

Mixed-ligand complexes of rhenium III*. Synthesis, characterisation and structures of [ReN(Me₂PhP)₂(mnt)] and [ReN(Me₂PhP)(2,6-DMTP)(morph tcb)] (Me₂PhP = dimethylphenylphosphine; 2,6-DMTP⁻ = 2,6-dimethyl- thiophenolate; morph tcb⁻ = *N*-(morpholinylthiocarbonyl)- benzamidinate)

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(Received June 28, 1993)

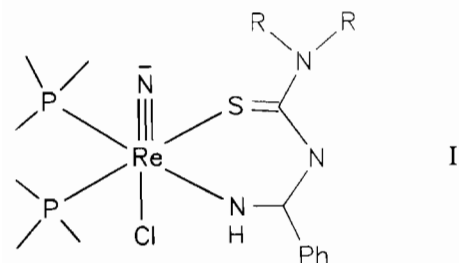
Abstract

Novel rhenium(V) nitrido complexes have been prepared by ligand exchange procedures starting from [ReN(Cl)(Me₂PhP)₂(morph tcb)] and 2,6-dimethylthiophenol, 2,6-DMTPH, or sodium 1,2-dicyanoethene-1,2-dithiolate, Na₂mnt. [ReN(Me₂PhP)(2,6-DMTP)(morph tcb)] and [ReN(Me₂PhP)₂(mnt)] are neutral, air-stable complexes which have been spectroscopically characterised and studied by X-ray diffraction. [ReN(Me₂PhP)₂(mnt)] crystallises triclinic in the space group *P*1̄ (*a* = 9.802(3), *b* = 10.215(2), *c* = 12.389(3) Å, α = 69.38(2), β = 85.84(2), γ = 78.84(6)°) with *Z* = 2. The final *R* value is 0.021. The rhenium atom is five-coordinate with the nitrido nitrogen at the apex of a distorted square pyramid. [ReN(Me₂PhP)(2,6-DMTP)(morph tcb)] crystallises monoclinic in the space group *P*2₁/*c* (*a* = 11.609(2), *b* = 11.677(1), *c* = 21.923(6) Å, β = 92.59(1)°) with *Z* = 4. Structure solution and refinement based on 4626 reflections converged at *R* = 0.032. The coordination polyhedron is a square pyramid which is significantly distorted towards a trigonal bipyramid.

Key words. Crystal structures; Rhenium complexes, Nitrido complexes

Introduction

Recently, we described the synthesis and characterisation of a novel class of rhenium(V) mixed-ligand complexes, [ReN(Cl)(Me₂PhP)₂(R₂tcb)] (I), by the reaction of [ReNCl₂(Me₂PhP)₃] with *N*-(*N,N*-dialkylthiocarbamoyl)benzamidines, HR₂tcb [1]. The complexes



*For Part II see ref. 2

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possess centres of different reactivities, namely the only weakly bonded chloro ligand, the two Me₂PhP and the chelate ligands as well as the nucleophilic nitrido nitrogen. With alkali halides and pseudohalides a selective exchange of Cl⁻ could be achieved to yield [ReN(X)(Me₂PhP)₂(R₂tcb)] complexes (X = I, CN, NCS, N₃), whereas with Me₃SiNCS the thionitrosyl-rhenium(I) complex [Re(NS)(NCS)₂(Me₂PhP)₃] is formed [2]

In the present paper, we study the reaction of [ReN(Cl)(Me₂PhP)₂(morph tcb)] (morph tcb⁻: R₂tcb⁻ with R₂ = morpholinyl) with 2,6-dimethylthiophenol (2,6-DMTPH) and disodium 1,2-dicyanoethene-1,2-dithiolate, Na₂mnt.

Experimental

Syntheses

[ReN(Cl)(Me₂PhP)₂(morph tcb)] was prepared as outlined in ref. 1. Na₂mnt was synthesised from sodium

cyanide and CS₂ [3]. 2,6-Dimethylthiophenol was purchased commercially (Aldrich).

[ReN(Me₂PhP)(2,6-DMTP)(morph tcb)]

76 mg (0.1 mmol) [ReN(Cl)(Me₂PhP)₂(morph tcb)] were dissolved in 50 ml methanol and an excess of 2,6-DMTPH (0.5 ml) was added. The mixture was refluxed for 2 h. During this time the colour changed from yellow to red. After removing the solvent in vacuum, a red oil remained which was redissolved in about 5 ml CHCl₃. 5 ml iso-propanol were added and after slow evaporation red crystals of [ReN(Me₂PhP)(2,6-DMTP)(morph tcb)] deposited which were filtered off and washed with iso-propanol and diethyl ether. Yield 54 mg (75% based on Re). *Anal.* Found: C, 45.9; H, 4.5; N, 7.3; S, 8.9. Calc. for C₂₈H₃₄N₄OS₂PRe: C, 46.4; H, 4.7; N, 7.7; S, 8.8%. IR (cm⁻¹): ν(Re≡N) 1072, ν(N-H) 3297. ¹H NMR (ppm): CH₃ (2,6-DMTP) 1.56 s (6H), CH₃ (phosphine) 2.0–2.2 m (6H), CH₂ 3.75 (broad) (4H) and 4.15 (broad) (4H), phenyl 6.8–7.9 m (13H). FAB-MS: *m/z* = 724 (*M*⁺), *m/z* = 587 [ReN(Me₂PhP)(morph tcb)]⁺, *m/z* = 586 [ReN(2,6-DMTP)(morph tcb)]⁺, *m/z* = 508 [ReN(Me₂PhP)(2,6-DMTP)S]⁺.

[ReN(Me₂PhP)₂(mnt)]

75 mg (0.1 mmol) [ReN(Cl)(Me₂PhP)₂(morph tcb)] were dissolved in about 50 ml methanol and 19 mg (0.1 mmol) Na₂mnt in about 10 ml methanol were added. The mixture was refluxed for about 2 h. A colourless solid (NaCl) was filtered off and upon standing overnight a yellow solid was precipitated, which was collected and washed with methanol and ether. Recrystallisation from CH₂Cl₂/iso-propanol gave yellow crystals. Yield 30 mg (48% based on Re). *Anal.* Found: C, 38.5; H, 3.4; N, 7.1; S, 11.0. Calc. for C₂₀H₂₂N₃S₂P₂Re: C, 38.9; H, 3.6; N, 6.8; S, 10.4%. IR (cm⁻¹): ν(Re≡N) 1071, ν(C≡N) 2200. ¹H NMR (ppm): CH₃ 1.2–2.1 m (12H), phenyl 6.9–7.7 m (10H). FAB-MS: *m/z* = 617 (*M*⁺), *m/z* = 540 [*M* – Ph]⁺, *m/z* = 479 [ReN(Me₂PhP)(mnt)]⁺.

Physical measurements

Routine IR spectra were recorded as KBr discs on a Specord 75 IR.

¹H NMR spectra were obtained in CDCl₃ solutions on a Bruker WM-400 spectrometer with TMS as internal standard.

Mass spectra were recorded on a MAT 701 A spectrometer (Finnigan). For the FAB⁺ measurements xenon was used as primary beam gas. The ion gun was

TABLE 1 Crystal data collection and structure refinement parameters

	[ReN(Me ₂ PhP)(2,6-DMTP)(morph tcb)]	[ReN(Me ₂ PhP) ₂ (mnt)]
Crystal dimensions (mm)	0.3 × 0.2 × 0.2	0.2 × 0.15 × 0.1
Formula	C ₂₈ H ₃₄ N ₄ OS ₂ PRe	C ₂₀ H ₂₂ N ₃ S ₂ P ₂ Re
Molecular weight	723.91	619.69
Space group	monoclinic <i>P</i> 2 ₁ / <i>c</i>	triclinic <i>P</i> $\bar{1}$
Lattice dimensions		
<i>a</i> (Å)	11.609(3)	9.802(3)
<i>b</i> (Å)	11.677(1)	10.215(2)
<i>c</i> (Å)	21.923(6)	12.389(3)
α (°)	90	69.38(2)
β (°)	92.59(1)	85.88(2)
γ (°)	90	78.84(2)
<i>V</i> (Å ³)	2968	1139
<i>D_c</i> (g cm ⁻³)	1.619	1.798
Radiation used, λ (Å)	Mo K α (0.70930)	Mo K α (0.70930)
Scan type	ω	$\omega/2\theta$
Absorption coefficient (cm ⁻¹)	46.63	28.66
Absorption correction	DIFABS	DIFABS
<i>T_{min}</i>	0.8254	0.9375
<i>T_{max}</i>	0.1492	1.0510
Range of <i>h, k, l</i>	0 → 14, 0 → 14, -27 → 27	0 → 11, -12 → 12, -14 → 14
Weighting scheme	1/ σ_F^2	1/ σ_F^2
Total unique data	6300	4206
Observed data (<i>I</i> > 3 σ (<i>I</i>))	4626	3549
No. parameters	334	319
<i>R</i>	0.032	0.021
<i>R_w</i>	0.042	0.027
Measuring temperature (°C)	-50	-50
Programs used	SDP [4]	SDP [4]

TABLE 2 Fractional positional parameters^a for [ReN(Me₂PhP)₂(2,6-DMTP)(morph tcb)]

Atom	x/a	y/b	z/c	B
Re	0.24180(2)	0.01634(2)	0.14277(1)	2.052(4)
S1	0.2528(2)	0.1829(2)	0.08392(9)	3.03(4)
S2	0.1119(2)	-0.1246(2)	0.17208(9)	2.97(4)
P	0.1514(2)	0.1337(2)	0.21637(9)	2.52(4)
O	0.4142(6)	0.4350(5)	-0.0795(3)	5.0(1)
N1	0.3629(5)	0.0025(6)	0.1851(3)	3.1(1)
N2	0.2607(5)	-0.0756(5)	0.0621(3)	2.6(1)
N3	0.3368(6)	0.0540(5)	-0.0105(3)	2.7(1)
N4	0.3833(6)	0.2420(5)	-0.0060(3)	3.0(1)
C1	0.3297(6)	0.1529(6)	0.0187(3)	2.5(1)
C2	0.2958(6)	-0.0464(6)	0.0080(3)	2.5(1)
C3	0.3898(8)	0.3584(7)	0.0200(4)	3.7(2)
C4	0.3471(9)	0.4432(7)	-0.0272(4)	4.2(2)
C5	0.4478(8)	0.2321(7)	-0.0623(4)	3.8(2)
C6	0.4036(9)	0.3224(8)	-0.1064(4)	4.5(2)
C10	0.2979(6)	-0.1368(6)	-0.0410(3)	2.4(1)
C11	0.3847(7)	-0.1349(7)	-0.0821(4)	3.1(2)
C12	0.3897(8)	-0.2225(7)	-0.1261(4)	3.9(2)
C13	0.3079(9)	-0.3051(7)	-0.1301(4)	4.1(2)
C14	0.2173(9)	-0.3065(7)	-0.0898(4)	3.9(2)
C15	0.2140(8)	-0.2223(7)	-0.0444(4)	3.4(2)
C21	0.0140(7)	0.1928(9)	0.1855(5)	4.8(2)
C22	0.1159(9)	0.0642(8)	0.2876(4)	4.4(2)
C30	0.2333(6)	0.2579(6)	0.2424(3)	2.4(1)
C31	0.1830(7)	0.3425(7)	0.2773(4)	3.5(2)
C32	0.2475(8)	0.4337(8)	0.3009(4)	4.2(2)
C33	0.3642(7)	0.4419(7)	0.2896(4)	3.5(2)
C34	0.4154(7)	0.3583(7)	0.2553(4)	3.4(2)
C35	0.3502(7)	0.2668(7)	0.2316(4)	3.1(2)
C40	0.1228(7)	-0.2579(7)	0.1327(3)	2.9(1)
C41	0.0357(7)	-0.2877(7)	0.0869(4)	3.5(2)
C42	0.0355(9)	-0.3993(8)	0.0632(4)	4.4(2)
C43	0.1202(9)	-0.4782(8)	0.0837(4)	5.0(2)
C44	0.2051(9)	-0.4474(8)	0.1272(4)	4.6(2)
C45	0.2073(8)	-0.3358(7)	0.1515(4)	3.5(2)
C51	0.2983(9)	-0.3040(8)	0.2000(5)	4.7(2)
C52	-0.0532(8)	-0.2031(9)	0.0644(5)	4.8(2)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\langle (4/3)[a^2B_{(1,1)} + b^2B_{(2,2)} + c^2B_{(3,3)} + ac(\cos \beta)B_{1,3}] \rangle (\text{\AA}^2)$.

operated at 8 kV and 100 μ A (probe temperature: 30 °C); nitrobenzylalcohol was used as matrix.

X-ray diffraction

X-ray data were collected on an Enraf-Nonius CAD 4 diffractometer. The unit cell dimensions were determined from the angular settings of 25 high angle reflections. The structures were solved by the heavy-atom Patterson method. All non-hydrogen atoms were located from successive Fourier maps. Empirical absorption correction (DIFABS) was applied. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed at calculated positions and included in the structure-factor calculations. The final difference Fourier maps showed

TABLE 3. Fractional positional parameters^a for [ReN(Me₂PhP)₂(mnt)]

Atom	x/a	y/b	z/c	B
Re	0.20932(2)	0.04386(2)	0.25455(2)	1.715(3)
S1	-0.0018(1)	-0.0016(1)	0.2072(1)	2.27(3)
S2	0.3152(1)	-0.0972(1)	0.1443(1)	2.64(3)
P1	0.0644(1)	0.2535(1)	0.2764(1)	1.90(3)
P2	0.4144(1)	0.1525(1)	0.1963(1)	2.12(3)
N1	-0.1479(6)	-0.2414(5)	0.1012(5)	4.3(1)
N2	0.2463(5)	-0.3424(5)	0.0019(4)	3.4(1)
N10	0.2453(5)	-0.0427(5)	0.3917(4)	3.0(1)
C1	0.0474(5)	-0.1276(5)	0.1397(4)	2.2(1)
C2	0.1800(5)	-0.1659(5)	0.1117(4)	2.2(1)
C3	-0.0610(6)	-0.1887(5)	0.1158(4)	2.7(1)
C4	0.2158(5)	-0.2649(5)	0.0510(5)	2.6(1)
C10	0.4550(5)	0.2705(5)	0.2650(4)	2.0(1)
C11	0.4736(6)	0.2183(6)	0.3834(5)	3.0(1)
C12	0.5133(7)	0.3035(7)	0.4378(5)	3.7(1)
C13	0.5330(6)	0.4382(6)	0.3749(5)	3.8(1)
C14	0.5129(7)	0.4919(6)	0.2572(5)	4.1(1)
C15	0.4755(6)	0.4071(6)	0.2015(5)	3.0(1)
C20	0.4115(6)	0.2535(6)	0.0428(4)	3.2(1)
C30	0.5753(6)	0.0228(6)	0.2179(6)	3.8(1)
C40	0.1216(5)	0.3235(5)	0.3778(4)	2.1(1)
C41	0.1321(6)	0.2376(6)	0.4933(5)	3.1(1)
C42	0.1648(6)	0.2899(7)	0.5761(5)	3.6(1)
C43	0.1856(6)	0.4266(6)	0.5437(5)	3.7(1)
C44	0.1759(6)	0.5122(6)	0.4306(6)	3.7(1)
C45	0.1442(6)	0.4603(5)	0.3470(5)	2.7(1)
C50	-0.1126(6)	0.2356(6)	0.3241(5)	3.5(1)
C60	0.0384(7)	0.3979(6)	0.1402(5)	3.4(1)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\langle (4/3)[a^2B_{(1,1)} + b^2B_{(2,2)} + c^2B_{(3,3)} + ab(\cos \gamma)B_{(1,2)} + ac(\cos \beta)B_{(1,3)} + bc(\cos \alpha)B_{(2,3)}] \rangle (\text{\AA}^2)$.

maximum peaks of 0.923 e/ \AA^3 for [ReN(Me₂PhP)₂(2,6-DMTP)(morph tcb)] and 0.975 e/ \AA^3 for [ReN(Me₂PhP)₂(mnt)]. Crystal data and more details of the refinements are summarised in Table 1. See also 'Supplementary material'. Positional parameters are given in Tables 2 and 3.

Results and discussion

The nitrido ligand is one of the most powerful π -donor ligands [5, 6] and stabilises metals preferably in their high formal oxidation states. The rhenium–nitrogen triple bond is very stable [7] and thus, numerous ligand exchange reactions can be performed with ReN complexes retaining the Re \equiv N unit. Recently, the synthesis of [ReN(Cl)(Me₂PhP)₂(R₂tcb)] complexes (**I**) was performed by the reactions of [ReNCl₂(Me₂PhP)₃] with *N*-(*N,N*-dialkylthiocarbamoyl)benzamidinates [1]. These complexes readily undergo ligand-exchange with alkali halides or pseudohalides to give compounds of the general formula [ReN(X)(Me₂PhP)₂(R₂tcb)] (X = I, NCS, CN, N₃) [2].

With sulfur-donor ligands the reactions are more complex. 2,6-Dimethylthiophenol reacts with $[\text{ReN}(\text{Cl})(\text{Me}_2\text{PhP})_2(\text{morph tcb})]$ under substitution of one Me_2PhP ligand by 2,6-DMTP. During the reaction the labilised Cl^- ligand is removed and the neutral, five-coordinate $[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$ is formed. In contrast to this reaction, the powerful chelating ligand mnt^{2-} does not attack the phosphine positions in $[\text{ReN}(\text{Cl})(\text{Me}_2\text{PhP})_2(\text{morph tcb})]$, but replaces morph tcb^- . The simultaneous abstraction of Cl^- also yields a five-coordinate, neutral complex: $[\text{ReN}(\text{Me}_2\text{PhP})_2(\text{mnt})]$.

Both complexes are air-stable as solids as well as in solution. Their IR spectra show intense bands between 1050 and 1100 cm^{-1} which can be assigned to the $\text{Re}\equiv\text{N}$ frequencies [5–7]. The complexes are diamagnetic as is expected for spin-paired $\text{Re}^{\text{V}}\text{N}$ complexes [1, 2]. Their ^1H NMR spectra are characterised by narrow lines and complex signal patterns due to ^{31}P couplings.

FAB mass spectrometric studies confirm the composition of the title complexes. Besides the molecular ions, fragments can be observed which result from the abstraction of complete ligands. The rhenium–nitrogen triple bond is not involved in the mass spectrometric fragmentation. This is in accordance with the behaviour of other nitrido complexes of rhenium and technetium [1, 2, 8–10] and confirms the extraordinary stability of the $\text{Re}\equiv\text{N}$ bonds. In contrast, the $\text{Re}=\text{O}$ bonds are included in the fragmentation of comparable oxorhenium complexes [11, 12].

Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of $\text{CH}_2\text{Cl}_2/\text{iso-propanol}$ solutions. Discrete, monomeric molecules, in which the rhenium atoms are five-coordinate, have been found for both compounds.

A SCHAKAL plot [13] of $[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$ is shown in Fig. 1. Table 4 contains selected bond lengths and angles of the complex. The $\text{Re}-\text{N1}$ distance is 1.65 \AA which is in the typical range of metal–nitrogen triple bonds [5, 6]. There are no differences in the ReS bond lengths due to the coordination of ‘thiolate sulfur’ and ‘thiocarbonyl sulfur’ donors. All C–N bond distances in the morph tcb chelate ring are almost equal, indicating a conjugated π -electron system as was also observed for other R_2tcb complexes of rhenium and technetium [1, 2, 9, 12]. The coordination geometry can be described as a strongly distorted square pyramid with the atoms S1, S2, P1 and N2 forming its basal plane and N1 as the apex. The rhenium atom is situated 0.65 \AA above the basal plane.

A plot of $[\text{ReN}(\text{Me}_2\text{PhP})_2(\text{mnt})]$ is given in Fig. 2. Selected bond distances and angles are summarised in Table 5. The main bonding situation is the same as in $[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$: a square-

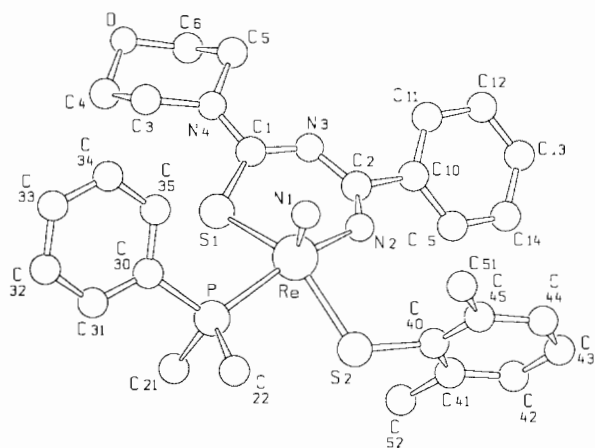


Fig. 1. SCHAKAL plot of $[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$ along with the atomic numbering scheme

TABLE 4. Selected bond lengths and angles in $[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$ with e.s.d.s in parentheses

Bond lengths (\AA)					
Re–N1	1.652(6)	Re–S2	2.334(2)	C2–N3	1.33(1)
Re–P	2.388(2)	S1–C1	1.75(1)	C2–N2	1.31(1)
Re–N2	2.081(6)	S2–C40	1.78(1)	C1–N4	1.34(1)
Re–S1	2.334(2)	C1–N3	1.32(1)		
Bond angles ($^\circ$)					
N1–Re–S1	108.9(2)	S2–Re–P	84.9(1)		
N1–Re–S2	108.6(2)	S2–Re–N2	87.9(2)		
N1–Re–P	93.7(2)	P–Re–N2	158.5(2)		
N1–Re–N2	107.8(3)	Re–S1–C1	108.9(2)		
S1–Re–P	86.0(1)	Re–S2–C40	114.8(3)		
S1–Re–S2	141.9(1)	Re–N2–C2	132.7(5)		
S1–Re–N2	87.2(2)	N2–C2–N3	128.9(7)		

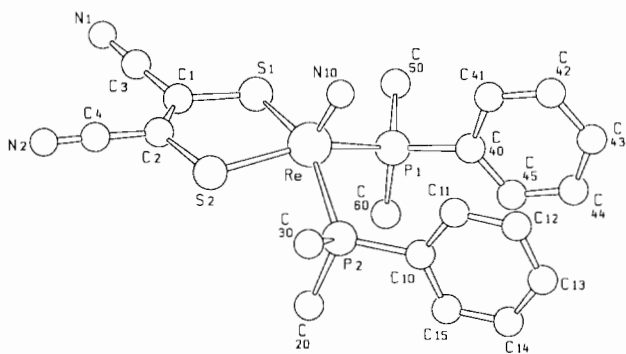


Fig. 2. SCHAKAL plot of $[\text{ReN}(\text{Me}_2\text{PhP})_2(\text{mnt})]$ along with the atomic numbering scheme.

pyramidal coordination sphere with the nitrido nitrogen at the apex and the metal atom situated 0.53 \AA above the basal plane of the atoms S1, S2, P1 and P2 which are coplanar within 0.03 \AA . The chelate ligand mnt^{2-} is almost planar and shows a dihedral angle to the S1, S2, P1, P2 plane of 10.8° . The $\text{Re}\equiv\text{N}$ bond length of

TABLE 5 Selected bond lengths and angles in $[\text{ReN}(\text{Me}_2\text{PhP})_2(\text{mnt})]$ with e.s.d.s in parentheses

Bond lengths (Å)					
Re–N10	1.644(4)	Re–P2	2.426(1)	C1–C3	1.43(1)
Re–S1	2.362(1)	S1–C1	1.75(1)	C2–C4	1.44(1)
Re–S2	2.371(2)	S2–C2	1.75(1)	C3–N1	1.15(1)
Re–P1	2.419(1)	C1–C2	1.34(1)	C4–N2	1.14(1)
Bond angles (°)					
N–Re–S1	102.9(2)	S2–Re–P3	87.56(3)		
N–Re–S2	104.0(1)	S2–Re–O2	85.94(5)		
N–Re–P2	97.8(1)	P2–Re–P3	96.63(3)		
N–Re–P3	90.4(1)	P2–Re–O2	73.03(5)		
N–Re–O2	168.0(1)	P3–Re–O2	83.3(1)		
S1–Re–S2	79.97(3)	Re–S1–P1	88.55(4)		
S1–Re–P2	91.15(3)	Re–S2–P1	88.86(4)		
S1–Re–P3	163.56(3)	S1–P1–S2	101.3(1)		
S1–Re–O2	85.22(6)	Re–O2–P1	155.6(1)		
S2–Re–P2	157.83(2)				

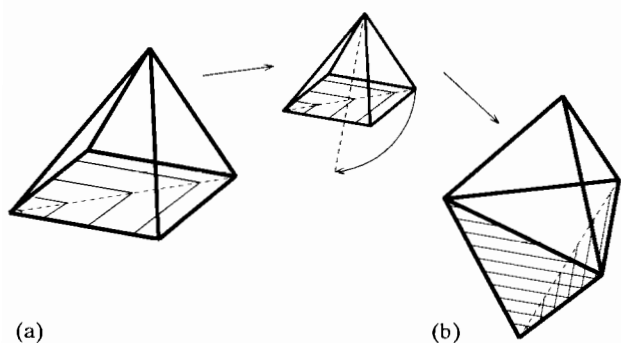


Fig. 3 Possible structures of five-coordinate complexes (a) square pyramid, (b) trigonal bipyramid with the shape determining angle (dihedral angle between the indicated plane).

1.66 Å is in the typical range [5, 6]. Due to the *trans* labilising influence of the phosphine ligands, the Re–S bonds (mean value 2.365 Å) are somewhat longer than the comparable Re–S bonds in the oxorhenium(V) complex $[\text{ReO}(\text{mnt})_2]^-$ which have a mean value of 2.315 Å [14].

Five-coordinate complexes can show two border-line structures, a square pyramid and a trigonal bipyramid. The degree of correspondence of a real structure with one of these idealised structures can be estimated by the evaluation of the shape determining angles which are associated with the edges *trans* to the nitrido ligand (0° for the square pyramidal and 53.1° for the trigonal bipyramidal geometry) as is suggested by Muetterties and Guggenberger [15] (see also Fig. 3). For the title complexes, the shape determining angles are 2.7° ($[\text{ReN}(\text{Me}_2\text{PhP})_2(\text{mnt})]$) and 17.7° ($[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$). This result is in accordance with the fact that distortion from the square pyramidal coordination towards the trigonal bipyramidal one is often observed when sterically hindered thiol ligands are involved [16–18].

Summarising it can be noted that ligand exchange reactions starting from $[\text{ReN}(\text{Cl})(\text{Me}_2\text{PhP})_2(\text{R}_2\text{tcb})]$ complexes can give coordination compounds with different structures dependent on the nature of the new ligand. Whereas only an exchange in the axial position *trans* to 'N³⁻' can be achieved when using KX salts ($X = \text{I}, \text{SCN}, \text{CN}, \text{N}_3$), the equatorial coordination sphere is influenced by sulfur-donor ligands. Five-coordinate complexes with different structures are obtained using 2,6-DMTP or Na_2mnt . The coordination of the sterically hindered 2,6-dimethylthiophenolate results in a strong distortion of the square pyramidal coordination sphere towards a trigonal bipyramid.

Supplementary material

Further details of the crystal structure determinations (F_oF_c lists, full lists of bond lengths and angles and isotropic thermal parameters) have been deposited with the Fachinformationszentrum, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, as Supplementary Publication Nos. CSD 56745 $[\text{ReN}(\text{Me}_2\text{PhP})(2,6\text{-DMTP})(\text{morph tcb})]$ and CSD 56788 $[\text{ReN}(\text{Me}_2\text{PhP})_2(\text{mnt})]$.

Acknowledgements

We acknowledge grants from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, and express our thanks to Professor J. Strähle (Tübingen) for his kind hospitality and for providing us with facilities.

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