Mixed-ligand complexes of rhenium
II. Synthesis and characterization of [ReN(X)($Me_2PhP)_2(R_2$tcb)] complexes (X=I, N_3, SCN, CN; R_2tcb^- =*N-(N,N*-dialkylthiocarbamoylbenzamidinate)). X-ray crystal structure of [ReN(N_3)($Me_2PhP)_2(Et_2$tcb)]

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(Received June 22, 1993, revised August 12, 1993)

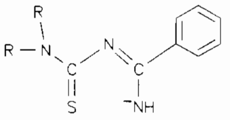
Abstract

Mixed-ligand complexes of rhenium(V) of the general formula [ReN(X)($Me_2PhP)_2(R_2$tcb)] with X=I, N_3, SCN and CN, have been synthesized from [ReN(Cl)($Me_2PhP)_2(R_2$tcb)] and NaX or KX salts. All complexes were characterized by IR and NMR spectroscopy and mass spectrometry. [ReN(N_3)($Me_2PhP)_2(Et_2$tcb)] was studied by X-ray diffraction. The complex crystallizes triclinic in the space group $P\bar{1}$, $Z=2$, $R=0.043$ for 4809 observed independent reflections. The lattice dimensions are $a=10.142(3)$, $b=11\,425(4)$, $c=13\,603(4)$ Å, $\alpha=88.52(2)$, $\beta=78.22(2)$ and $\gamma=88.30(2)°$ The azido ligand is coordinated *trans* to the ReN bond which is 1 733(8) Å. The Re–N_3 bond length is 2.323(9) Å. The coordination geometry is a distorted octahedron

Key words: Crystal structures; Rhenium complexes, Nitrido complexes, Bidentate ligand complexes; Chelate complexes

Introduction

Synthesis, structural characterization and reactions of rhenium nitrido compounds have been described in numerous papers [1–5]. The 'N^{3-}' ligand which is one of the strongest π-donor ligands preferably stabilizes high formal oxidation states of metals. The rhenium–nitrogen triple bond is very stable [1–5] and the equatorial coordination spheres of the compounds can readily be changed by ligand exchange reactions. Recently, we prepared novel nitridorhenium complexes of general formula [ReN(Cl)($Me_2PhP)_2(R_2$tcb)] by the reaction of [ReCl$_2$($Me_2PhP)_3$] with *N*-(*N,N*-dialkylthiocarbonylbenzamidines) (HR$_2$tcb, **I**) [5]. The resulting mixed-ligand complexes (**II**) have a potential as starting materials for further ligand-exchange reactions due to different reactivities of the Me_2PhP, R_2tcb^- and Cl^- ligands. Furthermore, an electrophilic attack on the coordinated nitrido ligand seems to be possible.



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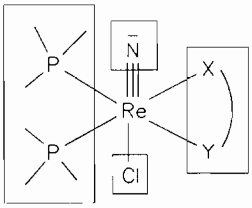

II

Here, we report the reactions of the [ReN(Cl)($Me_2PhP)_2(R_2$tcb)] complexes with alkali halides and pseudohalides which result in the selective exchange of the Cl^- ligand *trans* to the Re≡N bond.

Experimental

The [ReN(Cl)($Me_2PhP)_2(R_2$tcb)] complexes were prepared from [ReCl$_2$($Me_2PhP)_3$] [4, 6] and HR$_2$tcb as described previously [7, 8]. All other reagents were analytical grade.

Syntheses

[ReN(N_3)($Me_2PhP)_2(Et_2$tcb)]

100 mg (0.13 mmol) [ReN(Cl)($Me_2PhP)_2(Et_2$tcb)] were dissolved in 70 ml acetone and about 32 mg (0.5

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SSDI 0020-1693(93)03695-7

mmol) solid NaN_3 were added. The heterogeneous mixture was stirred for 4–5 h at room temperature and filtered. After evaporation of the solvent a yellow–orange solid remained. Recrystallization from acetone/iso-propanol gave yellow–orange crystals which were readily soluble in acetone, CH_2Cl_2, $CHCl_3$ and acetonitrile, but only slightly soluble in alcohols. Yield 37 mg (36% based on Re). *Anal.* Calc. for $C_{28}H_{38}N_7P_2SRe$: C, 44.7; H, 5.1; N, 13.0; S, 4.3. Found: C, 43.4; H, 5.2; N, 13.0; S, 4.3%. ^1H NMR (ppm): phenyl 6.8–8.0 m (15H), CH_2 3.5–4.1 m (broad) (4H), CH_3 0.8–2.6 m (18 H). ^{13}C NMR (ppm): phenyl 127.8–132.3; CH_2 44.4, 46.2; CH_3 10.3–19.9; C=S 166.9. FAB-MS: $m/z = 725$ (3% B) $[ReN(N)(Me_2PhP)_2(Et_2tcb)]^+$, 711 (100% B) $[ReN(Me_2PhP)_2(Et_2tcb)]^+$, 573 (10% B) $[ReN(Me_2PhP)(Et_2tcb)]^+$, 435 (13% B) $[ReN(Et_2tcb)]^+$. IR: $\nu(Re{\equiv}N)$ 1049, $\nu(N_3)$ 2048, ν(N–H) 3329 cm^{-1}.

$[ReN(NCS)(Me_2PhP)_2(morphtcb)]$

76 mg (0.1 mmol) $[ReN(Cl)(Me_2PhP)_2(morphtcb)]$ were dissolved in about 60 ml methanol and 19.4 mg (0.2 mmol) KSCN in 20 ml H_2O/methanol (1/20 vol./vol.) were added. The mixture was refluxed for 2 h and the solvent was removed in vacuum. The remaining solid was washed with H_2O, methanol and ether and recrystallized from CH_2Cl_2/iso-propanol to give yellow–orange crystals which were readily soluble in CH_2Cl_2, $CHCl_3$, acetone and acetonitrile, but only slightly soluble in alcohols. Yield 61 mg (78% based on Re). *Anal.* Calc. for $C_{29}H_{36}N_5OP_2S_2Re$: C, 44.4; H, 4.6; S, 8.2. Found: C, 44.2; H, 4.7; S, 7.6%. ^1H NMR (ppm): phenyl 6.7–7.7 (15H); CH_2 3.55 m (broad) (2H), 4.0 m (broad) (2H); CH_3 1.34 d (3H) $J(^1H–^{31}P)$ 9.69 Hz; 1.44 d (3H) $J(^1H–^{31}P)$ 9.31 Hz; 1.85 d (3H) $J(^1H–^{31}P)$ 9.28 Hz; 2.0 d (3H) $J(^1H–^{31}P)$ 9.44 Hz. ^{13}C NMR (ppm): phenyl 127–141; CH_2 46.6, 49.5; CH_3 13.6, 14.2, 18.9, 20.1; C=S 167.39. FAB-MS: $m/z = 783$ (6% B) $[ReN(NCS)(Me_2PhP)_2(morphtcb)]^+$ (M^+), 725 (85% B) $[ReN(Me_2PhP)_2(morphtcb)]^+$, 645 (99% B) $[ReN(NCS)(Me_2PhP)(morphtcb)]^+$, 587 (22% B) $[ReN(Me_2PhP)(morphtcb)]^+$, 535 (20% B) $[ReN(NCS)(Me_2PhP)_2]^+$. IR: $\nu(Re{\equiv}N)$ 1050, ν(NCS) 2060, ν(N–H) 3320 cm^{-1}.

$[ReN(CN)(Me_2PhP)_2(morphtcb)]$

The synthesis was performed as outlined above for $[ReN(NCS)Me_2PhP)_2(morphtcb)]$ with KCN instead of KSCN. The product was reprecipitated from CH_2Cl_2/iso-propanol to give a yellow–brown powder. Yield 38.3 mg (51% based on Re). *Anal.* Calc. for $C_{29}H_{36}N_5OP_2SRe$: C, 46.4; H, 4.8; N, 9.3. Found: C, 44.7; H, 4.5; N, 8.9%. The recorded NMR spectra of $[ReN(CN)(Me_2PhP)_2(morphtcb)]$ show the same high order patterns as those of $[ReN(NCS)(Me_2PhP)_2(morphtcb)]$. The chemical shifts and intensities of the observed signals are almost identical. FAB-MS: $m/z = 751$ (15% B) $[ReN(CN)(Me_2PhP)_2(morphtcb)]^+$ (M^+), 725 (5% B) $[ReN(Me_2PhP)_2(morphtcb)]^+$, 613 (48% B) $[ReN(CN)(Me_2PhP)(morphtcb)]^+$, 587 (10% B) $[ReN(Me_2PhP)(morphtcb)]^+$, 503 (11% B) $[ReN(CN)(Me_2PhP)_2]^+$. IR: $\nu(Re{\equiv}N)$ 1060, ν(CN) 2109, ν(N–H) 3329 cm^{-1}.

$[ReN(I)(Me_2PhP)_2(morphtcb)]$

The synthesis was performed as outlined above for $[ReN(NCS)(Me_2PhP)_2(morphtcb)]$ with NaI instead of KSCN. The product was reprecipitated from CH_2Cl_2/iso-propanol to give a yellow powder. Yield 45 mg (52.8% based on Re). *Anal.* Calc. for $C_{28}H_{36}N_4OP_2SIRe$: C, 39.5, H, 4.3; N, 6.6; S, 3.8, I, 14.9. Found: C, 40.3; H, 4.4; N, 7.0; S, 4.1; I, 14.6%. The recorded NMR spectra of $[ReN(I)(Me_2PhP)_2(morphtcb)]$ show the same high order patterns as those of $[ReN(NCS)(Me_2PhP)_2(morphtcb)]$. The chemical shifts and intensities of the observed signals are almost identical. FAB-MS: $m/z = 852$ (3% B) $[ReN(I)(Me_2PhP)_2(morphtcb)]^+$ (M^+), 725 (92% B) $[ReN(Me_2PhP)_2(morphtcb)]^+$, 604 (79% B) $[ReN(I)(Me_2PhP)_2]^+$, 587 (19% B) $[ReN(Me_2PhP)(morphtcb)]^+$. IR. $\nu(Re{\equiv}N)$ 1055, ν(N–H) 3330 cm^{-1}.

Physical measurements

Routine IR spectra were recorded as KBr discs on a Specord 75 IR instrument. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ 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 operated at 8 kV and 100 μA (probe temperature: 30 °C); nitrobenzylalcohol was used as matrix.

X-ray diffraction

X-ray data of $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$ were collected at $T = 223$ K on an automated Enraf-Nonius CAD 4 diffractometer with Mo Kα radiation ($\lambda = 0.7093$ Å). A crystal of approximate dimensions $0.2 \times 0.1 \times 0.5$ mm was chosen for the determination of the cell constants by least-squares from 25 reflections: $a = 10.142(2)$, $b = 11.425(4)$, $c = 13.603(4)$ Å, $\alpha = 88.52(2)$, $\beta = 78.22(2)$, $\gamma = 88.30(2)°$, $V = 1542$ Å^3 with $Z = 2$. The space group was found to be triclinic, $P\bar{1}$ (No. 2). Intensity data were collected for 6731 unique reflections of which 4809 were observed ($I \geq 3\sigma$). The structure was solved by automated heavy-atom Patterson method (SHELXS-86 [9]) and refined by full-matrix least-squares techniques (VAXSDP [10]) to a final $R = 0.043$ ($R_w = 0.049$) for 4573 observations and 353 parameters. All non-hydrogen atoms were treated anisotropically. Empirical absorption correction (DI-

TABLE 1. Fractional positional parameters[a] for $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$

Atom	*x/a*	*y/b*	*z/c*	*B*
Re	0.23201(4)	0.19569(3)	0.22546(3)	2.130(5)
S	0.3504(3)	0.1211(2)	0.0663(2)	2.99(5)
P1	0.2395(3)	0.3862(2)	0.1429(2)	2.70(5)
P2	0.1698(2)	0.2702(2)	0.3953(2)	2.31(4)
N1	0.4444(8)	0.2278(7)	0.2571(6)	3.5(2)
N2	0.5302(8)	0.2929(7)	0.2762(6)	3.3(2)
N3	0.604(1)	0.350(1)	0.2944(9)	6.0(3)
N4	0.2749(8)	0.0299(6)	0.2850(5)	2.6(1)
N5	0.3090(8)	−0.0995(6)	0.1477(5)	2.8(2)
N6	0.2943(9)	−0.0740(7)	−0.0150(5)	3.8(2)
N10	0.0639(7)	0.1893(6)	0.2179(6)	2.5(1)
C1	0.3131(8)	−0.0693(7)	0.2414(6)	2.2(2)
C2	0.3114(9)	−0.0261(7)	0.0707(6)	2.6(2)
C3	0.299(1)	−0.0042(9)	−0.1079(6)	4.3(2)
C4	0.168(1)	0.057(1)	−0.1112(9)	5.7(3)
C5	0.290(1)	−0.208(1)	−0.0225(9)	4.8(3)
C6	0.153(2)	−0.233(2)	−0.018(1)	8.0(4)
C10	0.1123(9)	0.4946(7)	0.1954(6)	2.5(2)
C11	0.139(1)	0.6050(8)	0.2232(7)	3.2(2)
C12	0.039(1)	0.6849(8)	0.2625(8)	3.9(2)
C13	−0.095(1)	0.6548(9)	0.2736(8)	3.9(2)
C14	−0.125(1)	0.543(1)	0.2474(9)	4.2(2)
C15	−0.022(1)	0.4645(8)	0.2090(8)	3.8(2)
C20	0.399(1)	0.4606(9)	0.1304(9)	4.1(2)
C30	0.216(1)	0.3823(9)	0.0140(7)	5.1(3)
C40	0.1950(9)	0.1640(7)	0.4937(6)	2.4(2)
C41	0.088(1)	0.1014(8)	0.5482(6)	3.0(2)
C42	0.111(1)	0.0167(8)	0.6187(7)	3.7(2)
C43	0.239(1)	−0.0085(9)	0.6340(6)	3.9(2)
C44	0.345(1)	0.055(1)	0.5790(7)	4.1(2)
C45	0.323(1)	0.1391(9)	0.5098(7)	3.3(2)
C50	0.255(1)	0.3984(8)	0.4269(7)	3.9(2)
C60	−0.007(1)	0.3132(9)	0.4318(7)	3.6(2)
C70	0.3623(8)	−0.1677(7)	0.3009(6)	2.4(2)
C71	0.461(1)	−0.2475(8)	0.2507(8)	3.3(2)
C72	0.506(1)	−0.3362(9)	0.3061(9)	4.6(3)
C73	0.461(1)	−0.3500(9)	0.4078(9)	5.1(2)
C74	0.367(1)	−0.2712(9)	0.4553(8)	4.3(2)
C75	0.3177(9)	−0.1804(8)	0.4043(7)	2.9(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ ($Å^2$)

FABS) was applied. Hydrogen atoms were calculated for idealized positions and introduced into the structure factor calculations. The final Fourier map showed maximum peaks less than 1.466 e/$Å^3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Table 1 contains the fractional positional parameters. Programs used: SHELXS-86, VAXSDP, SCHAKAL [11].

Results and discussion

$[ReN(Cl)(Me_2PhP)_2(R_2tcb)]$ (**II**) complexes undergo ligand-exchange reactions with alkali halides or pseudohalides to form mixed-ligand rhenium(V) compounds of general formula $[ReN(X)(Me_2PhP)_2(R_2tcb)]$ (X = I, N_3, NCS, CN) (eqn. (1)). The preferred substitution of the chloro ligand can be understood by the strong *trans*-labilizing effect of the 'N^{3-}' ligand which results in the extraordinary long Re–Cl bond of 2.673 Å in the starting complex [5].

$$[ReN(Cl)(Me_2PhP)_2(R_2tcb)] + X^- \longrightarrow [ReN(X)(Me_2PhP)_2(R_2tcb)] + Cl^- \quad (1)$$

X = N_3, SCN, CN, I, R_2 = Et_2, morph

All products are yellow to yellow–orange, neutral complexes which are readily soluble in $CHCl_3$, CH_2Cl_2, acetone, moderately soluble in alcohols and nearly insoluble in hydrocarbons. They are indefinitely stable as solids as well as in solution. Intense IR bands are observed between 1000 and 1100 cm^{-1}. These bands are in the typical range of $\nu(Re{\equiv}N)$ vibrations [2]. The $\nu(N–H)$ frequencies of the only singly deprotonated chelate ligands can be detected at about 3330 cm^{-1}. These values correspond to the frequencies which are observed in the $[ReN(Cl)(Me_2PhP)_2(R_2tcb)]$ complexes and the non-coordinated ligands [5]. The corresponding $\nu(NH)$ bands in the bis-chelates $[ReO(R_2tcb)_2]^+$ and $[TcO(R_2tcb)_2]^+$, however, are shifted to about 3200 cm^{-1} which was explained by the formation of hydrogen bonds to Ph_3PO and Cl^-, respectively [12, 13].

Fast atom bombardment mass spectrometry was used to study the fragmentation pattern of the new complexes. Molecular ion peaks could be observed for all compounds, with the exception of $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$. Their intensities, however, are low (3–5% beam). This is in agreement with the results of mass spectrometric studies on $[ReN(Cl)(Me_2PhP)_2(R_2tcb)]$ complexes [5]. Generally, fragmentation mainly occurs by the loss of complete ligands, e.g. $[M]^+$ peaks as well as $[ReN(Me_2PhP)_2(morphtcb)]^+$, $[ReN(X)(Me_2PhP)(morphtcb)]^+$ and $[ReN(X)(Me_2PhP)_2]^+$ are found in all spectra (Fig. 1 shows the spectrum of $[ReN(NCS)(Me_2PhP)_2(Et_2tcb)]$). The highest peak in the FAB mass spectrum of $[ReN(N_3)(Me_2PhP)(morphtcb)]$ is observed at $m/z = 725$ which corresponds to $[ReN(N)(Me_2PhP)_2(Et_2tcb)]^+$. This observation can be explained by the preferred loss of N_2 and gives the possibility of reactions on the intermediately formed 'dinitrido complex'.

The title compounds are diamagnetic as is expected for d^2 complexes with the 'N^{3-}' ligand, the electrons of which strongly interact with the rhenium d_{xz} and d_{yz} orbitals of π-symmetry. This results in the energetic separation of the essentially non-bonding d_{xy} orbital and the formation of spin-paired complexes.

All ^1H and ^{13}C NMR spectra are characterized by high order coupling patterns due to the ^{31}P nuclei of

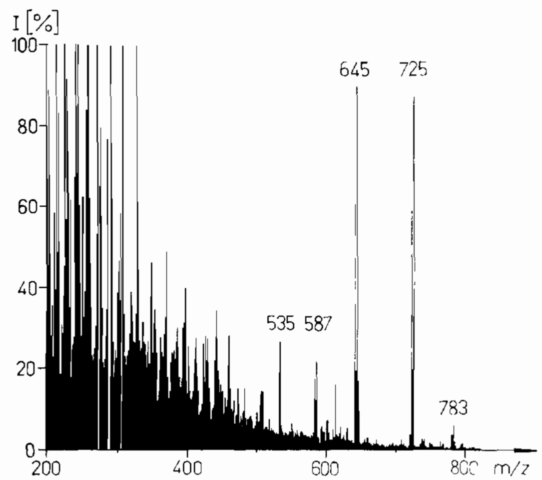

Fig. 1. FAB$^+$ mass spectrum of $[ReN(NCS)(Me_2PhP)_2(Et_2tcb)]$, matrix: 3-nitrobenzylalcohol For assignment of the fragments see 'Experimental'.

the phosphorus containing ligands and the formation of stereoisomers. The assignment of the ^{13}C signals was done by means of the DEPT 135 technique. The substitution of the ligands *trans* to the nitrido nitrogen does not influence the NMR signal positions.

Crystals of $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$ which were suitable for X-ray diffraction could be obtained by slow evaporation of an acetone/iso-propanol solution. The structure consists of discrete monomeric molecules. The molecular structure together with the atomic numbering scheme is given in Fig. 2 Selected bond lengths and angles are summarized in Table 2. The rhenium atom is six-coordinate with the azido ligand *trans* to the nitrido nitrogen and an N10–Re–N1 bonding angle of 170.2(4)°. The coordination geometry is best described as a distorted octahedron. The donor atoms of the chelating ligand $(Et_2tcb)^-$ are bent out of the equatorial plane away from the nitrido ligand, whereas the N10–Re–P angles are between 88.6(2) and 90.9(2)°. The linear azido ligand coordinates with an Re–N1–N2 angle of 151.6(7)°. The metal–nitride distance of 1.73(1) Å is larger than that in the comparable chloro compound (1.68(1) Å) which falls in the typical region of metal–nitrogen triple bonds [1–5] The *trans* effect of the nitrido ligand can be detected in the Re–N1 length of 2.32(1) Å. The title compound is directly comparable with the Re(V) anion *trans*-$[ReN(N_3)(CN)_4]^{3-}$ the structure of which was reported recently [14]. The metal–nitrido distance in $(Ph_4As)_3[ReN(N_3)(CN)_4]$ is 1.65(2) Å and the Re–N(N$_3$) length of 2.36(2) Å is similar to that in $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$. The structural *trans*-effect of the Me$_2$PhP ligands is evident in the Re–N4 and Re–S bond distances (2.111(7) and 2.414(2) Å) which are significantly longer than the corresponding values in $[ReO(Et_2tcb)_2]^+$ (Re–N 2.008 and 2.020, Re–S 2.309 and 2.315 Å) [12]. All C–N distances in the chelate ring are almost equal indicating the presence of an extended conjugated π-system as is already described for $[ReN(Cl)(Me_2PhP)_2(Et_2tcb)]$ [5]. The C–S bond length corresponds to values lying between single and double bonds.

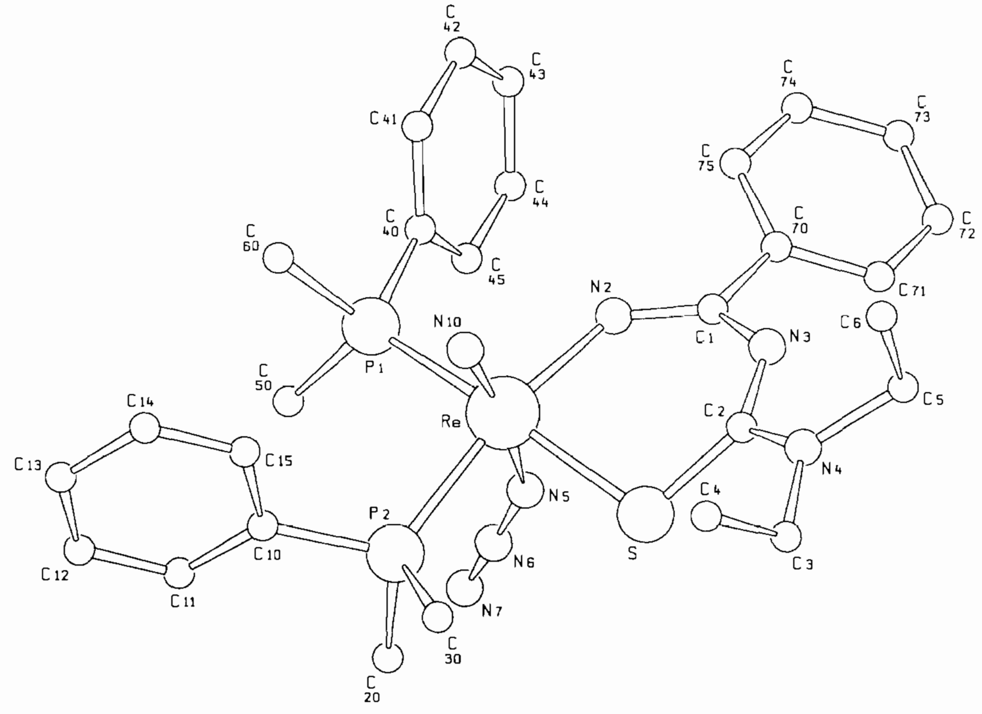

Fig. 2. SCHAKAL plot of $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$ with the atomic numbering scheme.

TABLE 2. Selected bond lengths and angles in [ReN(N_3)(Me_2PhP)$_2$(Et_2tcb)] with e.s.d.s

Bond lengths (Å)					
Re–N10	1.733(8)	Re–N4	2.111(7)	N2–N3	1.08(1)
Re–P1	2.420(2)	Re–N1	2.323(9)	N4–C1	1.32(2)
Re–P2	2.436(2)	S–C2	1.74(1)	N5–C1	1.34(1)
Re–S	2.414(2)	N1–N2	1.23(1)	N5–C2	1.32(2)
Bond angles (°)					
N10–Re–N1	170.2(4)	P2–Re–N4	89.3(2)		
N10–Re–P1	88.6(2)	S–Re–P2	165.4(9)		
N10–Re–P2	90.9(2)	S–Re–N1	85.6(3)		
N10–Re–S	103.6(2)	N1–Re–N4	79.8(3)		
N10–Re–N4	104.0(4)	P1–Re–N1	88.5(3)		
S–Re–N4	85.9(2)	P2–Re–N1	80.0(3)		
P1–Re–P2	95.3(1)	N3–Re–N4	87.6(3)		
S–Re–P1	86.7(1)	Re–N1–N2	151.6(7)		
P1–Re–N4	166.6(3)				

The mixed-ligand complexes described in this paper are products of selective ligand-exchange reactions which only substitute the *trans* positions to the ReN bonds in [ReN(Cl)(Me_2PhP)$_2$(R_2tcb)] complexes. This can be achieved by the use of alkali halides. A similar reaction with $(CH_3)_3$Si–NCS, however, gives the thionitrosylrhenium(I) complex *mer*-[Rc(NS)(NCS)$_2$(Me_2PhP)$_3$] which can also be obtained from [ReNCl_2(Me_2PhP)$_3$] and $(CH_3)_3$Si–NCS [15]. Reactions of the [ReN(Cl)(Me_2PhP)$_2$(R_2tcb)] complexes with HCl or sulfur donor ligands [16] will be published elsewhere.

Supplementary material

Further details of the crystal structure determination (F_oF_c list, full list 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, Germany, as Supplementary Publication No. CSD 56931.

Acknowledgements

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

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