DALTON
FULL PAPER

Sulfur–carbon bond cleavage in reactions of rhenium(V) complexes of NS_3 ligands with tertiary phosphines: crystal and molecular structures of $[ReO(SCH_2CH_2NCOCH_2S)(PMe_2Ph)]$ and $[ReO(SCMe_2CH_2NCOCH_2SCH_2CH_2S)(PMePh_2)]$

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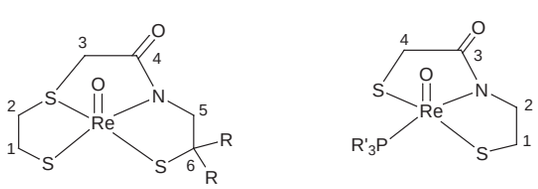
The neutral rhenium(V) oxo complex $[ReO\{S(CH_2)_2SCH_2CONCH_2S\}]$ reacted with tertiary phosphines PMe_2Ph or $PMePh_2$ to give the rhenium(V) species $[ReO(NS_2)(PR'_3)]$ ($PR'_3 = PMe_2Ph$ **1**, or $PMePh_2$ **2**), with loss of a SCH_2CH_2 group. The introduction of dimethyl substituents at C(6) of the tetradentate ligand prevents C–S bond cleavage and $[ReO(NS_2)(PR'_3)]$ type complexes were formed ($PR'_3 = PMe_2Ph$ **3**, or $PMePh_2$ **4**). The crystal and molecular structures of complexes **1** and **4** have been determined. Complex **1** is essentially square pyramidal with an apical oxo group and a PNS_2 donor set in the basal sites. The geometry of **4** is essentially octahedral with a thiolate sulfur of the NS_3 ligand *trans* to the oxo group.

Introduction

Tertiary phosphine ligands have a strong stabilising effect on rhenium and technetium complexes in both intermediate and low oxidation sites.[1] The stability of such complexes has been exploited in the development of cationic technetium complexes with tertiary and ditertiary phosphines for use as radiopharmaceuticals for heart imaging.[2] A common feature of the chemistry of tertiary phosphine complexes of Tc and Re is that they are prepared by the removal of the oxo groups of a high oxidation state precursor as the phosphine oxide. Thus technetium(V) oxo complexes of the type $[TcO(N_2O_2)Cl]$ (N_2O_2 = Schiff base tetradentate ligand) can be reduced to technetium(III) complexes $[Tc(N_2O_2)(PR_3)_2]$. It is also well established that alkyl substituted phosphines can reduce $[ReOCl_3(PPh_3)_2]$ to the rhenium(III) complexes $[ReCl_3(PR_3)_3]$.[3] We hoped to use an analogous reaction of $[ReO(NS_3)]$ with tertiary phosphines to produce complexes of the type $[Re(NS_3)(PR_3)_2]$. However, instead of the expected removal of the oxo group, cleavage of the NS_3 ligand occurred with loss of an SCH_2CH_2 group. We here describe the characterisation of the product of this reaction and the effects of variation of the type of phosphine used and the substituents on the tetradentate ligand backbone. The reaction of $[ReO(L^1)]$ and $[ReO(L^2)]$ with the ditertiary phosphine $Ph_2PCH_2CH_2PPh_2$ gives a much more complex series of reactions which will be reported elsewhere.



$R'_3P = PMe_2Ph, PMePh_2$
$R = R = H, L^1$
$R = R = Me, L^2$

Results and discussion

The reaction of $[ReO(L^1)]$ with PMe_2Ph or $PMePh_2$ in MeOH gave deep red complexes $[ReO(SCH_2CH_2NCOCH_2S)(PR'_3)]$ ($PR'_3 = PMe_2Ph$ **1** or $PMePh_2$ **2**) in *ca.* 50% yield. These complexes are stable in the solid and in solution, and are non-electrolytes in dichloromethane solution. In the IR spectra ν(Re=O) appears as a medium intensity band at around 965–970 cm^{-1} and the $^{31}P\{^1H\}$ NMR shows a singlet consistent with the presence of the single phosphine ligand. Analytical, NMR (^1H and ^{13}C) data and the crystal structure (see below) are consistent with loss of the C(1)–C(2)–S(1) group and formation of a novel trianionic NS_2 ligand. Full assignments of peaks in the ^1H and ^{13}C NMR spectra was made using two-dimensional correlation spectroscopy (COSY).

It is of interest in radiopharmaceutical terms that the complex is neutral, and that the phosphine ligand could provide a potential site of conjugation if activated carboxylic esters are introduced at the 4 positions of the phenyl ring.

By contrast, reaction of the same tertiary phosphines with $[ReO(L^2)]$ [L^2 is dimethylated at C(6) of the ligand backbone] results in six-co-ordinate complexes of the type $[ReO(L^2)(PR'_3)]$ ($PR'_3 = PMe_2Ph$ **3** or $PMePh_2$ **4**). The analytical, spectroscopic and the crystal structure data are consistent with retention of the ligand L^2 intact. For complex **4**, IR, the general broadness of the ^1H NMR, the observation of two species in the HPLC, and the two $^{31}P\{^1H\}$ signals of approximately 1:1 intensity suggest the presence of two isomers both in the solid state and in solution. There are several possibilities for isomers, one being the phosphine ligand *cis* or *trans* to the oxo group, but the similarity of the $^{31}P\{^1H\}$ NMR suggests this is not the case. The amount of the two isomers present is temperature dependent suggesting a fluxional process involving the orientation of the ligand backbone. The smaller PMe_2Ph ligand does not create as much steric pressure at the ligand backbone, and only one isomer is observed for complex **3**.

The dealkylation of thioethers in reactions with transition metal complexes is well known, and the formation of $[ReS(SCH_2CH_2S)_2]^-$ on reaction of $[ReOCl_3(PPh_3)_2]$ with $HSCH_2CH_2SH$ involves loss of an SCH_2CH_2 fragment.[4] Recently Blower and co-workers[5] have suggested that the reduction of $[Re([9]aneS_3)_2]^{2+}$ leads to population of C–S σ* orbitals and consequent loss of ethylene to give $[Re([9]aneS_3)(SCH_2CH_2SCH_2CH_2S)]^+$. In the systems reported here it is not immediately obvious why methylation of the backbone should inhibit C–S bond cleavage leading to the isolation of complex **4**, particularly as the methyl groups are remote from the cleavage site.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**.

Re–O	1.67(2)	Re–P	2.429(6)
Re–N	1.97(3)	N–C(3)	1.39(4)
Re–S(1)	2.263(7)	N–C(4)	1.46(4)
Re–S(2)	2.278(7)		
O–Re–N	110.0(9)	O–Re–P	99.6(7)
O–Re–S(1)	115.4(8)	N–Re–P	150.3(6)
N–Re–S(1)	83.2(8)	C(3)–N–C(2)	114(3)
O–Re–S(2)	113.2(8)	C(3)–N–Re	129(2)
N–Re–S(2)	80.7(8)	C(2)–N–Re	117(3)
S(1)–Re–S(2)	131.4(3)		

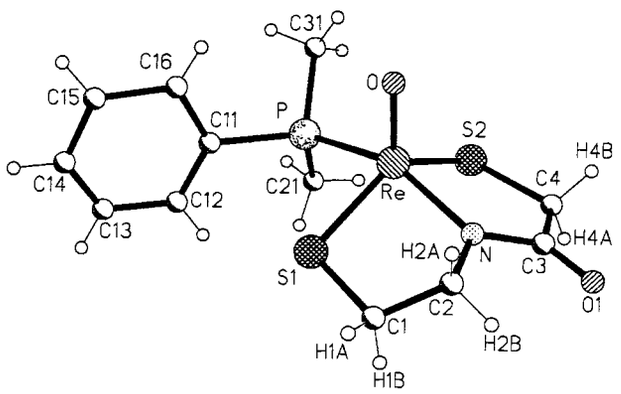


Fig. 1 Molecular structure of complex **1**.

However, the structures of **1** and **4** are very similar, with the main difference being the presence of the extra SCH_2CH_2 group in **4**. It is tempting to suggest that an intermediate analogous to **4** is involved in the formation of **1** but we were unable to detect this spectroscopically.

Crystal structures

[ReO(SCH$_2$CH$_2$NCOCH$_2$S)(PMe$_2$Ph)] 1. The molecular structure of complex **1** is shown in Fig. 1. Selected bond lengths and angles appear in Table 1. The overall geometry about the Re is best described as square pyramidal, with an apical oxo group. The rhenium–nitrogen bond distance of 1.97(3) Å is in the range observed in other rhenium(v) complexes with deprotonated nitrogen atoms.[6] The planar geometry about the N atom is also indicative of sp^2 hybridisation with donation of a nitrogen lone pair to the metal. The Re–S and Re–P distances are unremarkable, and typical of rhenium(v) complexes with such donors.

[ReO(L^2)(PMePh$_2$)] 4. The molecular structure of complex **4** is shown in Fig. 2. Selected bond lengths and angles appear in Table 2. The crystal consists of two monomeric neutral, independent and well separated [ReO(L^2)(PMePh$_2$)] molecules A and B. In both the overall geometry surrounding the rhenium is best described as distorted octahedral, with four sites in the plane S(1), O(3), N(1) and P(1), for A and S(4), O(1), N(2) and P(2) for B, while S(2) and S(3) occupy the other positions for A, with an S(2)–Re–S(3) angle of 163.46(10)°. The corresponding positions for B are occupied by S(5) and S(6) with an S(5)–Re–S(6) angle of 164.09(10)°. The rhenium–oxo bond distances are very similar, and within the range found for rhenium(v) mono-oxo-complexes.[7] The Re–P distances for A [2.440(3) Å] and B [2.442(3) Å] are unexceptional and fall within the range found for other rhenium(v) complexes.[6] The Re–S(1) [or Re–S(4)] bond distances of *ca.* 2.51 Å are greater than the Re–S(2) [or Re–S(5)] and Re–S(3) [or Re–S(6)] distances which can be attributed to the *trans* influence of the oxide ligand. This weakening of the Re–S bond may be significant in promoting the loss of the CH_2CH_2S unit. The two symmetry independent molecules A and B in the asymmetric unit are chemically

Table 2 Selected bond lengths (Å) and angles (°) for molecules A and B of complex **4**.

Molecule A		Molecule B	
Re(1)–S(1)	2.512(3)	Re(2)–S(4)	2.514(3)
Re(1)–S(2)	2.467(3)	Re(2)–S(5)	2.467(3)
Re(1)–S(3)	2.266(3)	Re(2)–S(6)	2.288(3)
Re(1)–P(1)	2.440(3)	Re(2)–P(2)	2.442(3)
Re(1)–O(3)	1.690(7)	Re(2)–O(1)	1.695(8)
Re(1)–N(1)	2.050(9)	Re(2)–N(2)	2.037(9)
N(1)–C(4)	1.315(14)	N(2)–C(4)	1.348(14)
N(1)–C(5)	1.488(14)	N(2)–C(5)	1.479(13)
S(3)–Re(1)–S(2)	163.46(10)	S(6)–Re(2)–S(5)	164.09(10)
S(3)–Re(1)–P(1)	90.04(10)	S(6)–Re(2)–P(2)	92.48(10)
O(3)–Re(1)–S(1)	162.2(3)	O(1)–Re(2)–S(4)	160.1(3)
O(3)–Re(1)–S(3)	107.1(3)	O(1)–Re(2)–S(6)	105.2(3)
O(3)–Re(1)–P(1)	91.1(3)	O(1)–Re(2)–P(2)	108.1(4)
O(3)–Re(1)–N(1)	106.7(4)	O(1)–Re(2)–N(2)	108.1(4)
N(1)–Re(1)–P(1)	162.2(3)	N(2)–Re(2)–P(2)	162.9(3)

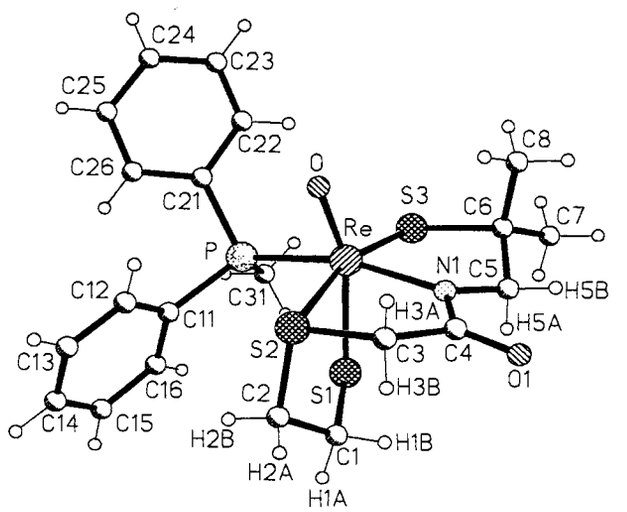


Fig. 2 Molecular structure of complex **4**.

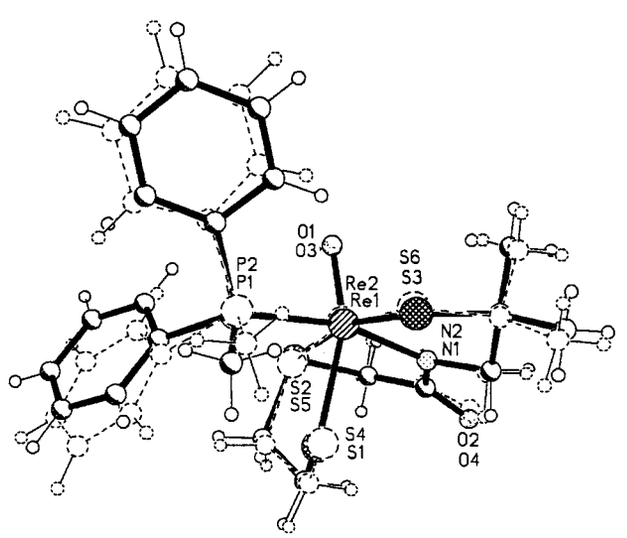


Fig. 3 Superposition of the symmetry independent molecules of complex **4**.

equivalent and differ only by a slightly different orientation of the phosphine phenyl groups (Fig. 3), arising from rotation about the Re–P bond.

Experimental

The complexes [ReO(L^1)] and [ReO(L^2)] were prepared

Table 3 Details of crystal structure determinations of complexes $[ReO(SCH_2CH_2NCOCH_2S)(PMe_2Ph)]$ **1** and $[ReO(L^2)(PMePh_2)]$ **4**.

	1	**4**
Empirical formula	$C_{12}H_{17}NO_2PReS_2$	$C_{21}H_{27}NO_2PReS_3$
M	488.56	638.79
T/K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	9.764(8)	10.172(2)
b/Å	20.168(3)	15.350(2)
c/Å	9.1109(10)	15.994(2)
α/°		73.73
β/°	116.602(3)	86.67(2)
γ/°		73.41(2)
U/Å^3	1604.3(13)	2296.8(6)
Z	4	4
μ/mm^{-1}	7.931	2.826
Reflections collected	1501	9462
Independent reflections (R_{int})	1501 (0.00)	6284 (0.1160)
Data/restraints/parameters	1451/0/173	6284/1/523
Goodness of fit on F^2	1.031	1.103
R indices [$I > 2\sigma(I)$]	$R1 = 0.0874$, $wR2 = 0.2211$ (for 1233)	0.0613, 0.1543 (for 5414)
Largest difference peak and hole/e Å^{-3}	3.224, −3.763	4.671, −2.670

according to the literature methods.[8] All other reagents were from Aldrich Chemical Co. Elemental analyses were performed by Anorganisch und Analytische Chemie, der Technischen Universität München and Brunel University (MEDAC Ltd., UK). The IR spectra were recorded as KBr discs or Nujol mulls (NaCl plates) using a Perkin-Elmer 1600 series FTIR spectrometer, NMR spectra on a JEOL EX 270 spectrometer at 270 (^{1}H) or 67.5 MHz (^{13}C) and fast-atom bombardment (FAB) mass spectra on an MS 50 instrument, using 3-nitrobenzyl alcohol as the matrix material.

The atom numbering scheme for the complexes is the same as that employed in the X-ray crystallography section.

Preparations

$[ReO(SCH_2CH_2NCOCH_2S)(PMe_2Ph)]$ 1. The compound PMe_2Ph (0.125 ml, 0.88 mmol) was added to a stirred solution of $[ReO(L^1)]$ (0.162 g, 0.39 mmol) in 30 ml MeOH, and the reaction mixture changed from orange to red-brown. The mixture was heated under reflux for 1 h then filtered, and the volume of the filtrate reduced to *ca.* 5 ml under reduced pressure. Diethyl ether (25 ml) was added and the brown precipitate filtered off. The filtrate was allowed to stand overnight to give red crystals, which were collected, washed with Et_2O and dried under vacuum to give 0.1 g (52%) of compound **1** (Found: C, 29.8; H, 3.6; N, 2.9. Calc. for $C_{12}H_{17}NO_2PReS_2$: C, 29.5; H, 3.5; N, 2.9%). IR (KBr disc): 1613 [ν(C=O)], 968 [ν(Re=O)], 747, 720 cm^{-1} (phenyl). NMR ($CDCl_3$): ^{1}H, δ 7.81–7.73 (2 H, m, Ph), 7.58–7.55 (3 H, m, Ph), 5.35 (1 H, d, d, J_{HH} = 6, 6.5, H2A), 4.16–3.98 (2 H, d, d, J_{HH} = 17, H4A, H4B), 3.49–3.19 (2 H, m, H1A, H2B), 2.76–2.65 (1 H, t, d, J_{HH} = 6.5, 6 Hz, H1B), 2.22 (3 H, s, Me) and 2.18 (3 H, s, Me); ^{13}C, δ 190.5 (C3), 131.9 (Ph), 131.3 (Ph), 13.2 (Ph), 129.2 (Ph), 129 (Ph), 56 (C2), 42.4 (d, J_{PC} = 4, C1), 41.2 (d, J_{PC} = 4.9, C4), 17.45 (d, J_{PC} = 31 Hz, Me) and 16.9 (d, J_{PC} = 31 Hz, Me); ^{31}P-{^{1}H}, δ 0.77, FAB mass spectrum: m/z = 490, $[M + 1]^+$. HPLC: retention time = 2.5 min, single species.

Crystals suitable for X-ray diffraction analysis were obtained by the addition of Et_2O to the reaction mixture.

$[ReO(SCH_2CH_2NCOCH_2S)(PMePh_2)]$ 2. The method used to prepare complex $[ReO(NS_2)(PMePh_2)]$ was used, with $PMePh_2$ (0.216 ml, 0.116 mmol) in place of PMe_2Ph. The quantities of other reagents were adjusted accordingly, and an identical work-up procedure was used to give 70 mg (52%) of the required compound **2** as deep red crystals (Found: C, 37.6; H, 3.5; N, 2.5. Calc. for $C_{17}H_{19}NO_2PReS_2$: C, 37.1; H, 3.5; N, 2.5%). IR (KBr disc): 1623 [ν(C=O)], 964 [ν(Re=O)], 760, 741 cm^{-1} (phenyl). NMR ($CDCl_3$): ^{1}H, δ 7.80–7.70 (4 H, m, Ph), 7.54–7.52 (6 H, m, Ph), 5.39 (1 H, d, d, J_{HH} = 5.5, 6, H2A), 4.13 (1 H, d, J_{HH} = 17, H4A), 4 (1 H, d, J_{HH} = 17, H4B), 3.38–3.21 (2 H, m, H1A, H2B), 2.75–2.65 (1 H, d, t, J_{HH} = 7, 6.5, 5, H1B) and 2.37 (3 H, d, J_{HH} = 10 Hz, Me); ^{13}C, δ 190.5 (C3), 132.9 (d, J_{PC} = 5, Ph), 132.7 (d, J_{PC} = 5, Ph), 131.9 (d, J_{PC} = 3, Ph), 131.1 (d, J_{PC} = 22.5, Ph), 130.3 (d, J_{PC} = 23.5, Ph), 129 (d, J_{PC} = 11, Ph), 56 (C2), 42.5 (d, J_{PC} = 4, C1), 41.4 (d, J_{PC} = 4, C4) and 17.33–16.76 (d, J_{PC} = 39 Hz, Me); ^{31}P-{^{1}H}, δ 14.30 (s). FAB mass spectrum: m/z = 552, $[M + 1]^+$; and 1103, $[2M + 1]^+$. HPLC: retention time = 1.5 min, single species.

$[ReO(L^2)(PMe_2Ph)]$ 3. The method used to prepare this complex was similar to that for **1**, with $[ReO(L^2)]$ (0.1 g, 0.22 mmol) in place of $[ReO(L^1)]$. The quantities of other reagents were adjusted accordingly. An identical work-up was used to give 71 mg (55%) of **3** as brown crystals (Found: C, 33.7; H, 4.5; N, 2.4. Calc. for $C_{16}H_{25}NO_2PReS_3$: C, 33.3; H, 4.4; N, 2.4%). IR (KBr disc): 1606 [ν(C=O)], 907 [ν(Re=O)], 750, 719 cm^{-1} (phenyl). NMR ($CDCl_3$): ^{1}H, δ 7.74–7.68 (2 H, m, Ph), 7.55–7.42 (3 H, m, Ph), 4.61 (1 H, d, J_{HH} = 13, H5B), 3.68 (2 H, s, H3A, H3B), 3.20 (1 H, d, J_{HH} = 12, H5A), 2.51 (3 H, m, H1B, H2A, H2B), 2.25 (3 H, d, J_{PH} = 10 Hz, Me), 2 (3 H, s, Me), 1.99 (3 H, s, Me_A), 1.71 (1 H, s, H1A) and 1.47 (3 H, s, Me_B); ^{13}C, δ 183.5 (C4), 139.2 (Ph), 131 (Ph), 130.5 (Ph), 128.5 (Ph), 128.4 (Ph), 67.2 (C5), 65.6 (d, J_{PC} = 6 Hz, C6), 44 (C3), 43.2 (C2), 34.2 (C1), 29.6 (6-Me_A), 27.8 (6-Me_B), 17.18 (d, J_{PC} = 28, PMe) and 14.4 (d, J_{PC} = 44 Hz, PMe); ^{31}P-{^{1}H}, δ −37.82 (s). FAB mass spectrum: m/z = 380, $[M - SCH_2CH_2 + PPhMe]^+$; 412, $[M - CH_2CH_2 + PPhMe_2]^+$; 440, $[M - PPhMe_2]^+$; 578, $[M + 1]^+$; and 1155, $[2M + 1]^+$. HPLC: retention time = 4 min, single species.

$[ReO(L^2)(PMePh_2)]$ 4. The method used to prepare this complex was similar to that for **3**, with $PMePh_2$ (0.14 ml, 0.75 mmol) in place of PMe_2Ph. The quantities of other reagents were adjusted accordingly. An identical work-up procedure was used to give **4** as deep brown crystals. Yield: 0.11 g (52%) (Found: C, 39.7; H, 4.3; N, 2.3. Calc. for $C_{21}H_{27}NO_2PReS_3$: C, 39.5; H, 4.3; N, 2.2%). IR (KBr disc): 1606 (isomer A), 1598 (isomer B) [ν(C=O)], 904 (isomer A), 895 (isomer B) [ν(Re=O)], 736, 692 cm^{-1} (phenyl). NMR ($CDCl_3$): δ (−50 °C), ^{1}H, 7.82–7.75 (2 H, t, $^3J_{HH}$ = 8, 9, Ph), 7.67–7.58 (6 H, m, Ph), 7.55–7.39 (2 H, m, Ph), 4.65 (1 H, d, J_{HH} = 13, H5B), 3.89 (2 H, s, H3A, H3B), 3.21 (1 H, d, J_{HH} = 13, H5A), 2.65–2.22 (3 H, m, H1B, H2A, H2B), 2.33 (3 H, d, J_{PH} = 9.5 Hz, PMe), 2.1 (3 H, s, Me_A), 1.6 (3 H, s, Me_B) and 1.17 (1 H, m, H1A); ^{13}C, δ 184.2

(C4), 135.6 (d, J_{PC} = 53, Ph), 134.5 (d, J_{PC} = 39, Ph), 133.2 (d, J_{PC} = 9.5, Ph), 132.5 (d, J_{PC} = 9.5, Ph), 130.8 (d, J_{PC} = 19.5, Ph), 128.4 (d, J_{PC} = 9 Hz, Ph), 66.70 (C6), 66.3 (C5), 43.7 (C1), 42.1 (C2), 34.8 (C3), 29.8 (6-Me_A), 27.6 (6-Me_B) and 17.7 (d, J_{PC} = 44 Hz, PMe); ^{31}P-{^{1}H}, δ (isomer A, isomer B, ratio A : B) (21 °C) −22.79, −22.42, 1.1 : 1; (−30 °C) −21.31, −25.89, 4.7 : 1; (−50 °C) −20.69, −26.01, 9 : 1. FAB mass spectrum: m/z = 352, $[M - SCH_2CH_2 + PPh_2Me]^+$; 412, $[M - (CH_2CH_2 + PPh_2Me)]^+$; 440, $[M - PPh_2Me]^+$; 640, $[M + 1]^+$. HPLC: retention time = 1.5, 4 min; two species, 1 : 1 ratio.

Crystals suitable for X-ray diffraction analysis were obtained by the addition of Et_2O to the reaction mixture.

Crystal structure determinations

Data collection. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer {or in the case of [ReO(L^2)-($PMePh_2$)] on a Delft instruments FAST area detector}[9] with monochromated Mo-Kα radiation. Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 2 h of exposure. Losses of intensity were observed and linearly corrected during processing. Three standard reflections were measured every 200 to check the crystal orientation. The data were corrected for Lorentz-polarisation factors and an absorption correction was applied using ψ scans of nine reflections

Structure analysis and refinement. The structures were solved by direct methods[10] and refined on F_o^2 by full matrix least squares.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealised positions with U_{iso} free to refine. The weighting schemes used gave satisfactory agreement analyses.

CCDC reference number 186/1111.

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