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The reactions of thiolate ligands with rhenium hydrides Part 1. The syntheses and structures of [ReO(SC_6H_3-2,6-Me_2)$_3$(PPh_3)] and [Re(SC_6H_3-2,6-Me_2)$_3$(PPh_2H)(PPh_3)]

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Abstract

A controlled substitution reaction of [$ReOCl_3(PPh_3)_2$] with DMT (DMT = 2.6-dimethylbenzenethiolate) was achieved using Me_3SiDMT to give [ReO(DMT)$_3$(PPh_3)] (**I**). The same complex was obtained from [$ReH_7(PPh_3)_2$] and the disulfide of DMT, but [Re(DMT)$_3$(PPh_3)($PHPh_2$)] (**IV**) was isolated from the reaction of [$ReH_7(PPh_3)_2$] with HDMT. X-ray diffraction studies show that both compounds have a distorted trigonal bipyramidal geometry. Crystal data: **I**: $C_{42}H_{42}OPS_3Re$, $M_r = 876.1$, monoclinic, space group $P2_1/n$, $a = 11.842(6)$, $b = 19.164(8)$, $c = 17.368(7)$, Å, $\beta = 104.01(4)°$, $V = 3824(3)$ Å^3, $Z = 4$, $R = 0.342$ ($R_w = 0.394$) for 4156 unique data having $F > 5\sigma(F)$; **IV**: $C_{54}H_{53}P_2ReS_3$, $M_r = 1045$, monoclinic, space group $P2_1/n$, $a = 11.014(4)$, $b = 23.064(4)$, $c = 19.017(5)$ Å, $\beta = 97.00(2)°$, $V = 4795(2)$ Å^3, $Z = 4$, $R = 0.060$, $R_w = 0.084$, for 4705 independent observed reflections having $F > 3\sigma(F)$.

Keywords: Crystal structures; Rhenium complexes; Oxo complexes; Thiolato complexes

1. Introduction

In an earlier publication, we reported the reaction of [$ReOCl_3(PPh_3)_2$] with an excess of a variety of sterically hindered thiolate anions in methanol to give the unreactive anions [$ReO(SAr)_4$]$^-$ [1] (SAr = 2,4,6-triisopropylbenzenethiolate (TIPT), 2,4,6-trimethylbenzenethiolate (TMT), 2,6-diisopropylbenzenethiolate (DIPT), 4-bromo-2,6-diisopropylbenzenethiolate (BIPT)). All have square pyramidal coordination with an apical oxo group [1]. The reactions proceeded with complete substitution of all the chloride ligands around Re except the oxo group and no intermediate product could be isolated despite intensive efforts. Here we report the synthesis of the oxo complex, [ReO(DMT)$_3$(PPh_3)] (**I**) (DMT = 2,6-dimethylbenzenethiolate) from the reaction of [$ReOCl_3(PPh_3)_2$] with trimethylsilyl-2,6-dimethylbenzenethiolate (Me_3SiDMT). The reactivity of this trithiolato–oxo complex is much greater than that of [$ReO(SAr)_4$]$^-$ (SAr = TIPT, DMT, BIPT) [1]. Alternatively [ReO(DMT)$_3$(PPh_3)] can be prepared from the oxidative reaction of [$ReH_7(PPh_3)_2$] with RSSR (SR = DMT) in methanol. However, the employment of HDMT instead of its dimer RSSR led to the unexpected formation of the Re(III) complex [Re(DMT)$_3$(PPh_3)($PHPh_2$)], the formation of $PHPh_2$ occurring by the unusual cleavage of a P–C(Ph) bond.

2. Experimental

2.1. Materials and methods

All manipulations were performed under dry nitrogen using standard Schlenk and vacuum-line and syringe techniques unless stated otherwise. 1,1,1,3,3,3-Hexamethyldisilazane was purchased from Aldrich and used

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without further purification. [$ReOCl_3(PPh_3)_2$] [2] and [$ReH_7(PPh_3)_2$] [3] were prepared by the literature procedures. Elemental analyses were performed by Medac Ltd., University of Brunel. IR spectra were recorded as nujol mulls (NaCl plates) on a Perkin-Elmer 1330 IR spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on an EX-270 JEOL (270 MHz) NMR spectrometer. FAB-MS spectra were obtained from the SERC facility at University College Swansea.

2.2. Preparation of $Me_3Si(DMT)$

Two equivalents HDMT (2 ml, ~14.47 mmol) with 1 equiv. of 1,1,1-3,3,3-hexamethyldisilazane (1.53 ml) were heated at 120 °C until evolution of NH_3 ceased to give colourless $Me_3Si(DMT)$. ^1H NMR (ppm): δ 0.29 (s, 9H, CH_3–Si), 2.53 (s, 6H, 2,6-CH_3Ph), 7.00–7.15 (m, 3H, SC_6H_3).

2.3. Synthesis of [$ReO(DMT)_3(PPh_3)$] (I)

Method A. [$ReOCl_3(PPh_3)_2$] (0.25 g, 0.3 mmol) in toluene was treated with $Me_3Si(DMT)$ (0.13 ml, ~0.6 mmol) and stirred at 45–55 °C for 4 h. Toluene was removed under reduced pressure. The resulting green residue was recrystallised from MeOH/CH_2Cl_2 under an N_2 atmosphere. The green crystals of [$ReO(DMT)_3(PPh_3)$] are stable in the air, although they decompose in solution in air. Yield 42.3%. *Anal.* Calc. for $C_{42}H_{42}OPReS_3$: C, 58.4; H, 4.9. Found: C, 57.3; H, 5.0%. IR (cm^{-1}): ν(ReO) 935. ^1H NMR ($CHCl_3$) (ppm): δ 1.181 (s, 3H, Me), 1.54 (s, 3H, Me), 1.62 (s, 3H, Me), 2.02 (s, 3H, Me), 2.26 (s, 3H, Me), 2.46 (s, 3H, Me), 7.38 (br s, 12H, Ph_3P), 7.96 (br s, 3H, SC_6H_3), 6.18–7.18 (m, 9H, PPh_3). ^{31}P NMR (ppm): δ 16.16 (s, PPh_3). FAB-MS(+) *m/z*: 876.17 (M^+), 739 ($M^+ - DMT$), 614 ($M^+ - Ph_3P$), 476 ($M^+ - DMT - Ph_3P - H^+$).

Method B. [$ReH_7(PPh_3)_2$] (0.2 g, 0.28 mmol) and RSSR (RS = DMT) (0.077 g, 0.28 mmol) in absolute ethanol (20 ml) were stirred at room temperature for 2 days, then stored at −20 °C for several days to produce a green precipitate. IR shows it to be the same product as that from Method A. Yield 53%.

2.4. Reaction of I with PPh_3 to give [$Re(DMT)_3(MeCN)(PPh_3)$] (II)

Compound **I** (0.2 g, 0.2 mmol) in MeCN (20 ml) with excess Ph_3P (0.5 g) was heated under reflux for 6 h. Then it was allowed to cool down to room temperature. The purple precipitate of [$Re(DMT)_3(MeCN)(PPh_3)$] (**II**) was recrystallised from CH_2Cl_2/EtOH. *Anal.* Calc. for $C_{44}H_{35}NPRe$: C, 58.6; H, 5.0; N, 1.6. Found: C, 58.5; H, 5.0; N, 1.7%. IR (cm^{-1}): ν(C≡N) 2260. ^{31}P NMR (ppm): δ 20.09 (s, PPh_3). ^1H NMR (ppm): δ 1.55 (s, 3H, CH_3CN), 1.93 (s, 18H, $(CH_3)_2Ar$), 6.80–7.82 (m, 24H, Ar*H*).

2.5. Reaction of complex I with excess of DMT

[$ReO(DMT)_3(PPh_3)$] (0.2 g, 0.26 mmol) was reacted with HDMT (0.036 g, ~0.04 ml, 0.26 mmol) and Et_3N (0.04 ml) in EtOH (25 ml) under reflux. After 30 min, the solution was cooled and excess [Ph_4P]Br was added to give brown [Ph_4P][$ReO(DMT)_4$] (**III**). IR (cm^{-1}): ν(Re=O) 965. ^1H NMR (ppm): δ 2.15 (s, 12H, CH_3), 2.37 (s, 12H, CH_3), 6.73–7.98 (m, 44H, ArH). ^{31}P NMR (ppm): δ 26.70 (s, PPh_4^+).

2.6. Synthesis of [$Re(DMT)_3(PPh_3)(PPh_2H)$] (IV)

Freshly prepared [$ReH_7(PPh_3)_2$] (0.5 g, 0.70 mmol) in toluene (40 ml) was treated with HMDT (0.29 ml, 2.1 mmol). The solution was stirred at room temperature for two days. The resulting purple solution was evaporated to dryness in vacuo and then extracted with hexane. In time, the extract deposited purple crystals of [$Re(DMT)_3(PPh_3)(PPh_2H)$]. The yield varied from 21 to 0%. *Anal.* Calc. for $C_{54}H_{53}P_2S_3Re$: C, 62.0; H, 5.1. Found: C, 61.9; H, 5.0%. IR (cm^{-1}): ν(P–H) 2320. ^1H NMR: δ 1.86 (s, 3H, Me), 2.30 (s, 3H, Me), 2.48 (s, 3H, Me). $^{31}P\{H\}$ NMR: δ 11.59 (d, PPh_3, *J*(P–P) 254.9 Hz), −11.745 (d, $PHPh_2$, *J*(P–P) 254.9 Hz). The colour of the hexane extract solution changed rapidly from purple to green due to oxidation. The residue left from the hexane extraction was recrystallised from toluene–hexane to give the complex [$Re(DMT)_3(PPh_3)$] in ~60% yield. The full details of the last complex which has an agostic interaction between the metal and a methyl hydrogen will be reported elsewhere.

2.7. X-ray structure determinations for complexes I and IV

The details of the experimental procedures and crystal data for the two structures are summarised in Table 1.

3. Results and discussion

3.1. Crystal structure of I

The molecular structure of **I** is shown in Fig. 1 together with the atom numbering scheme. The atomic coordinates are given in Table 2, and selected angles and bond distances are given in Table 3. The overall geometry about the Re atom is best described as distorted tbp (trigonal bipyramidal, see below). The equatorial plane comprises the oxo atom and two thiolate ligands while the third thiolate and triphenylphosphine

Table 1
X-ray structural data

	$[ReO(DMT)_3(PPh_3)]$	$[Re(DMT)_3(PPh_2H)(PPh_3)]$
Solution and refinement		
System used	Siemens SHELXTL PLUS	SHELX
Solution	direct methods	heavy atom method
Refinement method	full-matrix least-squares	full-matrix least-squares
Weighting scheme	$w^{-1}=\sigma^2(F)+0.0005F^2$	$w=1/[\sigma(F^2)+(0.04F)^2+4.0]$
No. parameters refined	433	
Final R indices (obs. data) (%)		
R	3.42	6.0
R_w	3.94	8.4
Data collection		
Diffractometer	Siemens R3m/V	Enraf Nonius CAD4
Radiation, λ (Å)	Mo Kα, 0.71069	
Temperature (K)	293	
Monochromator	highly orientated graphite crystal	
Scan type	ω–2θ	ω–θ
2θ Range (°)	4.0–48.0	scan width $0.7+0.35\tan\theta$
Scan speed	variable 1.5 to 15.0 min in ω	3.33 min^{-1}
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time	
Standard reflections	3 measured every 200 reflections	3 measured every 200 reflections
Reflections collected	6530	8171
Observed reflections	4156 ($F>5.0\sigma(F)$)	4705 ($I>3\sigma(I)$)
Absorption correction	semi-empirical	semi-empirical
Crystal data		
Empirical formula	$C_{42}H_{42}OPS_3Re$	$C_{54}H_{53}P_2S_3Re$
Colour	dark green prismatic	purple
Crystal size (mm)	0.44 × 0.28 × 0.19	0.4 × 0.3 × 0.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.842(6)	11.014(4)
b (Å)	19.164(8)	23.064(4)
c (Å)	17.368(7)	19.017(5)
β (°)	104.01(4)	97.00(2)
Volume ($Å^3$)	3824(3)	4795(2)
Density (calc.) (mg m^{-3})	1.522	1.593
Absorption coefficient (mm^{-1})	3.449	
$F(000)$	1760	2120

occupy the apical sites. The Re atom deviates from the equatorial S_2O plane by 0.2374 Å in a direction away from the triphenylphosphine ligand. The equatorial ligands and P–C bond of PPh_3 are staggered with torsion angles of average 162.1° (S(2)–Re–P–C(1) = 169.0; S(3)–Re–P–C(7) = 154.3, O–Re–P–C(13) = 163.0°) to minimise steric interactions. The aryl groups of the equatorial thiolates are disposed to the side of the equatorial plane away from the bulky triphenylphosphine ligand, the angle at S(2) being considerably larger (127°) than that at S(3), 113°.

3.2. Comparison of the structure of I with other five-coordinate complexes

Table 4 summarises details of the structures of a number of complexes of the type MXL_4, where X is a multiply bonded ligand such as oxo, nitrido, hydrazido or imido in combination with a range of other ligands. Muetterties and Guggenberger [4] have suggested the use of the shape determining dihedral angle associated with the edge opposite to the multiply bonded ligand (0.0° for an ideal sp and 53.1° for the ideal tbp) to define the amount of distortion from the idealised structures. Site preference and steric and electronic effects are interlinked, and together dictate the overall geometry of the complexes. A simple molecular orbital treatment of tbp structures with multiply bonded ligands [12] (Fig. 2) suggests that d^2 complexes will be marginally more stable with the oxo group in an equatorial site. However the energy differences between locating the oxo ligand in axial and equatorial sites are small, and the simple treatment neglects both the steric effects which must here be significant, and the p-donor or

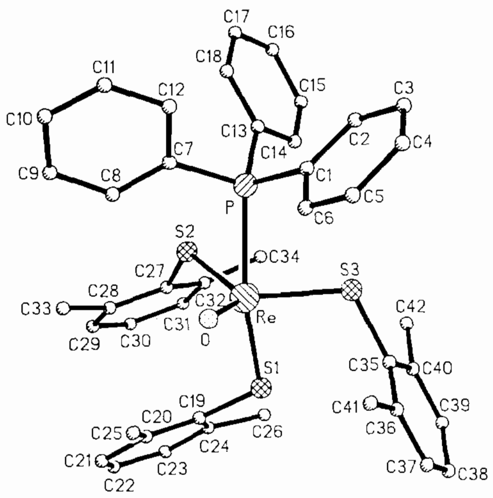

Fig. 1. An ORTEP representation of the structure of [ReO(DMT)$_3$(PPh$_3$)], together with a partial atom numbering scheme.

acceptor characteristics of the co-ligands. At first sight it is perhaps surprising that the bulky PPh$_3$ ligand should occupy an axial site, but this may reflect the tendency for p-acceptor ligands to do so, as in [Mo(CO)$_2$(TIPT)$_3$]$^-$ (TIPT = 2,4,6-tri-isopropylbenzene thiolate) [13]. Nevertheless, whatever the balance of effects responsible for the observed geometry, complex **I** remains an unusual example of a tbp d^2 oxo complex.

3.3. *Crystal structure of IV*

The ORTEP representation of the structure of complex **IV** is given in Fig. 3, together with the atom-labelling scheme. The atomic coordinates are given in Table 5 and selected bond lengths and angles are given in Table 6. The overall geometry about Re is best described as trigonal bipyramidal with three equatorial thiolate ligands and axial Ph$_3$P and Ph$_2$PH groups. The bond distance for Re–P(PPh$_3$) (2.455(4) Å) is found to be significantly greater than that of the Re–P(PHPh$_2$) bond (2.370(4) Å) due presumably to the bulk of the PPh$_3$ ligand. The equatorial thiolate ligands are orientated with one thiolate phenyl ring towards the PPh$_3$ and other two towards the PHPh$_2$, i.e. the 'two down one up' configuration [14]. Consequently the p orbitals of the thiolate sulfur atoms overlap with the $d_{x^2-y^2}$ or d_{xy} Re orbitals by alignment of the S–C(Ph) vectors approximately perpendicular to the equatorial plane as in compound **I**. Such a configuration is typical for five-coordinate sterically hindered thiolate metal complexes with an MS$_3$ core in the absence of multiply bonded ligands such as oxo or nitrido. Hitherto it has been observed that in this type of structure at least one of the axial ligands has to be a small molecule such as CO or MeCN owing to the steric hindrance exerted by the equatorial thiolate ligands. By contrast, compound **IV** tolerates both the bulky Ph$_3$P ligand together with the medium size ligand PHPh$_2$ as axial ligands. As a result, the Re–S–C(Ph) angles are straightened to some extent, due primarily to the steric forces exerted by the axial ligands. The angles Re–S–C(Ph) (122.0(6), 121.6(5), 123.6(6)) are significantly greater than the value (M–S–C(Ph) ~109–120°, mainly centred at 113°)

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement factors for [ReO(DMT)$_3$(PPh$_3$)]

	x	y	z	U_{eq}^{a}
Re	1851(1)	531(1)	2946(1)	384(1)
P	−131(2)	966(1)	3015(1)	407(6)
S(1)	3727(2)	389(1)	2787(1)	479(7)
S(2)	879(2)	478(1)	1634(1)	492(7)
S(3)	2523(2)	1530(1)	3642(1)	549(7)
O	1644(4)	−133(3)	3541(3)	545(20)
C(1)	−121(6)	1334(4)	3980(4)	464(27)
C(2)	−508(7)	2004(4)	4080(5)	544(31)
C(3)	−513(8)	2249(5)	4837(6)	674(38)
C(4)	−138(8)	1824(7)	5473(6)	771(44)
C(5)	265(9)	1178(6)	5378(5)	806(45)
C(6)	300(8)	939(5)	4645(5)	672(36)
C(7)	−1181(6)	248(4)	2948(4)	453(26)
C(8)	−1083(7)	−359(4)	2559(5)	545(31)
C(9)	−1923(9)	−877(5)	2484(5)	695(38)
C(10)	−2881(8)	−776(6)	2783(6)	768(41)
C(11)	−2962(7)	−179(6)	3183(5)	714(39)
C(12)	−2139(7)	336(5)	3273(5)	608(34)
C(13)	−844(6)	1606(4)	2278(4)	428(25)
C(14)	−202(7)	2091(4)	2000(5)	598(32)
C(15)	−732(8)	2545(5)	1404(6)	776(41)
C(16)	−1898(8)	2537(5)	1098(6)	773(40)
C(17)	−2554(8)	2060(5)	1380(6)	834(43)
C(18)	−2035(7)	1594(5)	1961(5)	683(36)
C(19)	3951(6)	−241(4)	2082(4)	445(25)
C(20)	3682(7)	−941(5)	2150(5)	537(30)
C(21)	3910(8)	−1413(5)	1606(5)	676(36)
C(22)	4424(9)	−1193(6)	1010(6)	817(45)
C(23)	4738(7)	−510(6)	975(5)	686(36)
C(24)	4508(6)	−29(4)	1508(5)	506(29)
C(25)	3191(8)	−1224(5)	2813(5)	673(36)
C(26)	4930(7)	710(5)	1477(5)	697(38)
C(27)	1575(6)	308(4)	844(4)	483(28)
C(28)	1470(7)	−357(5)	517(5)	597(33)
C(29)	1863(7)	−471(6)	−169(5)	735(37)
C(30)	2332(8)	68(7)	−506(5)	756(44)
C(31)	2397(7)	717(6)	−189(5)	749(42)
C(32)	2015(7)	869(5)	493(5)	578(31)
C(33)	919(8)	−958(5)	852(6)	756(40)
C(34)	2021(8)	1599(6)	792(6)	833(45)
C(35)	4092(6)	1573(4)	3956(5)	516(29)
C(36)	4650(7)	1203(5)	4627(5)	558(31)
C(37)	5860(8)	1250(5)	4868(5)	737(39)
C(38)	6478(8)	1652(6)	4469(7)	830(45)
C(39)	5920(8)	2033(5)	3825(6)	773(43)
C(40)	4708(8)	2003(5)	3536(6)	685(38)
C(41)	4006(8)	758(5)	5078(5)	719(38)
C(42)	4138(10)	2397(6)	2823(7)	984(54)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for [ReO(DMT)$_3$(PPh$_3$)]

Bond distances			
Re–P	2.521(2)	Re–S(1)	2.319(2)
Re–S(2)	2.293(2)	Re–S(3)	2.301(2)
Re–O	1.694(6)	P–C(1)	1.816(8)
P–C(7)	1.840(8)	P–C(13)	1.824(7)
S(1)–C(19)	1.786(8)	S(2)–C(27)	1.793(8)
S(3)–C(35)	1.807(7)		
Bond angles			
P–Re–S(1)	166.8(1)	P–Re–S(2)	79.2(1)
S(1)–Re–S(2)	98.1(1)	P–Re–S(3)	84.7(1)
S(1)–Re–S(3)	86.6(1)	S(2)–Re–S(3)	125.8(1)
P–Re–O	86.6(1)	S(1)–Re–O	105.6(2)
S(2)–Re–O	117.5(2)	S(3)–Re–O	112.8(2)
Re–S(1)–C(19)	117.8(2)	Re–S(2)–C(27)	123.7(2)
Re–S(3)–C(35)	113.4(3)		

Table 4
Core geometry determining angles for MXL$_4$[a] complexes

Complex	δ (°)	Reference
Ideal square pyramid	0.0	[4]
[TcO(TMT)$_4$]$^-$	0.0	[5]
[ReO(SPh)$_4$]$^-$	3.8	[6]
[ReO(DIPT)$_4$]$^-$	5.4	[1]
[ReO(TMT)$_4$]$^-$	13.6	[1]
[Mo(NNMe)$_2$O(SPh)$_3$]	16.5	[7]
[W(NPh)(NMe$_2$)$_4$]	17.5	[8]
[ReN(SC$_6$HMe$_4$)$_2$(HNC(NMe$_2$)$_2$)$_2$]	20.2	[9]
[TcO(TIPT)$_3$py]	32.0	[10]
[ReO(DMT)$_3$(PPh$_3$)]	40.8	this work
[VOCl$_2$(NMe$_3$)$_2$]	53.7	[11]
Ideal trigonal bipyramid	53.1	[4]

[a] X = multiply bonded atom.

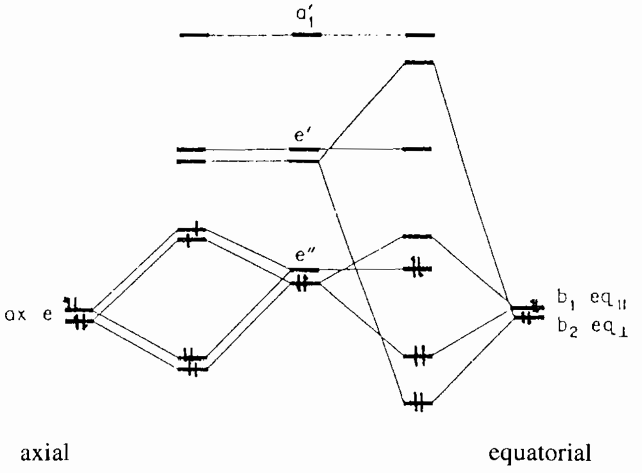

Fig. 2. An interaction diagram for a cylindrically symmetrical π-donor in a tbp complex. The left side represents occupation of an axial site, the right an equatorial site.

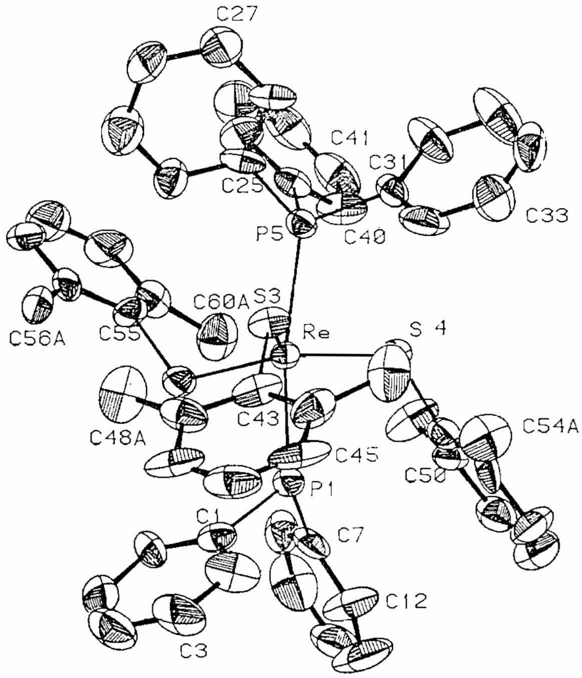

Fig. 3. The molecular structure of [Re(DMT)$_3$(PPh$_2$H)(PPh$_3$)], together with a partial atom numbering scheme.

observed previously. The formation of the PHPh$_2$ ligand is thought to arise from intermediate formation of an (η^6-C$_6$H$_5$)PPh$_2$ species and subsequent elimination of benzene [15].

3.4. Spectroscopic studies

The IR spectrum of compound **I** showed an Re=O stretching frequency at 935 cm^{-1}, significantly lower than that of [ReO(DMT)$_4$]$^-$. In the ^{1}H NMR spectra, six distinct singlets arise from the six methyl groups of three non-equivalent DMT ligands with restricted rotation about the S–C bonds. The relative integral intensities were consistent with the stoichiometry of complex **I**. The FAB-MS spectrum of **I** exhibited a molecular ion at 876 (M^+) and fragmentation peaks at 739 (M^+-DMT), 614 (M^+-Ph$_3$P). The presence of the fragments (M^+-DMT) and (M^+-Ph$_3$P) may reflect relative weaker ligation of the axial Ph$_3$P and DMT ligands.

Compound **II** showed a medium intensity IR band at 2260 cm^{-1} assigned to ν(C≡N). One singlet at δ = 20.085 ppm in the ^{31}P{^{1}H} NMR revealed the presence of PPh$_3$. The methyl groups of the DMT ligands appeared as one singlet at 1.93 ppm, confirming free rotation about the C–S bonds. Relative integral intensities for the aliphatic methyl protons versus aromatic protons were consistent with the proposed stoichiometry.

The IR spectrum of complex **III** showed ν(Re=O) at 965 cm^{-1}. Only two methyl environments were observed in the ^{1}H NMR. This was consistent with an

Table 5
Positional parameters and their e.s.d.s for [Re(DMT)$_3$(PPh$_3$)(PPh$_2$H)]

Atom	*x*	*y*	*z*	*B* (Å^2)
Re	0.12351(5)	0.08071(2)	0.26074(3)	2.228(9)
S1	−0.0465(4)	0.0802(2)	0.1810(2)	3.20(8)
S3	0.0866(4)	0.0644(2)	0.3731(2)	3.39(9)
S4	0.3134(4)	0.1009(2)	0.2343(3)	3.60(9)
P1	0.1403(4)	−0.0178(2)	0.2279(2)	2.77(8)
P5	0.1397(4)	0.1820(2)	0.3005(2)	2.70(8)
C1	0.023(1)	−0.0741(7)	0.2327(9)	3.4(3)
C2	0.047(2)	−0.1212(9)	0.278(1)	5.4(5)
C3	−0.040(2)	−0.1638(8)	0.280(1)	6.4(5)
C4	−0.147(2)	−0.1639(9)	0.234(1)	6.5(5)
C5	−0.166(2)	−0.1179(9)	0.187(1)	6.0(6)
C6	−0.085(1)	−0.0721(8)	0.185(1)	4.8(4)
C7	0.189(2)	−0.0364(7)	0.1412(9)	3.8(4)
C8	0.143(2)	−0.0058(9)	0.081(1)	4.6(4)
C9	0.171(2)	−0.024(1)	0.014(1)	6.7(6)
C10	0.245(2)	−0.0701(9)	0.010(1)	6.8(5)
C11	0.288(2)	−0.103(1)	0.069(1)	7.9(6)
C12	0.260(2)	−0.0841(9)	0.134(1)	6.2(5)
C25	0.032(2)	0.2089(6)	0.3604(8)	3.4(4)
C26	0.073(2)	0.2458(7)	0.4174(9)	4.4(4)
C27	−0.019(2)	0.2696(9)	0.457(1)	5.3(5)
C28	−0.142(2)	0.256(1)	0.440(1)	5.3(5)
C29	−0.174(2)	0.216(1)	0.385(1)	6.1(6)
C30	−0.087(1)	0.1930(8)	0.3467(9)	4.0(4)
C31	0.288(1)	0.1992(7)	0.3516(9)	3.6(3)
C32	0.341(2)	0.1566(8)	0.401(1)	6.2(5)
C33	0.454(2)	0.168(1)	0.439(1)	7.9(6)
C34	0.512(2)	0.217(1)	0.435(1)	6.4(5)
C35	0.462(2)	0.259(1)	0.388(1)	7.4(6)
C36	0.351(2)	0.2483(9)	0.347(1)	5.6(5)
C37	0.127(1)	0.2418(6)	0.2368(8)	3.1(3)
C38	0.038(2)	0.2818(8)	0.231(1)	4.7(4)
C39	0.031(2)	0.3278(9)	0.181(1)	6.5(6)
C40	0.122(2)	0.3298(8)	0.136(1)	5.9(5)
C41	0.210(2)	0.2898(9)	0.137(1)	5.5(5)
C42	0.216(2)	0.2434(7)	0.1854(9)	4.5(4)
C43	0.068(2)	−0.0077(7)	0.4057(9)	4.2(4)
C44A	0.287(2)	−0.004(1)	0.464(1)	6.4(6)
C44	0.161(2)	−0.0357(9)	0.448(1)	5.1(5)
C45	0.138(2)	−0.0898(7)	0.480(1)	5.6(5)
C46	0.028(2)	−0.1145(8)	0.468(1)	6.3(6)
C47	−0.068(2)	−0.0881(8)	0.431(1)	5.7(5)
C48A	−0.153(2)	−0.003(1)	0.355(1)	5.9(5)
C48	−0.053(2)	−0.0319(8)	0.397(1)	4.7(4)
C49	0.405(1)	0.0509(7)	0.1943(9)	3.7(4)
C50	0.423(2)	0.0585(7)	0.1230(9)	3.7(4)
C50A	0.358(2)	0.1051(9)	0.078(1)	5.9(5)
C51	0.505(2)	0.0233(8)	0.093(1)	4.6(4)
C52	0.572(2)	−0.020(1)	0.133(1)	6.4(6)
C53	0.557(2)	−0.0267(9)	0.205(1)	5.2(5)
C54	0.477(1)	0.0077(9)	0.236(1)	4.6(4)
C54A	0.465(2)	0.003(1)	0.317(1)	6.2(6)
C55	−0.131(1)	0.1461(7)	0.1555(9)	3.3(3)
C56	−0.242(1)	0.1542(7)	0.183(1)	4.3(4)
C56A	−0.294(2)	0.1138(8)	0.234(1)	5.0(5)
C57	−0.312(2)	0.2028(8)	0.157(1)	4.9(4)
C58	−0.273(2)	0.2374(9)	0.108(1)	5.7(5)
C59	−0.166(2)	0.2293(8)	0.079(1)	6.1(5)
C60A	0.023(2)	0.1660(9)	0.067(1)	5.2(5)
C60	−0.090(1)	0.1798(7)	0.1022(9)	3.5(3)

Table 6
Selected bond lengths (Å) and angles (°) for [Re(DMT)$_3$(PPh$_3$)(PHPh$_2$)]

Bond lengths			
Re–S(1)	2.261(4)	Re–S(3)	2.255(4)
Re–S(4)	2.258(4)	Re–P(1)	2.370(4)
Re–P(5)	2.455(4)		
Bond angles			
S(1)–Re–S(3)	113.9(2)	S(1)–Re–S(4)	124.4(2)
S(1)–Re–P(1)	84.4(1)	S(1)–Re–P(5)	103.6(2)
S(3)–Re–S(4)	121.6(1)	S(3)–Re–P(1)	96.8(2)
S(3)–Re–P(5)	83.2(1)	S(4)–Re–P(1)	92.0(2)
S(4)–Re–P(5)	80.6(1)	P(1)–Re–P(5)	171.3(1)
Re–S(1)–C(55)	122.0(6)	Re–S(3)–C(43)	121.6(5)
Re–S(4)–C(49)	123.6(6)		

approximate square pyramidal structure with four equivalent DMT ligands as in the analogous [ReO(SAr)$_4$]$^-$ (SAr = TIPT, TIMT, DIPT) [1]. One *ortho*-methyl on each DMT aryl ring is *syn* to the apical oxo group, with the other *anti*.

Compound **IV** has an IR band at 2320 cm^{-1} assigned to ν(P–H). The ^{31}P{^{1}H} NMR spectrum of **IV** shows doublets at δ 11.59 ppm due to PPh$_3$ and δ −11.745 ppm due to PHPh$_2$, with a coupling constant J(P–P) = 254.9 Hz. This value is typical for *trans* phosphine ligands. The Me groups of the thiolate ligands appear as singlets at 1.86, 2.30, 2.48 ppm (ratio 1:1:1) in the ^{1}H NMR spectrum, rather than the two singlets ratio 2:1 expected for the two up one down configuration. The integral ratios for the methyl and phenyl resonances were consistent with the proposed formulation. The observed pattern for the methyl groups presumably arises from inequivalence of the methyls of the thiolate ligand adjacent to the PPh$_3$ group.

4. Conclusions

The intermediate [ReO(DMT)$_3$(PPh$_3$)] in the substitution reaction of [ReOCl$_3$(PPh$_3$)$_2$] with DMT anion can be isolated by the use of Me$_3$SiDMT and exhibits significant differences both in structural geometry and chemical behaviour from [ReO(DMT)$_4$]$^-$. The synthesis of [Re(DMT)$_3$(PPh$_3$)(PHPh$_2$)] demonstrates that the M(SAr)$_3$ core (SAr = sterically hindered aromatic thiolate) can in fact accommodate both the bulky PPh$_3$ and another moderately sized PHPh$_2$ ligand in the axial sites.

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