,[*,a] **Jin Hu,**[a] **John R. Miller,**[a] **David L. Hughes,**[b] **Jon A. Zubieta**[c] **and Qin Chen**[c]

[a] *Department of Biological and Chemical Sciences, Central Campus, University of Essex, Colchester CO4 3SQ, UK*
[b] *Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK*
[c] *Chemistry Department, University of Syracuse, Syracuse, NY 13244, USA*

The hydride $[ReH_7(PPh_3)_2]$ reacted with 2,6-dimethylbenzenethiol in toluene to give a complex of stoichiometry $[Re(SC_6H_3Me_2\text{-}2,6)_3(PPh_3)]$ **1**. A crystal structure showed a trigonal-bipyramidal geometry about the Re with an agostic interaction to a thiolate methyl occupying an apical site, *trans* to the PPh_3 ligand. Complex **1** reacts rapidly with MeCN to give the known $[Re(SC_6H_3Me_2\text{-}2,6)_3(MeCN)(PPh_3)]$ **2** and with Bu^tNC to form $[Re(SC_6H_3Me_2\text{-}2,6)_3(Bu^tNC)_2]$ **3**. The crystal structure of **3** showed trigonal-pyramidal geometry about the Re with asymmetric co-ordination of the isocyanide ligands and an unusual configuration for the thiolate aromatic groups. The reactions of the hydrides $[ReH_7(PPh_3)_2]$ and $[ReH_5(PPh_3)_3]$ with 2,4,6-triisopropyl-, 2,6-dimethoxy-benzenethiol and tris(2-sulfanylphenyl)phosphine were also studied. With $HSC_6H_2Pr^i_3\text{-}2,4,6$ the dinitrogen complex $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4** was formed and its structure determined. The preparations and structures of the complexes $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$, $[Re\{SC_6H_3(OMe)_2\text{-}2,6\}_3(PPh_3)]$ and $[Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)]$ are also discussed. An alternative convenient route to $[ReH_4(PPh_3)_4]^+$ from $[ReH_5(PPh_3)_3]$ is presented.

Sterically hindered thiolates have been studied extensively owing to their ability to generate metal complexes with unusual geometries and low co-ordination numbers.[2,3] Such complexes are potentially capable of binding small molecules, but this ability is a sensitive function of the nature of the substituents on the thiolate ligand. In the case of aromatic thiolates with phenyl or alkyl substituents in the 2,6 positions metal–carbon σ or π bonds can be formed. Thus 2,6-diphenylbenzenethiol forms η^6-arene complexes $[Mo(SC_6H_3Ph_2\text{-}2,6)(\eta^6\text{-}SC_6H_3Ph_2\text{-}2,6)(CO)]$[4] and $[RuCl_2(\eta^6\text{-}SC_6H_3Ph_2\text{-}2,6)(PPh_3)]$,[5] where η^6-$SC_6H_3Ph_2$-2,6 indicates the ligand is bound *via* sulfur and a η^6-bonding interaction with a phenyl substituent. However the same thiol reacts with $RhCl_3$ to form the complex $[Rh_2(\mu\text{-}SC_6H_3Ph\text{-}2\text{-}C_6H_4\text{-}6)_2(SC_6H_3Ph_2\text{-}2,6)_2(MeCN)_2]$[4] where μ-SC_6H_3Ph-2-C_6H_4-6 denotes a ligand which bridges two Rh atoms and is bound *via* S and a σ bond to a phenyl substituent. A variant of this type of chemistry is seen with 2,4,6-triisopropylbenzenethiol which reacts with $RhCl_3$ to give the dimeric complex $[Rh_2(\mu\text{-}SC_6H_2Pr^i_2\text{-}2,4\text{-}CMe{=}CH_2\text{-}6)_2(SC_6H_2Pr^i_3\text{-}2,4,6)_2(MeCN)]$, where μ-$SC_6H_2Pr^i_2$-2,4-CMe=CH_2-6 is a bridging ligand bound *via* S and a prop-1-ene group formed by dehydrogenation of a Pr^i substituent.[6] In the case of $[Ru(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ an agostic interaction between a methine hydrogen and the Ru occurs, conferring an overall trigonal-bipyramidal structure.[7] There are few examples of rhenium hydrido-complexes with sulfur ligands, and $[ReH_4(NC_9H_6SH\text{-}8)(PPh_3)_4]$ (NC_9H_6SH-8 = 8-sulfanylquinoline),[8] $[ReH(NC_5H_4SH\text{-}2)_2(PPh_3)_2]$ (NC_5H_4SH-2 = 2-sulfanylpyridine),[9] $[ReCl(H)(S_2CNR_2)(PMe_2Ph)_3]$ and $[ReH(S_2CNR_2)_2(PMe_2Ph)_2]$ (R = Me or Et)[10] have been reported.



As part of a systematic study of the reactions of bulky aromatic thiolates with rhenium polyhydrides we report here the reactions of 2,6-dimethylbenzenethiol with $[ReH_7(PPh_3)_2]$[11] to give a further example of a complex with an agostic M ··· H interaction. We also report the reactions of the hydrides $[ReH_7(PPh_3)_2]$ and $[ReH_5(PPh_3)_3]$ with 2,4,6-triisopropylbenzenethiol, 2,6-dimethoxybenzenethiol and tris(2-sulfanylphenyl)phosphine. With $HSC_6H_2Pr^i_3$-2,4,6 the dinitrogen complex $[ReSC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ is formed, and we now give full details of its synthesis, reactions and structure.[12a] The preparations and structures of $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$, $[Re\{SC_6H_3(OMe)_2\text{-}2,6\}_3(PPh_3)]$ and $[Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)]$ are also discussed. A summary of the reactions involved appears in Scheme 1.

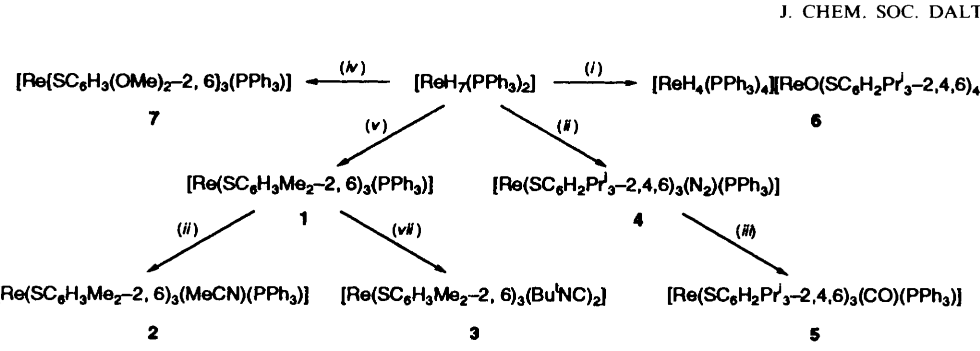
Results and Discussion

Reactions of $[ReH_7(PPh_3)_2]$ *with* $HSC_6H_3Me_2$-2,6.—The hydride complex $[ReH_7(PPh_3)_2]$ reacted with 3 equivalents of $HSC_6H_3Me_2$-2,6 in toluene at room temperature over 48 h to give a deep purple solution. Removal of the solvent gave a dark

---

† The Reactions of Rhenium Hydrido-complexes with Thiolate Ligands. Part 2.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 (*i*) $HSC_6H_2Pr^i{}_3$-2,4,6, O_2; (*ii*) $HSC_6H_2Pr^i{}_3$-2,4,6, N_2; (*iii*) CO; (*iv*) $HSC_6H_3(OMe)_2$-2,6; (*v*) $HSC_6H_3Me_2$-2,6; (*vi*) MeCN; (*vii*) Bu^tNC

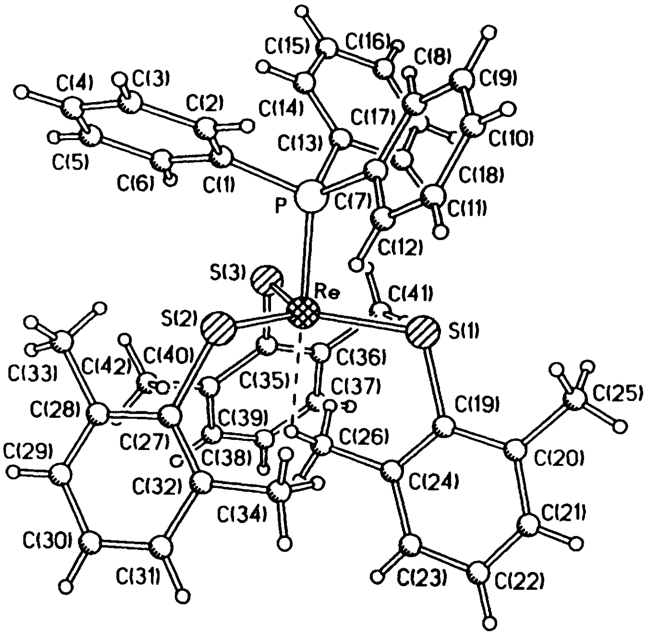


Fig. 1 Graphical representation of the structure of $[Re(SC_6H_3Me_2$-$2,6)_3(PPh_3)]$ **1**[12b]

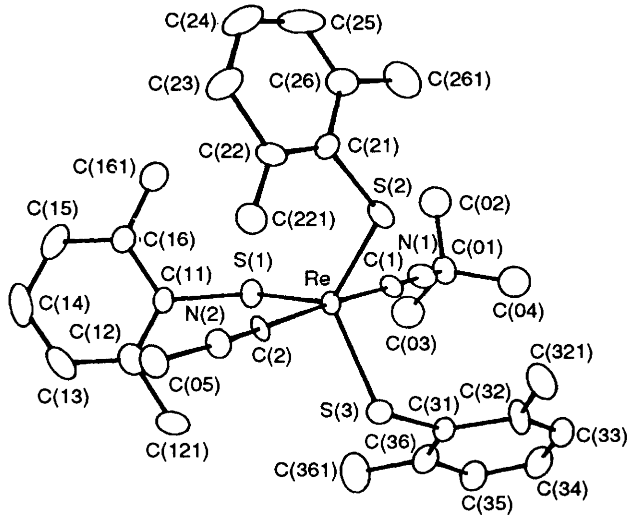


Fig. 2 An ORTEP representation of the structure of $[Re(SC_6H_3Me_2$-$2,6)_3(Bu^tNC)_2]$ **3** with some isocyanide methyl groups omitted for clarity and including an atom labelling scheme

residue which was freed from purple $[Re(SC_6H_3Me_2$-$2,6)_3(PPh_2H)(PPh_3)]$[1] by washing with hexane to give a dark green precipitate. The reaction mixture is intensely air sensitive and introduction of any oxygen leads to $[ReO(SC_6H_3Me_2$-$2,6)_3(PPh_3)]$[1] as the only isolable product. Elemental analysis of the green product after recrystallisation from toluene–hexane suggested the stoichiometry $[Re(SC_6H_3Me_2$-$2,6)_3(PPh_3)]$.

The IR spectrum showed no bands ascribable to ν(Re–H) in the 1900–2100 cm^{-1} region and a complex pattern of peaks due to the thiolate and PPh_3. The ^{31}P NMR spectrum showed the expected singlet at δ 20.1 for the single phosphorus ligand. The ^1H NMR spectrum showed three singlets due to the thiolate methyls at δ 1.59 (3 H), 1.82 (12 H) and 1.94 (3 H). This suggested that one of the thiolate groups was structurally different from the other two with distinct environments for its two methyl groups. The nature of the inequivalence could not be established from the spectroscopic data, and a structure determination was undertaken on crystals obtained from toluene–hexane.

Crystal Structure of $[Re(SC_6H_3Me_2$-$2,6)_3(PPh_3)]$ **1**.—A graphical representation of the structure appears in Fig. 1 together with a partial atom labelling scheme. Full details will appear elsewhere,[12b] and we restrict ourselves to a brief description of the salient features. The overall geometry about the Re is trigonal bipyramidal with the three thiolate sulfurs occupying the equatorial sites and one axial site occupied by a triphenylphosphine. It is clear that H(26b) approaches closely to Re (Re···H 2.07 Å), within the range normally found for metal–hydrogen agostic interactions. As a result of the formation of the chelate ring the Re–S(1) bond lies in approximately the same plane as that of the thiolate aryl group, while the remaining Re–S bonds adopt the more usual conformation perpendicular to the corresponding phenyl rings. The two singlets integrating as three hydrogens in the ^1H NMR spectrum can then be assigned to the methyls of the thiolate involved in the agostic interaction. The peak to highest field at δ 1.59 is ascribed to the agostic hydrogen, and its appearance as a singlet indicates that some fluxionality must be present to render all three hydrogens equivalent. The three S–Re–S angles in the equatorial plane add up to 359.9° indicating that the Re atom is precisely located in the plane of the three S atoms. The comparative bulk of the PPh_3 ligand causes all three thiolate aryl groups to be disposed to one side of the equatorial plane in the so-called 'three up' configuration.

The formation of the agostic bond in complex **1** is in marked contrast to the behaviour with 2,4,6-triisopropylbenzenethiol which reacts with the hydride precursor under similar conditions to give $[Re(SC_6H_2Pr^i{}_3$-$2,4,6)_3(N_2)(PPh_3)]$ **4**, rather than a species with the agostic interaction (see below).

Reactions of $[Re(SC_6H_3Me_2$-$2,6)_3(PPh_3)]$.—(*a*) *With methyl cyanide*. Complex **1** reacts rapidly with MeCN at room temperature to give the known complex $[Re(SC_6H_3Me_2$-$2,6)_3(MeCN)(PPh_3)]$ **2** in near-quantitative yield. This was identified by comparison with an authentic sample prepared from $[ReCl_3(MeCN)(PPh_3)_2]$.[13]

(*b*) *With* tert-*butyl isocyanide*. There is a similarly rapid reaction with Bu^tNC, but here the stronger π-acceptor isocyanide ligand also replaces the PPh_3 to give $[Re(SC_6H_3Me_2$-$2,6)_3(Bu^tNC)_2]$ **3**. The complex was isolated as

Table 1 Summary of experimental data for crystal structure determinations

	3	**4**	**6**
Formula	$C_{34}H_{45}N_2ReS_3$	$C_{63}H_{84}N_2PReS_3 \cdot 0.5C_7H_8$	$C_{72}H_{64}P_4Re,C_{60}H_{92}OReS_4 \cdot C_4H_8O$
M	764.1	1228.8	2455.3
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/n$
a/Å	10.624(2)	17.642(3)	23.172(7)
b/Å	15.842(3)	21.545(3)	23.051(7)
c/Å	10.823(2)	18.402(2)	23.410(5)
α/°		76.783(10)	
β/°	106.798(8)	94.073(10)	90.86(2)
γ/°		108.979(12)	
U/Å^3	1743.8(9)	6439.2(16)	12 503(6)
D_c/g cm^{-3}	1.455	1.267	1.304
Z	2	4	4
μ(Mo-Kα)/cm^{-1}	37.3	20.7	
F(000)	772	2556	4424 (H excluded)
Crystal dimensions/mm	0.30 × 0.40 × 0.10	0.45 × 0.45 × 0.50	0.25 × 0.25 × 0.25
T/°C	18	20	23
Scan range/°	$1.5 < \theta < 25°$	$\theta < 20$	$\theta < 20$
Reflections collected	3625	11 980	12 486
Observed reflections	3078 ($I > 3\sigma_I$)	9303 ($I > 2\sigma_I$)	7443 ($I > 3\sigma_I$)
R	0.044	0.055	0.068
R'	0.047	0.058	0.076
No. reflections used	3078	10 861	7443

Table 2 Fractional atomic coordinates for $[Re(SC_6H_3Me_2\text{-}2,6)_3(Bu^tNC)_2]$ **3**

Atom	x	y	z	Atom	x	y	z
Re	0.796 18(2)	0.396	0.484 40(3)	C(15)	0.310(1)	0.240(1)	0.335(2)
S(1)	0.677 3(2)	0.297 7(2)	0.541 1(3)	C(16)	0.439(1)	0.245 7(9)	0.373(1)
S(2)	0.878 6(2)	0.389 5(4)	0.314 8(2)	C(21)	0.784(1)	0.351 5(8)	0.170 5(9)
S(3)	0.851 7(3)	0.518 6(2)	0.609 0(3)	C(22)	0.667 3(9)	0.395(2)	0.094 3(9)
N(1)	1.032(1)	0.286 9(9)	0.655(1)	C(23)	0.598(2)	0.346(1)	−0.022(1)
N(2)	0.549 4(9)	0.505 1(8)	0.330(1)	C(24)	0.649(3)	0.274(1)	−0.058(2)
C(1)	0.945 3(9)	0.332 6(8)	0.587(1)	C(25)	0.768(2)	0.237(1)	0.022(2)
C(01)	1.108(1)	0.236(2)	0.736(1)	C(26)	0.836(1)	0.276 3(9)	0.133(1)
C(2)	0.635 8(6)	0.469 7(6)	0.380 5(9)	C(31)	0.994 1(9)	0.502 5(7)	0.744(1)
C(02)	1.117(3)	0.149(2)	0.664(3)	C(32)	1.128 9(9)	0.524(1)	0.736(1)
C(03)	1.050(3)	0.216(2)	0.855(3)	C(33)	1.231(1)	0.517(1)	0.835(2)
C(04)	1.249(3)	0.265(2)	0.788(3)	C(34)	1.217(2)	0.490(1)	0.957(2)
C(05)	0.426(1)	0.549 0(8)	0.257(1)	C(35)	1.093(1)	0.473(1)	0.969(1)
C(06)	0.340(2)	0.481(1)	0.168(2)	C(36)	0.980(1)	0.478(1)	0.860(1)
C(07)	0.467(2)	0.621(2)	0.179(2)	C(121)	0.490(2)	0.420(1)	0.629(1)
C(08)	0.361(2)	0.588(1)	0.347(2)	C(161)	0.515(2)	0.176(1)	0.333(2)
C(11)	0.501 6(9)	0.305 7(7)	0.476(1)	C(221)	0.612(1)	0.467(1)	0.125(2)
C(12)	0.428(1)	0.359(1)	0.522(1)	C(261)	0.968(2)	0.240(1)	0.215(3)
C(13)	0.293(1)	0.359(1)	0.475(2)	C(321)	1.138(1)	0.553(1)	0.604(1)
C(14)	0.231(1)	0.303(2)	0.379(3)	C(361)	0.850(2)	0.454(2)	0.879(2)

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Re–S(1)	2.204(3)	Re–S(2)	2.253(2)
Re–S(3)	2.336(3)	Re–C(1)	1.93(1)
Re–C(2)	2.101(8)	N(1)–C(1)	1.24(2)
N(1)–C(01)	1.29(4)	N(2)–C(2)	1.08(2)
N(2)–C(05)	1.49(1)		
S(1)–Re–S(2)	125.6(3)	S(1)–Re–S(3)	119.8(1)
S(1)–Re–C(1)	84.9(4)	S(1)–Re–C(2)	95.7(3)
S(2)–Re–S(3)	114.6(3)	S(2)–Re–C(1)	89.8(4)
S(2)–Re–C(2)	92.1(3)	S(3)–Re–C(1)	94.2(4)
S(3)–Re–C(2)	83.1(3)	C(1)–Re–C(2)	177.2(5)
Re–S(1)–C(11)	117.0(4)	Re–S(2)–C(21)	120.0(4)
Re–S(3)–C(31)	111.4(4)	Re–C(1)–N(1)	174(1)
Re–C(2)–N(2)	176(1)	C(1)–N(1)–C(01)	171(2)
C(2)–N(2)–C(05)	176(2)		

a dark green moderately air-stable solid with an elemental analysis consistent with the above formulation. Its IR spectrum shows two intense bands at 2060 and 2090 cm^{-1} due to ν(N≡C) together with a complex pattern of bands assignable to the thiolate groups. The methyl groups of the isocyanide ligands give rise to two singlets in the ^1H NMR spectrum with appropriate integration at δ 1.11 and 0.60. The apparent inequivalence of the isocyanide ligands was somewhat unexpected, and a structure determination was carried out on crystals obtained from toluene–hexane.

Crystal Structure of $[Re(SC_6H_3Me_2\text{-}2,6)_3(Bu^tNC)_2]$ **3**.—An ORTEP[14] representation of the structure is shown in Fig. 2, together with a partial atom labelling scheme. Details of the structure determination appear in Table 1, atomic coordinates in Table 2 and selected bond lengths and angles in Table 3. The overall geometry about the Re is trigonal bipyramidal with equatorial thiolate and axial isocyanide ligands. The configuration of the thiolate aryl groups is unusual as it is neither 'two up, one down' nor 'three up' as have been found for other five-co-ordinate complexes of sterically hindered aromatic thiols. One[13,15] thiolate ligand [S(1)–C(11)] lies with its phenyl ring directed above the equatorial plane and another [S(3)–C(31)] has the phenyl ring below the plane. The third [S(2)–C(21)] is rotated about the Re–S bond so that the C–S bond is inclined towards the equatorial plane. This has the effect of placing the C(21) aryl ring almost at right angles to the plane of the three equatorial sulfurs and the Re atom. As a result of this unusual orientation the S(1)–Re–S(2) angle of 125.6(3)° is larger than the two other S–Re–S angles (119.8 and 114.6°). Examination of torsion angles about the Re–S bonds shows that the S–C bonds of the 'up' and 'down' thiolates lie close to planes involving the isocyanide ligands *e.g.* [C(2)–Re–S(1)–C(11) 4.92(0.48) and C(1)–Re–S(3)–C(31) −2.99(0.50)°]. By contrast the C(2)–Re–S(2)–C(21) angle is −55.9° showing that the unique thiolate aryl ring is not symmetrically disposed with repect to the equatorial plane. It is this asymmetry which probably accounts for the inequivalence of the isocyanide ligands, as each experiences different steric constraints. It is reflected in the Re–C distances of 2.101(8) and 1.93(1) Å and the corresponding C–N distances of 1.08(2) and 1.24(2) Å, although both have essentially linear Re–C–N systems.

The unusual configuration of one of the thiolate ligands results in the absence of the mirror-plane symmetry found for the 'two up, one down' arrangement, and the complex is chiral. We have not however been able to determine the absolute configuration, possibly as the chiral centre is not close to the Re. The presence of the two relatively bulky isocyanide ligands is undoubtedly a dominant effect in determining the geometry of the molecule. The complex $[Re(SC_6H_2Me_3\text{-}2,4,6)_3(MeCN)_2]$[16] has the more usual 'two up, one down' disposition of the aryl groups with Re–S–C angles in the range 113.0(3)–114.6(3)°. Increasing the size of the axial ligands in $[Re(SC_6H_3Me_2\text{-}2,6)_3(PHPh_2)(PPh_3)]$[1] results in an increase in the Re–S–C angles to relieve the steric pressure. In the case of complex **3** the *tert*-butyl groups exert steric repulsions at a distance of two or more atoms from the metal, and the complex responds by reorientating one aryl group rather than expanding the Re–S–C angles.

Reactions of $[ReH_7(PPh_3)_2]$ *with* $HSC_6H_2Pr^i_3\text{-}2,4,6$.—The hydride $[ReH_7(PPh_3)_2]$ reacts with $HSC_6H_2Pr^i_3\text{-}2,4,6$ in toluene under a dinitrogen atmosphere at room temperature to give the extremely air- and moisture-sensitive green complex $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4**. This precipitated in high yield on the addition of dry methanol to the concentrated reaction solution. However controlled injection of air into the reaction solution led to isolation of $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ **6**. Analogously, the reaction between $[ReH_7(PPh_3)_2]$ and $HSC_6H_2Br\text{-}4\text{-}Pr^i_2\text{-}2,6$ gave $[Re(SC_6H_2Br\text{-}4\text{-}Pr^i_2\text{-}2,6)_3(N_2)(PPh_3)]$. Use of the pentahydride $[ReH_5(PPh_3)_3]$ as starting material also gives $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4**, but the yield is very low. After separation of **4** by filtration, complex **6** slowly precipitates from the filtrate. The same cationic tetrahydride complex can also be isolated in very low yield from the reaction of the heptahydride with the thiol. The higher proportion of triphenylphosphine in $[ReH_5(PPh_3)_3]$ favours the hydride product **6** rather than the dinitrogen complex. The previously unreported $[ReH_4(PPh_3)_4]^+$ cation was also conveniently prepared in high yield as the tetrafluoroborate salt $[ReH_4(PPh_3)_4]BF_4$ from the reaction of $[ReH_7(PPh_3)_2]$ with PPh_3 and $[PPh_3H][BF_4]$.

The ^1H NMR spectrum of $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4** in $CDCl_3$ indicated that the three thiolate ligands are equivalent. Two doublets centred at δ 0.97 and 1.15 were assigned to methyl groups of the 2,6- and 4-isopropyl groups respectively, and indicated high symmetry with the 2- and 6-isopropyl groups equivalent. Resonances due to the methine protons of the 2-isopropyl groups were located at δ 3.53 and for the 4-isopropyl at δ 2.85 as well defined septets. The thiolate aromatic protons appeared as a singlet at δ 6.88. The relative integral intensities for aliphatic methyl protons *vs.* aromatic protons were consistent with the proposed stoichiometry. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet resonance at δ 26.01 with respect to an H_3PO_4 reference. In the IR spectrum a strong band at 2130 cm^{-1} was assigned to $\nu(N\equiv N)$. This value is relatively high compared to the values in the range 1900–2050 cm^{-1} for most dinitrogen complexes. This is not surprising in view of the relatively high oxidation state of the metal $[Re^{III}]$ and suggests that the ligated N_2 is likely to be extremely substitution labile, and this is supported by the observed substitution chemistry. The $\nu(N\equiv N)$ for $[Re(SC_6H_2Br\text{-}4\text{-}Pr^i_2\text{-}2,6)_3(N_2)(PPh_3)]$ appeared at 2130 cm^{-1} in its IR spectrum, identical to the value found for the $SC_6H_2Pr^i_3\text{-}2,4,6$ complex. The ^1H NMR spectrum showed a complex series of peaks for the methyl and methine protons. However the relative integral intensities for aliphatic methyl *vs.* aromatic protons were consistent with the proposed stoichiometry. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at δ 24.3.

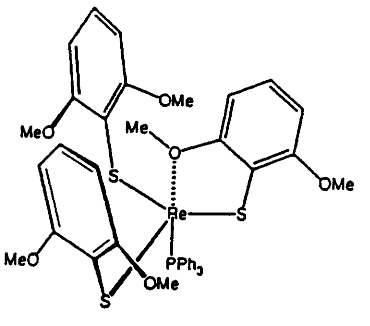
For the complex $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ **6** the four thiolate ligands in the anion are equivalent in solution. They gave rise to three septets [relative integrated ratios 1 : 1 : 1, δ 2.80, 3.40, 4.17; ^3J(H–H), 6.86 Hz] in the ^1H NMR spectrum arising from the methine protons. This suggests that the *o*-Pr^i groups of the ligands are not equivalent, one set being *syn* to the oxo group, the other *anti*. The methyl protons gave rise to a very complex series of peaks in the range δ 0.83–1.5, and detailed assignment is not possible. The cation $[ReH_4(PPh_3)_4]^+$ (in both **6** and the BF_4 salt) displayed a quintet centred at δ −2.60 due to the hydride protons. The splitting pattern is consistent with the presence of four equivalent phosphine ligands. The relative integration in the ^1H NMR spectrum of $[ReH_4(PPh_3)_4]BF_4$ indicated the presence of four hydride ligands ruling out structures such as $[ReH_2(PPh_3)_4]^+$. In the $^{31}P\text{-}\{^1H\}$ NMR spectra the four equivalent PPh_3 ligands appeared as a singlet at δ 21.6.

The IR spectrum of $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ **6** showed $\nu(Re{=}O)$ at 953 cm^{-1}, which is identical to $\nu(Re{=}O)$ for the known complex $[PPh_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$.[17] Both **6** and $[ReH_4(PPh_3)_4]BF_4$ showed the ν(Re–H) stretching frequency at 2020 cm^{-1} in their IR spectra; the latter also showed broad bands at 1050 and 1070 cm^{-1} due to ν(B–F).

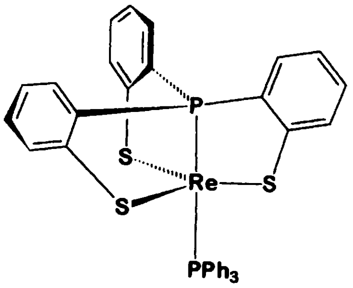
Reactivity of $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4**.—The co-ordinated dinitrogen in complex **4** was readily displaced by two-electron ligands such as CO and MeCN to give the known complexes $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)(PPh_3)]$, $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)_2]$ and $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(MeCN)(PPh_3)]$.[13] Bubbling NH_3(g) through a toluene solution of the complex produced a hygroscopic purple crystalline solid, the IR spectrum of which showed a strong sharp ν(N–H) band at 3320 cm^{-1} arising from ligated NH_3. The product is presumably $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(PPh_3)]$, but the elemental analyses were variable, possibly due to the loss of NH_3, and complete characterisation was not possible.

Reaction of $[ReOCl_3(PPh_3)_2]$ *with* $NaBH_4$ *and* $HSC_6H_2Pr^i_3\text{-}2,4,6$.—Although $[ReH_7(PPh_3)_2]$ is a good precursor for the preparation of complex **4** its preparation is difficult, and the former is not stable enough to be stored for a long period. We therefore investigated whether the dinitrogen complex could be prepared from $[ReOCl_3(PPh_3)_2]$ by direct reaction with thiol and tetrahydroborate in ethanol. When this reaction mixture was heated under reflux for 3–5 h a dark green precipitate formed on cooling.

The IR spectrum of the product showed two sharp bands at 2130 and 1935 cm^{-1}, the first being much more intense than the second. The band at 2130 cm^{-1} disappeared after exposure to air for 15 min and is assigned to $\nu(N{=}N)$; it is in an identical position to that found for $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4** above. The pattern of the IR spectrum is elsewhere generally quite similar to that of **4** except for the extra band at 1935 cm^{-1}. Under an argon atmosphere the reaction gave green crystals without the IR band at 2130 cm^{-1}, but that at 1935 cm^{-1} was retained. The ^{31}P NMR spectrum of the product in $[^2H_8]$-toluene showed a singlet at precisely the same position as that



A



B

for **4**. We conclude on the basis of the above spectra and elemental analyses that the product obtained under dinitrogen is essentially the dinitrogen complex with a small amount of contamination by a hydrido-complex by-product. We were unable to identify any peaks in the ^1H NMR spectrum due to the hydride impurity, possibly due to instability or concealment by peaks due to the thiol ligands.

Other reactions of $[ReH_7(PPh_3)_2]$.—*With* 2,6-*dimethoxybenzenethiol.* The heptahydride $[ReH_7(PPh_3)_2]$ reacted with $HSC_6H_3(OMe)_2$-2,6 in toluene at room temperature to give a purple-brown precipitate. This was recrystallised from dichloromethane–toluene to produce purple-brown crystals, which analysed as $[Re\{SC_6H_3(OMe)_2\text{-}2,6\}_3(PPh_3)]$ **7**. The proposed structure based on spectroscopic and elemental analyses is shown in **A**. The complex has a trigonal-bipyramidal geometry with one axial PPh_3 and three equatorial thiolate ligands bound to the metal *via* their sulfur atoms. One of the thiolates provides additional ligation to the Re *via* an oxygen atom of a methoxy group. In the ^1H NMR spectrum the MeO group protons appeared as singlets at δ 3.86, 3.70, 2.40 and 2.29 (integrated ratio 2 : 2 : 1 : 1) consistent with the proposed ligation of a methoxy oxygen. In the ^{31}P NMR spectrum the ligated PPh_3 generated a singlet at δ 19.35. The FAB mass spectrum showed the molecular ion at *m/z* 956, which exactly fits the formulation. The isotope distribution pattern for this ion was also consistent with the proposed formulation.

With $P(C_6H_4S\text{-}2)_3$. The reaction of $[ReH_7(PPh_3)_2]$ with tris(2-sulfanylphenyl)phosphine in toluene gave red-brown cube-like crystals. The complex was formulated as $[Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)]$ **8** based on spectroscopic data and elemental analysis. The proposed structure is shown in **B**. The Re has trigonal-bipyramidal co-ordination with axial P donors and the three thiolate sulfurs in the equatorial plane. The complex shows a pair of doublets in its ^{31}P NMR spectrum. One at δ 35.52 is assigned to triphenylphosphine, the other at δ 138.20 to the tris(2-sulfanylphenyl)phosphine. The coupling constant ^3J(P–P) 349.5 Hz is typical for *trans*-phosphine donors. Complex **8** is directly analogous to $[Tc\{P(C_6H_4S\text{-}2)_3\}(Pr^iNC)]$ which has been prepared from $[TcOCl_4]^-$,[18] the sulfanylphosphine and 1 equivalent of isocyanide in MeCN and characterised crystallographically.

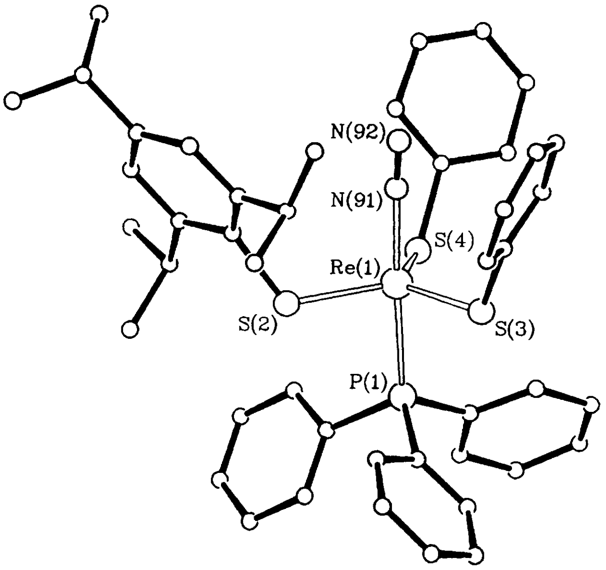


Fig. 3 An ORTEP representation of one of the two virtually identical molecules of $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4** with some isopropyl groups omitted for clarity and with a partial atom labelling scheme

Crystal Structures.—$[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]\cdot 0.5C_6H_5Me$ **4**. A single-crystal structure determination was carried out for complex **4** and a perspective view of one of the two very similar, independent molecules in the unit cell is presented in Fig. 3. Atomic coordinates are given in Table 4 and selected bond lengths and angles in Table 5. The overall geometry about the rhenium is trigonal bipyramidal with the dinitrogen and phosphine ligands occupying the axial sites and the thiolate sulfurs in the equatorial plane. The Re atoms in the two molecules are displaced by 0.12 and 0.17 Å from the equatorial planes towards the dinitrogen ligands. The molecules have a 'three up' configuration. All the aromatic groups are disposed to the same side of the equatorial plane towards the N_2, presumably owing to the steric effect exerted by the triphenylphosphine ligand. The thiolate phenyl groups thus comprise an umbrella-like structure providing a cavity for the dinitrogen ligand, and this may contribute to the relative stability of the fourteen-electron complex. The Re–N bond distances of 1.994(10) and 2.004(12) Å are shorter than single-bond distance of 2.16(2) Å in $[ReCl_2(NH_3)(NNCOPh)(PPh_3)_2]$,[19] but not as short as the formal double-bond distance of 1.837(5) Å in the $NNPh_2$ ligand in $[ReCl_2N(NNPh_2)(PPh_3)]$.[19] The Re–N (N_2) distances are therefore indicative of some multiple bonding between the nitrogen and the metal. In general the N–N distances observed for terminal dinitrogen ligands vary only slightly and are often, within experimental error, the same as that of free dinitrogen (1.0976 Å). The N–N distances for complex **4** are similar to those encountered in other terminal dinitrogen complexes.

A disordered toluene solvate molecule was located with one major, resolved orientation and one minor, less resolved, overlapping arrangement.

$[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)(PPh_3)]$ **5**. The crystal structure of the carbonyl complex revealed that it was essentially as expected isostructural with the dinitrogen complex. Full details will be published elsewhere.[12]

$[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]\cdot$thf **6**. A dark orange crystal of $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ **6** suitable for an X-ray study was obtained from tetrahydrofuran (thf)–MeOH. The structure was found to comprise well separated cations and anions. An ORTEP diagram

Table 4 Fractional atomic coordinates ($\times 10^4$) for $[\mathrm{Re(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(N_2)(PPh_3)]\cdot 0.5C_6H_5Me}$ **4**

Atom	*x*	*y*	*z*
Re(1)	1235.8(2)	202.0(2)	2427.1(2)
P(1)	425(1)	907(1)	2089(1)
C(11a)	−672(5)	500(4)	2114(5)
C(12a)	−1016(6)	−10(5)	2704(6)
C(13a)	−1847(7)	−302(6)	2767(7)
C(14a)	−2303(7)	−85(6)	2228(6)
C(15a)	−1985(7)	420(6)	1632(6)
C(16a)	−1161(6)	722(5)	1575(6)
C(11b)	609(5)	1422(4)	1138(5)
C(12b)	756(6)	2097(6)	991(6)
C(13b)	899(8)	2463(7)	235(7)
C(14b)	865(7)	2134(6)	−327(7)
C(15b)	715(6)	1479(6)	−180(6)
C(16b)	590(6)	1131(5)	568(5)
C(11c)	548(5)	1508(5)	2659(5)
C(12c)	1312(6)	1881(5)	2836(5)
C(13c)	1421(7)	2384(6)	3246(6)
C(14c)	768(7)	2495(6)	3481(6)
C(15c)	−5(8)	2150(6)	3288(6)
C(16c)	−112(7)	1647(5)	2869(6)
S(2)	370(1)	−516(1)	1806(1)
C(21)	410(5)	−1365(4)	1968(5)
C(22)	1021(6)	−1511(5)	1684(5)
C(23)	953(6)	−2188(5)	1804(6)
C(24)	312(7)	−2696(5)	2162(6)
C(25)	−284(6)	−2550(5)	2426(6)
C(26)	−255(6)	−1865(5)	2343(5)
C(221)	1694(6)	−1011(5)	1200(6)
C(222)	1431(8)	−931(7)	383(6)
C(223)	2494(7)	−1134(7)	1306(9)
C(241)	264(8)	−3454(7)	2257(8)
C(242)	448(11)	−3707(8)	3072(10)
C(243)	−446(9)	−3845(6)	1911(10)
C(261)	−954(6)	−1714(5)	2617(6)
C(262)	−1443(7)	−2266(7)	3285(7)
C(263)	−1567(6)	−1621(7)	1980(6)
S(3)	2231(1)	1072(1)	1798(1)
C(31)	3138(5)	892(4)	1710(5)
C(32)	3347(6)	863(5)	998(5)
C(33)	4057(6)	714(5)	932(6)
C(34)	4532(7)	607(5)	1529(6)
C(35)	4338(6)	671(5)	2219(6)
C(36)	3649(6)	835(5)	2319(5)
C(321)	2859(6)	1006(5)	306(6)
C(322)	3007(7)	1778(5)	52(6)
C(323)	3033(8)	738(6)	−363(6)
C(341)	5310(9)	416(7)	1470(8)
C(342)	5058(10)	−311(9)	1371(11)
C(343)	5875(10)	958(10)	884(12)
C(361)	3506(7)	971(5)	3063(6)
C(362)	3701(8)	1749(7)	2956(8)
C(363)	3925(7)	657(7)	3742(6)
S(4)	950(2)	122(1)	3620(1)
C(41)	1552(6)	−229(5)	4331(5)
C(42)	2025(6)	215(5)	4757(6)
C(43)	2482(7)	−61(6)	5348(6)
C(44)	2475(7)	−700(6)	5460(6)
C(45)	2016(6)	−1127(6)	5051(6)
C(46)	1524(6)	−907(5)	4470(6)
C(421)	2016(7)	937(6)	4668(7)
C(422)	2756(8)	1431(7)	4952(7)
C(423)	1227(8)	975(8)	5004(7)
C(441)	2984(8)	−958(7)	6108(7)
C(442)	3785(9)	−519(10)	6176(11)
C(443)	2478(9)	−1350(9)	6807(7)
C(461)	940(7)	−1423(6)	4112(7)
C(462)	196(8)	−1765(9)	4648(8)
C(463)	1283(9)	−1959(6)	3921(7)
N(91)	1966(6)	−358(5)	2715(6)
N(92)	2363(9)	−611(7)	2846(7)
Re(2)	3539.2(2)	5310.5(2)	2472.3(2)
P(5)	4470(2)	4699(1)	2506(1)
C(51a)	4488(5)	4108(5)	3375(5)
C(52a)	4409(6)	4264(5)	4041(6)
C(53a)	4438(7)	3835(6)	4733(7)
C(54a)	4537(7)	3211(6)	4726(7)
C(55a)	4633(7)	3053(7)	4088(7)
C(56a)	4602(7)	3512(6)	3388(7)
C(51b)	5519(6)	5224(5)	2346(5)
C(52b)	5703(7)	5785(5)	1793(6)
C(53b)	6516(7)	6205(6)	1650(7)
C(54b)	7109(8)	6042(7)	2069(7)
C(55b)	6925(8)	5498(7)	2618(7)
C(56b)	6116(7)	5064(6)	2772(7)
C(51c)	4267(6)	4196(5)	1804(5)
C(52c)	4813(9)	4338(7)	1246(8)
C(53c)	4619(11)	3911(9)	697(10)
C(54c)	3893(9)	3446(8)	739(9)
C(55c)	3345(8)	3334(6)	1256(7)
C(56c)	3541(7)	3725(6)	1783(6)
S(6)	3663(2)	5530(1)	1219(1)
C(61)	3063(5)	5991(5)	672(5)
C(62)	3194(6)	6660(5)	669(5)
C(63)	2715(7)	6990(6)	234(6)
C(64)	2141(8)	6671(7)	−205(7)
C(65)	2061(7)	6008(6)	−232(7)
C(66)	2508(6)	5666(5)	182(6)
C(621)	3878(6)	7071(5)	1103(6)
C(622)	4658(7)	7341(7)	614(7)
C(623)	3708(8)	7639(6)	1394(7)
C(641)	1562(13)	7058(11)	−691(12)
C(642)	1771(18)	7246(17)	−1453(14)
C(643)	880(16)	6985(16)	−305(14)
C(661)	2428(7)	4967(6)	98(7)
C(662)	1612(8)	4627(6)	−280(7)
C(663)	3136(8)	4967(7)	−344(7)
S(7)	2682(2)	4332(1)	3077(1)
C(71)	1717(6)	4309(5)	3354(5)
C(72)	1554(6)	4127(5)	4133(5)
C(73)	767(6)	4034(5)	4341(6)
C(74)	184(7)	4109(6)	3844(6)
C(75)	358(7)	4271(5)	3103(6)
C(76)	1126(6)	4378(5)	2841(5)
C(721)	2161(7)	3990(6)	4727(6)
C(722)	2255(7)	3285(6)	4771(6)
C(723)	1985(8)	4068(6)	5516(6)
C(741)	−703(9)	3964(8)	4110(8)
C(742)	−1218(9)	3292(8)	4034(11)
C(743)	−955(11)	4511(9)	3931(15)
C(761)	1226(6)	4501(5)	2012(5)
C(762)	766(7)	4943(6)	1542(7)
C(763)	1026(8)	3830(6)	1774(6)
S(8)	4458(1)	5934(1)	3155(1)
C(81)	4324(6)	6672(5)	3360(5)
C(82)	4933(6)	7288(5)	3099(5)
C(83)	4893(6)	7854(5)	3314(6)
C(84)	4282(7)	7841(6)	3735(6)
C(85)	3707(7)	7243(6)	3988(6)
C(86)	3705(6)	6634(5)	3808(5)
C(821)	5650(6)	7331(5)	2663(6)
C(822)	6292(6)	7103(6)	3195(6)
C(823)	6052(7)	8045(6)	2165(7)
C(841)[a]	4239(12)	8483(7)	3974(10)
C(842)[b]	4765(27)	8585(16)	4657(19)
C(843)[b]	3522(28)	8520(23)	4098(26)
C(844)[b]	3677(32)	8736(26)	3475(29)
C(845)[c]	4234(33)	8973(26)	3357(28)
C(846)[c]	4286(64)	8481(47)	4724(55)
C(847)[c]	5177(38)	8709(32)	4488(37)
C(848)[c]	4896(48)	8935(37)	4152(43)
C(861)	3099(6)	5959(6)	4209(6)
C(862)	3416(8)	5721(7)	4999(7)
C(863)	2249(7)	6005(7)	4249(8)
N(93)	2770(5)	5822(4)	2426(4)
N(94)	2341(6)	6107(5)	2382(5)

Table 4 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Toluene molecule, disordered							
C(101)[d]	6118(12)	2794(10)	2138(11)	C(107)	5640(13)	2472(11)	1560(12)
C(102)	6589(14)	3456(11)	1948(13)	C(112)[e]	5984(34)	2221(25)	2235(17)
C(103)[d]	7034(16)	3822(13)	2445(14)	C(114)[e]	6050(29)	3161(15)	1432(23)
C(104)[d]	6922(14)	3581(12)	3195(13)	C(116)[e]	6510(36)	3159(16)	2709(18)
C(105)[d]	6489(14)	2908(11)	3406(12)	C(117)[e]	6302(33)	2329(31)	3695(19)
C(106)	6081(11)	2466(10)	2892(11)				

Site occupancy factors: [a] 0.5; [b] 0.3; [c] 0.2; [d] 0.74; [e] 0.26.

Table 5 Selected bond lengths (Å) and angles (°) for complex **4**

Molecule 1		Molecule 2	
Re(1)–P(1)	2.366(3)	Re(2)–P(5)	2.406(3)
Re(1)–S(2)	2.250(2)	Re(2)–S(6)	2.257(2)
Re(1)–S(3)	2.257(3)	Re(2)–S(7)	2.249(2)
Re(1)–S(4)	2.242(3)	Re(2)–S(8)	2.254(2)
Re(1)–N(91)	2.004(12)	Re(2)–N(93)	1.994(10)
N(91)–N(94)	1.007(21)	N(93)–N(94)	1.108(16)
P(1)–Re(1)–S(2)	87.6(1)	P(5)–Re(2)–S(6)	85.7(1)
P(1)–Re(1)–S(3)	86.2(1)	P(5)–Re(2)–S(7)	86.3(1)
S(2)–Re(1)–S(3)	119.6(1)	S(6)–Re(2)–S(7)	120.0(1)
P(1)–Re(1)–S(4)	87.3(1)	P(5)–Re(2)–S(8)	85.4(1)
S(2)–Re(1)–S(4)	117.7(1)	S(6)–Re(2)–S(8)	120.5(1)
S(3)–Re(1)–S(4)	121.9(1)	S(7)–Re(2)–S(8)	117.9(1)
P(1)–Re(1)–N(91)	177.4(3)	P(5)–Re(2)–N(93)	179.0(2)
S(2)–Re(1)–N(91)	94.7(3)	S(6)–Re(2)–N(93)	93.3(2)
S(3)–Re(1)–N(91)	91.6(3)	S(7)–Re(2)–N(93)	94.3(2)
S(4)–Re(1)–N(91)	92.7(3)	S(8)–Re(2)–N(93)	95.0(2)
Re(1)–S(2)–C(21)	118.1(3)	Re(2)–S(6)–C(61)	117.4(4)
Re(1)–S(3)–C(31)	114.9(3)	Re(2)–S(7)–C(71)	119.5(3)
Re(1)–S(4)–C(41)	117.1(4)	Re(2)–S(8)–C(81)	120.1(3)

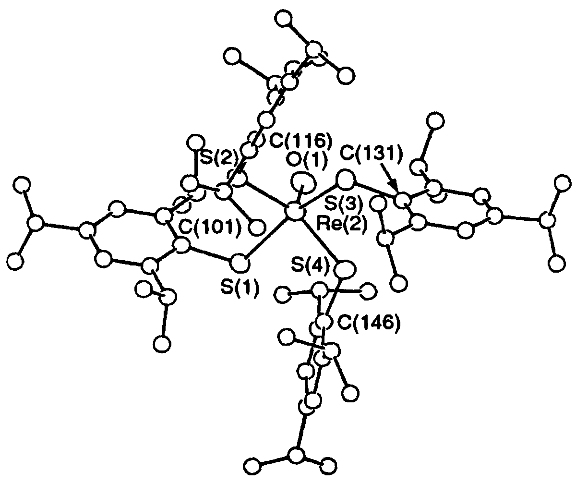


Fig. 4 An ORTEP representation of the structure of the anion $[ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]^-$ of complex **6** with a partial atom labelling scheme

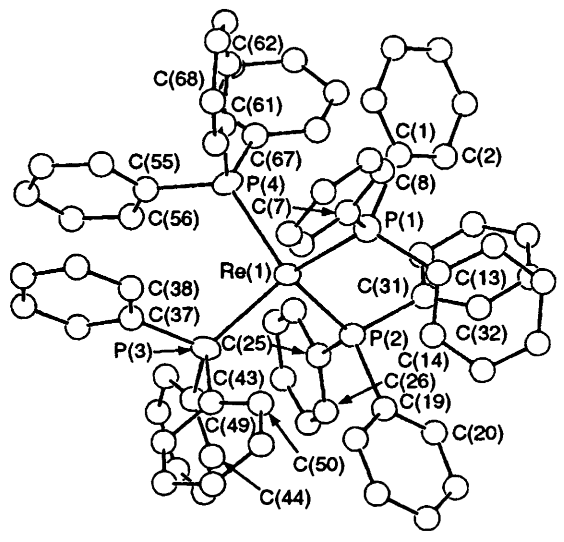


Fig. 5 An ORTEP representation of the structure of the cation $[ReH_4(PPh_3)_4]^+$ of complex **6** with a partial atom labelling scheme

of the anion $[ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]^-$ is shown in Fig. 4. The atomic coordinates are given in Table 6, selected bond distances and angles for both the cation and anion in Table 7. The structure of the anion was found to be square pyramidal with an apical oxo group, and the four thiolate ligands lying in the basal plane. A comparison of related structures given in Table 8 indicates that *ortho* substituents have little influence on the main features of the structure. The most obvious effect of the steric bulk of the thiolate ligands is on the alignment of the arene rings. In $[ReO(SPh)_4]^-$ the normals to the planes of the arene rings make varying angles with the Re–O vector (67–108°),[22] whereas in $[ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]^-$ all the normals are close to orthogonal to the Re–O vector.

The ORTEP diagram of the cation is shown in Fig. 5. Since the hydride hydrogens in the cation could not be detected from the X-ray diffraction data, the following discussion will focus on the non-hydrogen-atom geometry about the cation. The cation has an ReP_4 geometry which is intermediate between tetrahedral and planar. This geometry has been termed 'flattened tetrahedral'.[23] The close approach to T_4 symmetry is, however, consistent with an $[ReH_4(PPh_3)_4]^+$ formulation with dodecahedral co-ordination geometry. The structure of $[ReH_4(PPh_3)_4]^+$ is very similar to that of dodecahedral $[MoH_4(PMePh_2)_4]$[24] and $[ReH_4(PMe_2Ph)_4]^+$.[18] A comparison of such hydrides with 'MP_4' tetrahedral geometries in Table 9 indicates that the extent of 'flatness' increases as the bulk of the phosphine ligands reduces from PPh_3 through $PMePh_2$ to PMe_2Ph. A thf solvate molecule was identified in the lattice.

Redox Behaviour of some Trigonal-bipyramidal Rhenium(III) *Thiolate Complexes containing the* 'ReS_3' *Core.*—The electrochemical behaviour of $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ **4** was studied in toluene saturated with $[NBu^n_4][BF_4]$.[21] The only redox behaviour seen for this complex was a one-electron irreversible oxidation at $E_p = +0.27$ V (see Table 10). The irreversible nature of the oxidation process is apparent from the absence of a backward peak in the cyclic voltammogram. This is in contrast to the behaviour of $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)(PPh_3)]$ **5** which displays a one-electron reversible oxidation at $E_{\frac{1}{2}}$ +0.78 V at a scan rate of 0.2 V s^{-1}. The reversibility of this process and the others discussed below was confirmed by E_{pa} and E_{pc} peak separations in the range 65–85

Table 6 Fractional atomic coordinates for $[ReH_4(PPh_3)_4][ReO(SC_6H_2Pr^i{}_3\text{-}2,4,6)_4]\cdot$thf **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	0.287 74(4)	0.184 42(3)	0.172 42(3)	C(203)	0.204 2(3)	0.052 9(2)	0.601 9(3)
Re(2)	0.791 75(4)	0.086 51(4)	0.154 15(3)	C(204)	0.250 3(4)	0.027 6(4)	0.579 5(3)
S(1)	0.798 7(2)	0.151 8(2)	0.077 6(2)	C(1)	0.176 1(5)	0.163 9(5)	0.280 6(6)
S(2)	0.886 6(2)	0.114 9(2)	0.175 1(2)	C(2)	0.123 0(6)	0.156 5(5)	0.252 7(5)
S(3)	0.781 6(2)	0.067 2(2)	0.251 7(2)	C(3)	0.086 2(4)	0.111 9(6)	0.269 4(5)
S(4)	0.695 9(2)	0.116 2(2)	0.158 9(2)	C(4)	0.102 4(5)	0.074 8(5)	0.313 8(6)
P(1)	0.226 8(2)	0.218 0(2)	0.251 1(2)	C(5)	0.155 6(6)	0.082 3(5)	0.341 7(5)
P(2)	0.221 7(2)	0.210 9(2)	0.092 8(2)	C(6)	0.192 4(4)	0.126 8(6)	0.325 0(5)
P(3)	0.378 3(2)	0.214 9(2)	0.130 6(2)	C(7)	0.265 9(6)	0.247 2(6)	0.315 5(5)
P(4)	0.315 1(2)	0.090 5(2)	0.213 7(2)	C(8)	0.236 8(4)	0.250 3(6)	0.367 2(6)
O(1)	0.793 7(5)	0.019 8(5)	0.122 4(5)	C(9)	0.264 0(6)	0.274 4(6)	0.415 2(4)
O(2)	0.251 9(3)	0.035 8(5)	0.526 9(4)	C(10)	0.320 2(6)	0.295 5(6)	0.411 5(5)
C(101)	0.869 7(8)	0.166 0(8)	0.052 9(7)	C(11)	0.349 3(4)	0.292 4(6)	0.359 8(6)
C(102)	0.901 0(8)	0.123 8(8)	0.021 9(7)	C(12)	0.322 2(6)	0.268 3(6)	0.311 9(4)
C(103)	0.951 1(8)	0.138 5(8)	−0.007 7(8)	C(13)	0.179 1(6)	0.282 8(5)	0.240 6(6)
C(104)	0.970 6(9)	0.196 2(9)	−0.006 5(8)	C(14)	0.197 4(5)	0.324 9(6)	0.202 1(5)
C(105)	0.941(1)	0.239(1)	0.025 2(9)	C(15)	0.164 8(6)	0.375 1(5)	0.193 6(5)
C(106)	0.890 9(8)	0.223 7(8)	0.054 8(8)	C(16)	0.113 9(6)	0.383 2(5)	0.223 6(6)
C(107)	0.879 5(9)	0.059 8(9)	0.017 3(8)	C(17)	0.095 5(5)	0.341 1(6)	0.262 1(5)
C(108)	0.923(1)	0.018(1)	0.046 2(9)	C(18)	0.128 1(6)	0.290 9(5)	0.270 6(5)
C(109)	0.870(1)	0.044(1)	−0.046 9(9)	C(19)	0.216 4(6)	0.285 6(4)	0.064 5(5)
C(110)	1.027(1)	0.216(1)	−0.037(1)	C(20)	0.168 5(5)	0.304 3(5)	0.032 8(5)
C(111)	1.064(1)	0.167(1)	−0.057(1)	C(21)	0.166 8(5)	0.360 7(6)	0.011 1(5)
C(112)	1.012(2)	0.251(2)	−0.084(2)	C(22)	0.213 0(6)	0.398 3(4)	0.021 2(5)
C(113)	0.859(1)	0.271(1)	0.089 7(8)	C(23)	0.260 9(5)	0.379 5(6)	0.053 0(5)
C(114)	0.822(1)	0.306(1)	0.048(1)	C(24)	0.262 6(5)	0.323 2(6)	0.074 6(5)
C(115)	0.901(1)	0.308(1)	0.124(1)	C(25)	0.233 2(6)	0.168 7(5)	0.026 1(4)
C(116)	0.910 3(8)	0.098 7(8)	0.246 8(7)	C(26)	0.230 8(6)	0.196 2(4)	−0.027 0(6)
C(117)	0.920 7(9)	0.146(1)	0.284 2(9)	C(27)	0.230 2(6)	0.163 3(6)	−0.077 0(4)
C(118)	0.937 6(9)	0.133(1)	0.343 5(9)	C(28)	0.232 0(6)	0.102 9(5)	−0.074 0(4)
C(119)	0.941(1)	0.074(1)	0.359(1)	C(29)	0.234 5(6)	0.075 4(4)	−0.020 9(6)
C(120)	0.935 5(9)	0.028 7(9)	0.322 9(9)	C(30)	0.235 1(5)	0.108 3(6)	0.029 1(4)
C(121)	0.920 7(9)	0.039 4(9)	0.264 0(8)	C(31)	0.144 6(4)	0.196 0(6)	0.107 7(5)
C(122)	0.915 9(9)	0.208 6(9)	0.263 9(8)	C(32)	0.107 4(6)	0.239 9(4)	0.125 1(5)
C(123)	0.965(1)	0.248(1)	0.289(1)	C(33)	0.049 6(6)	0.227 3(5)	0.135 7(5)
C(124)	0.857(1)	0.233(1)	0.278(1)	C(34)	0.029 1(4)	0.170 8(6)	0.128 8(5)
C(125)	0.953(1)	0.058(1)	0.426(1)	C(35)	0.066 4(6)	0.126 9(4)	0.111 4(6)
C(126)	1.013(1)	0.059(1)	0.442(1)	C(36)	0.124 1(6)	0.139 5(5)	0.100 8(5)
C(127)	0.908(1)	0.085(1)	0.461(1)	C(37)	0.444 5(5)	0.181 9(6)	0.161 1(6)
C(128)	0.919(1)	−0.009(1)	0.220 1(9)	C(38)	0.456 3(5)	0.193 2(5)	0.218 7(6)
C(129)	0.981(1)	−0.017(1)	0.198(1)	C(39)	0.507 3(6)	0.172 9(6)	0.243 9(4)
C(130)	0.894(1)	−0.065(1)	0.246(1)	C(40)	0.546 5(5)	0.141 3(6)	0.211 7(6)
C(131)	0.709 0(8)	0.055 4(8)	0.275 8(8)	C(41)	0.534 7(5)	0.130 1(5)	0.154 1(6)
C(132)	0.680 4(8)	0.003 7(8)	0.266 3(7)	C(42)	0.483 7(6)	0.150 4(6)	0.128 9(4)
C(133)	0.628 3(8)	−0.009 6(8)	0.298 4(8)	C(43)	0.380 0(6)	0.205 9(6)	0.052 1(4)
C(134)	0.610 2(9)	0.031(1)	0.338 2(8)	C(44)	0.375 8(6)	0.254 2(4)	0.016 3(6)
C(135)	0.635 9(9)	0.084(1)	0.346 6(8)	C(45)	0.374 8(6)	0.246 9(5)	−0.042 8(5)
C(136)	0.687 3(9)	0.096 9(9)	0.315 6(8)	C(46)	0.377 9(6)	0.191 4(6)	−0.066 3(4)
C(137)	0.700(1)	−0.040(1)	0.222 4(9)	C(47)	0.382 1(6)	0.143 1(4)	−0.030 5(6)
C(138)	0.649(1)	−0.053(1)	0.181(1)	C(48)	0.383 2(6)	0.150 4(5)	0.028 7(5)
C(139)	0.721(1)	−0.094(1)	0.251(1)	C(49)	0.403 4(6)	0.291 2(4)	0.140 9(6)
C(140)	0.555(1)	0.010(1)	0.375(1)	C(50)	0.374 0(4)	0.332 9(6)	0.172 3(5)
C(141)	0.515(1)	0.057(1)	0.378(1)	C(51)	0.396 6(6)	0.388 8(5)	0.177 9(5)
C(142)	0.579(1)	−0.012(1)	0.432(1)	C(52)	0.448 6(6)	0.402 9(4)	0.152 0(5)
C(143)	0.715(1)	0.154(1)	0.323 1(9)	C(53)	0.478 0(4)	0.361 1(6)	0.120 6(5)
C(144)	0.760(1)	0.153(1)	0.374(1)	C(54)	0.455 4(6)	0.305 3(5)	0.115 1(5)
C(145)	0.672(1)	0.206(1)	0.334(1)	C(55)	0.381 0(5)	0.053 9(5)	0.188 9(6)
C(146)	0.669 1(8)	0.160 3(9)	0.100 7(8)	C(56)	0.382 2(5)	0.035 5(6)	0.132 1(5)
C(147)	0.656 8(9)	0.136 1(9)	0.046 4(9)	C(57)	0.429 4(6)	0.004 2(6)	0.112 4(4)
C(148)	0.630(1)	0.171(1)	0.004(1)	C(58)	0.475 4(5)	−0.008 6(5)	0.149 3(6)
C(149)	0.609(1)	0.227(1)	0.021(1)	C(59)	0.474 2(5)	0.009 8(6)	0.206 1(5)
C(150)	0.621(1)	0.251(1)	0.073(1)	C(60)	0.427 0(6)	0.041 0(6)	0.225 8(4)
C(151)	0.650(1)	0.218(1)	0.115 0(9)	C(61)	0.325 2(6)	0.085 0(6)	0.292 0(4)
C(152)	0.676 6(9)	0.074(1)	0.029 6(8)	C(62)	0.304 6(5)	0.037 3(5)	0.322 1(6)
C(153)	0.699(1)	0.071(1)	−0.033(1)	C(63)	0.312 9(6)	0.034 1(5)	0.381 2(6)
C(154)	0.623(1)	0.034(1)	0.037(1)	C(64)	0.341 8(6)	0.078 7(6)	0.410 1(4)
C(155)	0.575(2)	0.264(2)	−0.027(1)	C(65)	0.362 4(5)	0.126 4(5)	0.379 9(6)
C(156)	0.611(2)	0.300(2)	−0.056(2)	C(66)	0.354 1(6)	0.129 6(5)	0.320 9(6)
C(157)	0.527(2)	0.234(2)	−0.046(2)	C(67)	0.262 0(5)	0.030 4(5)	0.199 9(5)
C(158)	0.660(1)	0.241(1)	0.173 5(9)	C(68)	0.282 1(4)	−0.026 3(6)	0.194 4(5)
C(159)	0.721(1)	0.268(1)	0.175(1)	C(69)	0.243 0(6)	−0.072 0(4)	0.188 1(5)
C(160)	0.613(1)	0.288(1)	0.189(1)	C(70)	0.183 8(5)	−0.060 9(5)	0.187 4(5)
C(201)	0.2058(3)	0.066 2(2)	0.509 8(4)	C(71)	0.163 7(4)	−0.004 2(6)	0.193 0(5)
C(202)	0.172 6(4)	0.080 3(5)	0.557 9(2)	C(72)	0.202 8(6)	0.041 5(4)	0.199 3(5)

mV, $i_{pa}:i_{pc}$ ratios of near unity and linear plots of i_{pa} *vs.* $v^{\frac{1}{2}}$ where v is the scan rate. The likely explanation is that the ligated N_2 is very labile compared to the carbonyl, and when the complex is electrochemically oxidised the complex probably decomposes by dissociation of the N_2. The greater π-acceptor character of the CO ligand also results in the carbonyl complex being considerably harder to oxidise than the dinitrogen analogue. Neither complex showed any reduction processes in the range accessible.

Table 7 Selected bond lengths (Å) and angles (°) for complex **6**

Re(2)–O(1)	1.71(1)	Re(2)–S(1)	2.347(5)
Re(2)–S(2)	2.338(5)	Re(2)–S(3)	2.342(5)
Re(2)–S(4)	2.328(2)	Re(1)–P(1)	2.463(5)
Re(1)–P(2)	2.470(5)	Re(1)–P(3)	2.432(6)
Re(1)–P(4)	2.450(5)		
S(1)–Re(2)–S(2)	84.6(2)	S(1)–Re(2)–S(3)	151.1(2)
S(1)–Re(2)–S(4)	85.7(2)	S(2)–Re(2)–S(3)	87.5(2)
S(2)–Re(2)–S(4)	143.3(2)	S(3)–Re(2)–S(4)	84.2(2)
S(1)–Re(2)–O(1)	104.0(4)	S(2)–Re(2)–O(1)	108.2(4)
S(3)–Re(2)–O(1)	104.9(4)	S(4)–Re(2)–O(1)	108.5(4)
Re(2)–S(1)–C(101)	116.1(6)	Re(2)–S(2)–C(116)	114.3(6)
Re(2)–S(3)–C(131)	116.2(6)	Re(2)–S(4)–C(146)	116.6(7)
P(1)–Re(1)–P(4)	97.5(2)	P(2)–Re(1)–P(3)	98.8(2)
P(1)–Re(1)–P(2)	97.5(2)	P(1)–Re(1)–P(3)	135.9(2)
P(2)–Re(1)–P(4)	132.0(2)	P(3)–Re(1)–P(4)	101.2(2)

The complex [Re{$SC_6H_3(OMe)_2$-2,6}$_3$(PPh_3)] **7** was found to undergo a one-electron reversible oxidation process at $E_{\frac{1}{2}} = -0.02$ V and a further quasi-reversible one-electron oxidation centred at $E_{\frac{1}{2}} = +0.56$ V (Table 10). The relevant redox processes are

$$[ReL_3(PPh_3)] \underset{+e}{\overset{-e}{\rightleftharpoons}} [ReL_3(PPh_3)]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} [ReL_3(PPh_3)]^{2+}$$

where HL = thiol. The electrochemical accessibility of the rhenium(V) oxidation state is attributed to the fact that ligation of the Re atom by the oxygen donor of the methoxy group increases electron density at the metal centre and hence facilitates the oxidation process. In addition, the chelating structure in the molecule also promotes the stability of [Re{$SC_6H_3(OMe)_2$-2,6}$_3$(PPh_3)]$^{2+}$. No reduction processes were detectable up to the limit of solvent (CH_2Cl_2) reduction.

The complex [Re{P(C_6H_4S-2)$_3$}(PPh_3)] **8** showed a partially reversible one-electron oxidation centred at $E_{\frac{1}{2}} = +0.53$ V, and a partially reversible one-electron reduction centred at $E_{\frac{1}{2}} = -1.43$ V (see Table 10). The relevant electrode processes are

$$[Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)]^- \underset{+e}{\overset{-e}{\rightleftharpoons}} [Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)] \underset{+e}{\overset{-e}{\rightleftharpoons}} [Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)]^+$$

Table 8 Comparative dimensions of [ReO(SR)$_4$]$^-$ anions (distances in Å, angles in °)

	R			
Parameter	Ph[20]	$C_6H_2Me_3$-2,4,6[17]	$C_6H_3Pr^i_2$-2,6[21]	$C_6H_2Pr^i_3$-2,4,6[a]
Re–O	1.686(9)	1.65(1)	1.70(2)	1.71(1)
Re–S (mean)	2.341(3)	2.334(4)	2.35(1)	2.336(4)
O–Re–S (mean)	108.3(1)	107.7(4)	106.3(10)	106.4(3)
S–Re–S (*cis*) min.	83.3(1)	83.1(1)	83.4(4)	84.2(2)
S–Re–S (*cis*) max.	86.5(1)	87.0(1)	86.3(4)	87.5(2)
Re–S–C (mean)	114.3(3)	114.3(5)	113.6(13)	115.8(6)
X[b]	0.73	0.71	0.66	0.66
θ[c]	3.8	13.6	5.4	7.69

[a] This work. [b] Displacement of Re atom from least-squares plane of sulfur atoms. [c] Basal fold angle [dihedral angle of S(1)–S(2)–S(3)–S(4), equal to zero for ideal tetragonal pyramid].

Table 9 Comparative dimensions (°) for some tetrahydride complexes

Angle	[$ReH_4(PPh_3)_4$]$^+$	[$MoH_4(PMePh_2)_4$][24]	[$ReH_4(PMe_2Ph)_4$]$^+$[18]
P(1)–Re–P(2)	97.5(2)	94.17(7)	92.83(13)
P(1)–Re–P(4)	97.5(2)	95.06(6)	94.45(12)
P(2)–Re–P(3)	98.8(2)	93.15(7)	94.35(13)
P(3)–Re(1)–P(4)	101.2(2)	100.71(5)	94.88(13)
Av. P–Re–P (*cis*)	98.8	95.77	94.12
P(1)–Re(1)–P(3)	135.9(2)	141.50(7)	148.74(13)
P(2)–Re(1)–P(4)	132.0(2)	144.07(8)	148.98(13)
Av. P–Re–P (*trans*)	134.0	142.79	148.81

Table 10 Redox-potential data for complexes with ReS_3 cores

Complex	Re^{II}–Re^{III} $E_{\frac{1}{2}}$/V	Re^{III}–Re^{IV} E_p/V	Re^{III}–Re^{IV} $E_{\frac{1}{2}}$/V	Re^{IV}–Re^{V} $E_{\frac{1}{2}}$/V	Scan rate, v/V s^{-1}
4		+0.27			0.2
5			+0.78		0.2
7			−0.02	+0.56	0.2
8	−2.07	−1.43	+0.53		0.1

Measured in [NBu^n_4][BF_4]–toluene solvent system. Potentials relative to ferrocene–ferrocenium couple taken as 0.0 V.

For this complex the presence of three chelating rings in the molecule plays an important role in stabilising the electrochemically generated rhenium-(II) and -(III) species.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using conventional Schlenk-tube and syringe techniques. All solvents were freshly distilled from appropriate drying agents under dinitrogen. Elemental analyses were carried out by the Microanalytical Laboratory, University of Manchester. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Perkin-Elmer 1330 spectrometer, ^{1}H and ^{31}P NMR spectra on a EX-270 JEOL spectrometer.

Unless otherwise stated, all the cyclic voltammograms were measured at a platinum electrode with 0.2 mol dm^{-3} $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ as the supporting electrolyte in dichloromethane, and a silver-wire pseudo-reference electrode at room temperature under a nitrogen atmosphere. Potentials are quoted *versus* the ferrocene–ferrocenium couple taken as zero and used as an internal standard. The measurements were made on an EG+G PAR model 362 scanning potentiostat. Data were manipulated on an Elonex PC-320X microcomputer using an EG+G Condecon™ 300 hardware/software package.

The compounds $[\mathrm{ReH_7(PPh_3)_2}]$,[11] $[\mathrm{ReOCl_3(PPh_3)_2}]$,[15] $\mathrm{HSC_6H_2Pr^i_3}$-2,4,6[25] and tris(2-sulfanylphenyl)phosphine[26] were prepared by the literature methods. A sample of $\mathrm{HSC_6H_3(OMe)_2}$-2,6 was kindly provided by Dr. P. T. Bishop. The remaining thiols were prepared as described earlier.[15]

Tris(2,6-*dimethylbenzenethiolato*)(*triphenylphosphine*)*rhenium*(III) **1**.—Freshly prepared $[\mathrm{ReH_7(PPh_3)_2}]$ (0.5 g, 0.7 mmol) in toluene (40 cm^3) was treated with $\mathrm{HSC_6H_3Me_2}$-2,6 (0.29 cm^3, 2.1 mmol) and the solution stirred at room temperature for 2 d. The resulting purple solution was evaporated to dryness and the residue washed with hexane and recrystallised from toluene–hexane in *ca.* 60% yield (Found: C, 59.1; H, 5.1; P, 3.5; S, 10.6. Calc. for $\mathrm{C_{42}H_{42}PReS_3}$: C, 59.8; H, 5.0; P, 3.5; S, 10.5%). NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 1.59 (s, 3 H, $\mathrm{CH_3}$), 1.82 (s, 12 H, $\mathrm{CH_3}$), 1.94 (3 H, $\mathrm{CH_3}$) and 6.75–7.75 (m, 24 H, Ph); ^{31}P, δ 20.12 (s).

Tris(2,6-*dimethylbenzenethiolato*)(*methyl cyanide*)(*triphenylphosphine*)*rhenium*(III) **2**.—Complex **1** was heated under reflux in dry methyl cyanide for 10 min to produce a clear dark purple solution. This was cooled at −20 °C overnight to produce complex **2** in *ca.* 90% yield. It was identified by comparison with an authentic sample prepared by the literature route.[13]

Bis(tert-*butyl isocyanide*)*tris*(2,6-*dimethylbenzenethiolato*)*rhenium*(III) **3**.—Complex **1** (0.15 g, 0.17 mmol) and *tert*-butyl isocyanide (0.1 cm^3) were heated under reflux for 30 min. The solvent was removed *in vacuo* and the green residue recrystallised from toluene–hexane, yield 62% (Found: C, 53.1; H, 5.9; N, 3.7. Calc. for $\mathrm{C_{34}H_{45}N_2ReS_3}$: C, 53.4; H, 5.9; N, 3.7%). IR 2060 and 2090 cm^{-1}, ν(N≡C). NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 0.60 (s, 9 H, $\mathrm{Bu^t}$), 1.11 (s, 9 H, $\mathrm{Bu^t}$), 2.22 (s, 6 H, thiolate $\mathrm{CH_3}$), 2.25 (s, 6 H, thiolate $\mathrm{CH_3}$), 2.28 (s, 6 H, thiolate $\mathrm{CH_3}$) and 6.86–7.05 (m, 9 H, Ph).

$[\mathrm{Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)}]\cdot0.5\mathrm{C_6H_5Me}$ **4**.—A suspension of $[\mathrm{ReH_7(PPh_3)_2}]$ (0.25 g, 0.35 mmol) in toluene (20 cm^3) with $\mathrm{HSC_6H_2Pr^i_3}$-2,4,6 (0.25 g, *ca.* 0.25 cm^3, 1.1 mmol) was stirred for 3 d at room temperature. Extremely air- and moisture-sensitive green crystals were obtained by adding dry methanol to the concentrated reaction solution and standing for 2 d (75% yield) (Found: C, 65.2; H, 7.2; N, 1.8; P, 2.3; S, 7.5. $\mathrm{C_{63}H_{84}N_2PReS_3\cdot0.5C_7H_8}$ requires C, 65.1; H, 7.1; N, 2.3; P, 2.5; S, 7.8%). IR 2130 cm^{-1}, ν(N≡N). NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 0.97 (d, 36 H, $\mathrm{CH_3}$), 1.15 (d, 18 H, $\mathrm{CH_3}$) and 7.50–7.67 (m, 15 H, phosphine Ph); ^{31}P, δ 26.01.

$[\mathrm{Re(SC_6H_2Br\text{-}4\text{-}Pr^i_2\text{-}2,6)_3(N_2)(PPh_3)}]$.—The complex $[\mathrm{ReH_7(PPh_3)_2}]$ (0.15 g, 0.21 mmol) was treated with $\mathrm{HSC_6H_2Br}$-4-$\mathrm{Pr^i_2}$-2,6 (0.17 g, 0.63 mmol) in an analogous manner to that for the preparation of complex **4** to give green crystals (71.2% yield). The complex was shown to be directly analogous to **4** by IR and NMR spectroscopy. IR 2130 cm^{-1}, ν(N≡N). NMR ($\mathrm{CDCl_3}$): δ 0.65–1.87 (m, 36 H, $\mathrm{CH_3}$), 2.28–3.37 (6 H, C*H*$\mathrm{CMe_2}$), 7.07 (s, 6 H, thiolate Ph) and 7.36–7.74 (15 H, phosphine Ph); ^{31}P, δ 24.32 (s).

Reaction between $[\mathrm{ReOCl_3(PPh_3)_2}]$, $\mathrm{HSC_6H_2Pr^i_3}$-2,4,6 *and* $\mathrm{NaBH_4}$.—The complex $[\mathrm{ReOCl_3(PPh_3)_2}]$ (0.25 g, 0.3 mmol) and $\mathrm{NaBH_4}$ (0.25 g, excess) in absolute ethanol (20 cm^3) were treated with $\mathrm{HSC_6H_2Pr^i_3}$-2,4,6 (0.28 g, 1.2 mmol). The reaction solution was heated under reflux for 5 h, then filtered and on standing for 2 d gave green crystals of complex **4** (68.2% yield).

Reactions of Complex **4**.—*With carbon monoxide*. Complex **4** (0.10 g, 0.08 mmol) in toluene (20 cm^3) in a flask (100 cm^3) was stirred under CO at room temperature for 2 d. Addition of methanol and standing for several days gave red-orange crystals (0.07 g, 75% yield) (Found: C, 65.2; H, 7.4. $\mathrm{C_{64}H_{84}OPReS_3\cdot0.5C_7H_8}$ requires C, 66.0; H, 7.2%). IR 1930 cm^{-1}, ν(C≡O). NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 0.73 [s, 18 H, CH(C*H*$_3$)$_2$], 0.92 [s, 18 H, CH(C*H*$_3$)$_2$] 1.14 [d, 18 H, CH(C*H*$_3$)$_2$], 2.78 (m, 3 H, C*H*$\mathrm{Me_2}$), 3.05 (m, 6 H, C*H*$\mathrm{Me_2}$), 6.82 (s, 6 H, thiolate Ph) and 7.39–7.91, (15 H, phosphine Ph); ^{31}P, δ 33.48 (s).

Treatment of the reaction solution with a stream of CO gave a mixture of $[\mathrm{Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)(PPh_3)}]$ and $[\mathrm{Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)_2}]$.

With MeCN. Complex **4** (0.3 g) was stirred at 40 °C in dry MeCN (40 cm^3) for 2 h at room temperature to give a purple microcrystalline complex. This was identified as $[\mathrm{Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(MeCN)(PPh_3)}]$ by comparison with an authentic sample made by the literature method.[13]

$[\mathrm{Re\{SC_6H_3(OMe)_2\text{-}2,6\}_3(PPh_3)}]$ **7**.—The complex $[\mathrm{ReH_7(PPh_3)_2}]$ (0.15 g, 0.2 mmol) in toluene (20 cm^3) was treated with $\mathrm{HSC_6H_3(OMe)_2}$-2,6 (0.11 g, 0.63 mmol). It was stirred for 2 d to precipitate a purple-brown solid. This was recrystallised from $\mathrm{CH_2Cl_2}$ and toluene to give purple needle-like crystals (42% yield) [Found: C, 56.0; H, 5.0%; FAB *m/z* 956 (M^+). $\mathrm{C_{42}H_{42}O_6PReS_3\cdot C_7H_8}$ requires C, 56.1; H, 4.8%]. NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 2.29 (s, 3 H, OMe), 2.40 (s, 3 H, OMe), 3.70 (s, 6 H, OMe), 3.86 (s, 6 H, OMe) and 5.97–7.69 (m, 24 H, Ph); ^{31}P, δ 19.35 (s).

$[\mathrm{Re\{P(C_6H_4S\text{-}2)_3\}(PPh_3)}]$ **8**.—The complex $[\mathrm{ReH_7(PPh_3)_2}]$ (0.15 g, 0.21 mmol) in toluene (20 cm^3) was treated with $\mathrm{P(C_6H_4SH\text{-}2)_3}$ (0.075 g, 0.25 mmol) and stirred for 2 d at room temperature. Addition of methanol and standing for several days gave red-brown crystals (54% yield) (Found: C, 53.8; H, 3.4. $\mathrm{C_{36}H_{27}P_2ReS_3}$ requires C, 53.8; H, 3.4%). ^{31}P NMR ($\mathrm{CDCl_3}$): δ 35.52 (d, $\mathrm{PPh_3}$) and 138.20 [d, $\mathrm{P(C_6H_4S)_3}$], ^{3}J(P–P) = 349.5 Hz.

$[\mathrm{ReH_4(PPh_3)_4}][\mathrm{ReO(SC_6H_2Pr^i_3\text{-}2,4,6)_4}]$ **6**.—The preparation of complex **4** was carried out as above, and air (5 cm^3) was introduced into the reaction flask with a syringe. Evaporation of the solvent to *ca.* 10 cm^3, and refridgeration overnight gave the complex as dark orange crystals in 38% yield, suitable for structure determination (Found: C, 65.3; H, 6.7; P, 5.1. $\mathrm{C_{132}H_{160}OP_4Re_2S_4\cdot C_4H_8O}$ requires C, 66.5; H, 6.6; P, 5.2%). IR, ν(Re–H) 2020, ν(B–F) 1050, 1080 cm^{-1}. NMR ($\mathrm{CDCl_3}$): ^{1}H, δ −2.60 [q, 4 H, Re–H, *J*(P–H) = 25.6], 0.83 (m, 72 H, Me), 2.80 [spt, 4 H, C*H*$\mathrm{Me_2}$, *J*(H–H) = 6.86], 3.40 [spt, 4 H, C*H*$\mathrm{Me_2}$, *J*(H–H) = 6.86], 4.17 [spt, 4 H, C*H*$\mathrm{Me_2}$, *J*(H–H) = 6.86 Hz] and 6.9–7.27 (m, 68 H, Ph); ^{31}P, δ 17.40 (s).

[ReH$_5$(PPh$_3$)$_3$].—A slurry of [ReOCl$_3$(PPh$_3$)$_2$] (1.00 g, 1.2 mmol) and PPh$_3$ (1.00 g, 3.8 mmol) together with NaBH$_4$ (1.00 g, excess) in absolute ethanol (20 cm^3) was heated under reflux for 3 h. After filtration, the yellow solid was extracted with toluene. A yellow powder was obtained by removal of the toluene *in vacuo* and washed with methanol and then diethyl ether. Yield 61%.

[PPh$_3$H]BF$_4$.—Triphenylphosphine (2.6 g, 0.01 mol) was dissolved in diethyl ether (30 cm^3) and 1 equivalent of a solution of HBF$_4$·Et$_2$O added. The resulting white solid was filtered off and washed with additional diethyl ether to give a virtually quantitative yield of the phosphonium salt.

[ReH$_4$(PPh$_3$)$_4$]BF$_4$.—The complex [ReH$_5$(PPh$_3$)$_3$] (1.0 g, 1 mmol) and [PPh$_3$H]BF$_4$ (0.35 g, 1 mmol) were stirred in thf (20 cm^3) at room temperature for 2 h. Removal of the solvent and addition of diethyl ether gave the tetrahydride as an off-white solid in 74% yield. The ^{1}H NMR spectrum in the hydride region was identical to that of complex **6**.

Crystallography.—The numerical details of the crystal structure determinations are summarised in Table 1.

Complex **3**. *Data collection.* Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $23 < \theta < 25°$. The data were collected in the ω–2θ scan mode and three standard reflections were measured every hour of exposure; 0.9% loss of intensity was observed which was linearly corrected during processing. Three standard reflections were measured every 200 to check the crystal orientation. The data were corrected for Lorentz and polarisation factors and an absorption correction was applied using ψ scans of nine reflections.[26]

Structure solution and refinement. The structure was solved using the Patterson heavy-atom method (MOLEN).[27] Remaining non-hydrogen atoms were located in subsequent cycles of Fourier-difference syntheses and least-squares refinement. Full-matrix least-squares refinement on F converged with $R = 0.044$, $R' = 0.047$, maximum (shift/error) < 0.01 and $S = 3.5$. The weighting scheme used was of the form $w = 1/[\Sigma\sigma^2(F) + (0.02F)^2 + 1.0]$. In the last few cycles the extinction coefficient was refined to a g value of 1.57×10^{-8}. Hydrogen atoms were added in calculated positions with $B_{iso} = 1.3B_{eq}$ of the attached atom; they were included in structure-factor calculations but were not refined. Neutral atom scattering factors were used.[28]

Complex **4**. *Data collection.* Following photographic examination, data were collected as for complex **3**. Accurate cell parameters were determined from goniometer settings of 25 reflections with θ *ca.* 10.5°, each reflection centred in four orientations. Diffraction intensities to $\theta_{max} = 20°$ were measured. During processing data were corrected for Lorentz-polarisation effects, slight loss of intensity (*ca.* 6.3% overall), absorption (by semiempirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods).

Structure solution and refinement. A total of 11 980 reflections were entered into the program SHELXN[29] for structure determinations and for refinement by large-block least-squares methods. The Re, P, S and N atoms were refined anisotropically. Hydrogen atoms were included in idealised positions in phenyl and methine groups, those in methyl groups were not included, but the methyl C atoms were allowed anisotropic thermal parameters. Disorder was noted in one Pr^i group, with the pair of Me groups in any of at least four orientations; here the part C atoms were refined isotropically with site occupancies set between 0.2 and 0.5. A toluene solvent molecule was located, also disordered, with one major resolved orientation and one minor, less well resolved, overlapping arrangement. These molecules were refined with geometrical restraints. Refinement was terminated with $R = 0.055$, $R' = 0.058$ and $R_g = 0.069$[28] for the 10 861 reflections with $I > \sigma_I$, weighted $w = (\sigma_F^2 + 0.0041F^2)^{-1}$. In a final difference map the major peaks of residual electron density *ca.* 0.8 e Å^{-3} were close to the Re atoms with nothing else of significance in the map. Scattering factor curves for neutral atoms were used.[27] Computer programs used in this analysis were run on the MicroVAX II machine at the Nitrogen Fixation Laboratory at the University of Sussex.

Complex **6**. *Data collection.* Intensity data were collected on a Rigaku AFC5S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $15 < \theta < 20°$. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 150. No loss of intensity was observed. The data were corrected for Lorentz and polarisation factors and an absorption correction applied as for complex **3**.

Structure solution and refinement. The structure was solved using direct methods (TEXSAN[30]). Remaining non-hydrogen atoms were located as for complex **3**. Full-matrix least-squares refinement on F converged with $R = 0.068$, $R' = 0.076$, maximum (shift/error) 0.08 and $S = 2.22$. Hydrogen atoms were not included. Neutral atom scattering factors were used.[27]

Additional material available from the Cambridge Crystallographic Date Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are indebted to Professor J. A. K. Howard, Professor Shi-Xiong-Lu and Dr. A. Batsanov, University of Durham for the determination of the crystal structure of complex **1**. J. H. thanks the Committee of Vice Chancellors and Principals for an Overseas Research Student award, and we are also grateful to Hermann Starck GmbH, Berlin, for the generous provision of rhenium metal. J. A. Z. gratefully acknowledges partial support of this research by the Petroleum Research Fund.

References

1 J. R. Dilworth, J. Hu, S. X. Liu, D. Povey, G. Smith and J. Howard, *Inorg. Chim. Acta*, 1994, **223**, 63.

2 J. R. Dilworth and P. J. Blower, *Coord. Chem. Rev.*, 1987, **76**, 121.

3 J. R. Dilworth and J. Hu, *Adv. Inorg. Chem.*, 1994, **40**, 411.

4 P. T. Bishop and J. R. Dilworth, *J. Chem. Soc., Dalton Trans.*, 1991, 385.

5 J. R. Dilworth, S. Lu, Q. Wu and Y. Zheng, *Inorg. Chim. Acta*, 1992, **194**, 99.

6 P. T. Bishop, J. R. Dilworth, T. Nicholson and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1986, 1123.

7 S.-L. Soong, J. H. Hain, M. Millar and S. Koch, *Organometallics*, 1988, **7**, 556.

8 M. Leaphon, K. Rohl, R. J. Thomas, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1993, **32**, 5562.

9 M. Leaphon, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1991, **30**, 4986.

10 J. Chatt, R. H. Crabtree, J. R. Dilworth and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2358.

11 J. Chatt and R. S. Coffey, *J. Chem. Soc.*, 1969, 1963.

12 (*a*) J. R. Dilworth, J. Hu, R. M. Thompson and D. L. Hughes, *J. Chem. Soc., Chem. Commun.*, 1992, 551; (*b*) J. R. Dilworth, J. Hu, Shi-Xiong Lu, A. Batsanov and J. Howard, unpublished work.

13 P. J. Blower and J. R. Dilworth, *J. Chem. Soc., Dalton Trans.*, 1985, 2305.

14 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

15 P. J. Blower, J. R. Dilworth, J. Hutchinson, T. Nicholson and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1985, 2639.

16 N. de Vries, J. C. Dewan, A. G. Jones and A. Davison, *Inorg. Chem.*, 1988, **27**, 1574.

17 P. J. Blower, J. R. Dilworth, J. Hutchinson, T. Nicholson and J. Zubieta, *Inorg. Chim. Acta*, 1984, **90**, 27.

18 N. de Vries, A. Davison and A. Jones, *Inorg. Chim. Acta*, 1989, **165**, 9.

19 J. R. Dilworth, P. Jobanputra, J. R. Miller, S. J. Parrot and J. R. Miller, *Polyhedron*, 1993, **12**, 513.

20 A. C. McDonnell, T. N. Maribley, M. R. Snow and A. G. Wedd, *Aust. J. Chem.*, 1983, **36**, 253.

21 J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.

22 A. C. McDonnell, T. N. Maribley, M. R. Snow and A. G. Wedd, *Aust. J. Chem.*, 1983, **36**, 253.

23 L. J. Guggenburger, *Inorg. Chem.*, 1973, **12**, 2295.

24 D. M. Lunder, M. A. Green, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 4527.

25 E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 2327.

26 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

27 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, 1990.

28 D. T. Cromer and J. T. Weber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

29 G. M. Sheldrick, SHELXN, extended version of SHELX 76, University of Cambridge, 1977.

30 TEXSAN, Single Crystal Structure Analysis Software, Version 1.6, Molecular Structure Corporation, Houston, TX, 1993.

Received 4*th April* 1995; *Paper* 5/02165K