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Mixed-ligand complexes of rhenium
I. The reaction of $ReNCl_2(Me_2PhP)_3$ with bidentate chelate ligands. X-ray crystal structures of chloro-[*N*-(*N*,*N*-diethylthiocarbamoyl)-benzamidinato]bis(dimethylphenylphosphine)nitridorhenium(V), $[ReN(Cl)(Me_2PhP)_2(Et_2tcb)]$, and {bis(*μ*-ethyldithiophosphato-*S*,*S*′,*O*)di[bis(dimethylphenylphosphine)nitridorhenium(V)]}, $[ReN(Me_2PhP)_2Etdtp)]_2$

Ulrich Abram* and Simone Ritter

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen (Germany)

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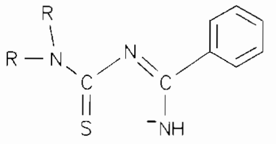
Abstract

Novel mixed-ligand complexes of rhenium(V) with tertiary phosphines and bidentate chelate ligands have been synthesized from $[ReNCl_2(Me_2PhP)_3]$. With diethyldithiocarbamate (Et_2dtc^-), *N*-(*N*,*N*-dialkylthiocarbamoyl)benzamidinates (R_2tcb^-) and diphenyldithiophosphinate ($S_2PPh_2^-$) monomeric, neutral complexes of the general formula $[ReN(Cl)(Me_2PhP)_2L]$ are formed. The analogous reaction with *O*,*O*′-diethyldithiophosphate (Et_2dtp^-) yields the dimeric compound $[ReN(Me_2PhP)_2(Etdtp)]_2$, where each one ethyl group of the dithiophosphates is removed and the resulting $Etdtp^{2-}$ acts as a tridentate bridging ligand. $[ReN(Cl)(Me_2PhP)_2(Et_2tcb)]$ crystallizes triclinic in the space group $P\bar{1}$ with $a=9.774(3)$, $b=11.993(3)$, $c=13.707(4)$ Å, $\alpha=92.29(2)$, $\beta=91.00(2)$ and $\gamma=98.03(6)°$, $Z=2$. The final R value is 0.026 on the basis of 6532 reflections. The chloro ligand is coordinated *trans* to the ReN bond which is 1.678(4) Å. The dimeric complex $[ReN(Me_2PhP)_2(Etdtp)]_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a=9.971(3)$, $b=10.837(3)$, $c=11.888(5)$ Å and $\alpha=89.18(2)$, $\beta=74.76(2)$ and $\gamma=69.15(3)°$. Structure resolution and refinement based on 7608 reflections converged at $R=0.021$. Two $[ReN(Me_2PhP)_2(Etdtp)]$ units are connected by the oxygen donor site of the monoethyldithiophosphate ligand occupying the position *trans* to the ReN bond with a Re–O bond length of 2.347(3) Å.

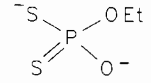
Introduction

Synthesis, structural characterization and reactions of rhenium nitrido compounds have been described in numerous papers [1–3]. The 'N^{3-}' ligand which is one of the strongest π-donor ligands preferably stabilizes high formal oxidation states of the metal. The Re≡N core is a very stable unit. Thus, new ReN complexes can easily be achieved via ligand exchange reaction. Usual starting materials for this approach are phosphine complexes of rhenium(V). The five-coordinate triphenylphosphine complex $[ReNCl_2(Ph_3P)_2]$ [4] reacts with bidentate chelate ligands commonly under complete substitution of the equatorial ligands [5].

In this paper, we describe ligand exchange reactions of $[ReNCl_2(Me_2PhP)_3]$ with diethyldithiocarbamate, diphenyldithiophosphinate, *N*-(*N*,*N*-dialkylthiocarbamoyl)benzamidinates (I) and *O*,*O*′-diethyldithiophosphate. In contrast to corresponding reactions with $[ReNCl_2(Ph_3P)_2]$, the phosphine ligands are not completely removed and mixed-ligand complexes are formed.



I



II

Experimental

Synthesis

$[ReNCl_2(Me_2PhP)_3]$ was prepared from $[ReNCl_2(Ph_3P)_2]$ according to a literature procedure [4,

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*Author to whom correspondence should be addressed.

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5]. HEt$_2$tcb, Hmorphtcb and Hpiptcb were synthesized from the corresponding *N*-(*N*,*N*-dialkylthiocarbamoyl)benzimide chlorides [6] and aqueous ammonia [7]. The other ligands were purchased commercially.

[ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$dtc)]

70 mg (0.1 mmol) [ReNCl$_2$(Me$_2$PhP)$_3$] were dissolved in 100 ml cold methanol and 70 mg (0.3 mmol) NaEt$_2$dtc·3H$_2$O were added. After a refluxing period of 1 h and cooling the solution was filtered to remove NaCl. The volume was reduced to about 20 ml and upon standing overnight yellow crystals deposited which were collected and recrystallized from CHCl$_3$/MeOH. Yield 43 mg (65% based on Re). *Anal.* Found: C, 38.5; H, 4.5; N, 4.0; S, 10.2. Calc. for $C_{21}H_{32}N_2P_2S_2ClRe$: C, 38.2; H, 4.8; N, 4.2; S, 9.7%. IR: ν(Re≡N) 1052, ν(C–N) 1508 cm^{-1}. ^{1}H NMR (ppm): CH$_3$ 1.37–2.28 m (18H), CH$_2$ 3.75 m (2H) and 4.02 m (2H), phenyl 7.15–7.98 m (10H); ^{13}C NMR (ppm): CH$_3$ 11.1, 16.8, 18.1, 19.1, 19.5, 20.0, CH$_2$ 44.5, phenyl 128.1–139.9, C–N 221.5. FAB-MS: $m/z = 660$ (7% B) [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$dtc)]$^+$ (M^+), $m/z = 625$ (65% B) [ReN(Me$_2$PhP)$_2$(Et$_2$dtc)]$^+$, $m/z = 522$ (100% B) [ReN(Cl)(Me$_2$PhP)(Et$_2$dtc)]$^+$, $m/z = 512$ (12% B) [ReN(Cl)(Me$_2$PhP)$_2$]$^+$, $m/z = 487$ (10% B) [ReN(Me$_2$PhP)(Et$_2$dtc)]$^+$, $m/z = 384$ (10% B) [ReN(Cl)(Et$_2$dtc)]$^+$.

[ReN(Cl)(Me$_2$PhP)$_2$(S$_2$PPh$_2$)]

70 mg (0.1 mmol) [ReNCl$_2$(Me$_2$PhP)$_3$] were dissolved in about 100 ml methanol and 100 mg (0.4 mmol) dithiophosphinic acid (HS$_2$PPh$_2$) were added. After stirring for 5 h, the solvent was removed in vacuum leaving a yellow oil. 50 ml diethyl ether were added and the mixture was stirred overnight, resulting in a yellow powder. The product was filtered and washed twice with diethyl ether. Yield 61 mg (80% based on Re). *Anal.* Found: C, 43.5; H, 4.0; N, 1.5; S, 9.1. Calc. for $C_{28}H_{32}NP_3S_2ClRe$: C, 44.2; H, 4.2; N, 1.8; S, 8.4%. IR: ν(Re≡N) 1050 cm^{-1}. ^{1}H NMR (ppm): CH$_3$ 1.65 and 1.71 m (12H), phenyl 6.82–7.40 m (20H); ^{13}C NMR (ppm): CH$_3$ 16.01 and 19.23, phenyl 128.2–142.0. FAB-MS: $m/z = 761$ (5% B) [ReN(Cl)(Me$_2$PhP)$_2$(S$_2$PPh$_2$)]$^+$ (M^+), m/z = 726 (100% B) [ReN(Me$_2$PhP)$_2$(S$_2$PPh$_2$)]$^+$, $m/z = 623$ (71% B) [ReN(Cl)(Me$_2$PhP)(S$_2$PPh$_2$)]$^+$, $m/z = 588$ (23% B) [ReN(Me$_2$PhP)(S$_2$PPh$_2$)]$^+$. FD-MS: $m/z = 761$ [ReN(Cl)(Me$_2$PhP)$_2$(S$_2$PPh$_2$)]$^+$, $m/z = 726$ [ReN(Me$_2$PhP)$_2$(S$_2$PPh$_2$)]$^+$, $m/z = 623$ [ReN(Cl)(Me$_2$PhP)(S$_2$PPh$_2$)]$^+$.

[ReN(Me$_2$PhP)$_2$(Etdtp)]$_2$

70 mg (0.1 mmol) ReNCl$_2$(Me$_2$PhP)$_3$ were dissolved in 100 ml methanol and 100 mg (0.5 mmol) (NH$_4$)Et$_2$dtp were added. The mixture was refluxed for 2 h and the solvent was removed in vacuum. Extraction of the oily residue with 2×5 ml CHCl$_3$ gave a clear yellow solution to which 20 ml iso-propanol were added. Slow evaporation of this mixture resulted in pale-yellow crystals. Yield 38 mg (60% based on Re). *Anal.* Found: C, 33.9; H, 4.7; N, 2.2; S, 10.6. Calc. for $C_{36}H_{54}N_2O_4P_6S_4Re_2$: C, 34.1; H, 4.3; N, 2.2; S, 10.1%. IR: ν(Re≡N) 1033 cm^{-1}. ^{1}H NMR (ppm): CH$_3$ (ethyl) 1.33 tr (3H), CH$_3$ 1.74 d (6H) and 1.94 d (6H), CH$_2$ 4.12 qu (2H), phenyl 7.25–7.67 m (10H). FAB-MS: $m/z = 634$ (25% B) [ReN(Me$_2$PhP)$_2$(EtHdtp)]$^+$, $m/z = 509$ (10% B) [ReN(Me$_2$PhP)$_2$S]$^+$. FD-MS: $m/z = 1266$ [ReN(Me$_2$PhP)$_2$(Etdtp)]$_2^+$ (M^+).

[ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)]

70 mg (0.1 mmol) [ReN(Cl)$_2$(Me$_2$PhP)$_3$] were dissolved in about 40 ml MeOH and 47 mg (0.2 mmol) HEt$_2$tcb in 10 ml methanol and 2–3 drops Et$_3$N were added. The mixture was refluxed for 1 h. After cooling a yellow product precipitated from the brown solution. The solid was filtered off and from the filtrate a second crop of product could be obtained. Recrystallization from CH$_2$Cl$_2$/iso-propanol gave yellow crystals which were easily soluble in CH$_2$Cl$_2$, CHCl$_3$, acetone and acetonitrile, but only slightly soluble in alcohols. Yield 47 mg (63% based on Re). *Anal.* Found: C, 44.1; H, 5.2; N, 6.0; Cl, 5.0; S, 4.0. Calc. for $C_{28}H_{38}N_4ClP_2SRe$: C, 45.0; H, 5.1; N, 7.5; Cl, 4.7; S, 4.3%. IR: ν(Re≡N) 1060, ν(N–H) 3340 cm^{-1}. ^{1}H NMR (ppm): CH$_3$ 1.05–2.08 m (18H); CH$_2$ 3.5–3.9 m (4H); phenyl 6.75–7.7 (15H). ^{13}C NMR (ppm): CH$_3$ 11.0–20.8, CH$_2$ 44.7 and 46.6, phenyl 127.6–141.4, C(N)Ph 166.0, C=S 172.4. FAB-MS: $m/z = 746$ (2% B) [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)]$^+$ (M^+), $m/z = 512$ (50% B) [ReN(Cl)(Me$_2$PhP)$_2$]$^+$, $m/z = 608$ (100% B) [ReN(Cl)(Me$_2$PhP)(Et$_2$tcb)]$^+$, $m/z = 711$ (76% B) [ReN(Me$_2$PhP)$_2$Et$_2$tcb]$^+$.

[ReN(Cl)(Me$_2$PhP)$_2$(morphtcb)]

The compound was prepared as outlined above for [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)]. Yield 56 mg (74% based on Re). *Anal.* Found: C, 44.0; H, 4.7; N, 7.2; S, 4.0. Calc. for $C_{28}H_{36}N_4ClP_2SRe$: C, 44.2; H, 4.7; N, 7.4; S, 4.2%. IR: ν(Re≡N) 1050, ν(N–H) 3320 cm^{-1}. ^{1}H NMR (ppm): CH$_3$ 1.47–2.24 m (12H), CH$_2$ 3.77 m (broad) (4H) and 4.24 m (broad) (4H), phenyl 6.9–8.0 m (15H). ^{13}C NMR (ppm): CH$_3$ 10.9–20.8, CH$_2$ 47.9 and 48.2, phenyl 127.4–140.9, C(N)Ph and C=S 161.8, 166.9, 173.3 and 187.9. FAB-MS: $m/z = 760$ (4% B) [ReN(Cl)(Me$_2$PhP)$_2$(morphtcb)]$^+$ (M^+), $m/z = 512$ (29% B) [ReN(Cl)(Me$_2$PhP)$_2$]$^+$, $m/z = 622$ (69% B) [ReN(Cl)(Me$_2$PhP)(morphtcb)]$^+$, $m/z = 725$ (70% B) [ReN(Me$_2$PhP)$_2$(morphtcb)].

[ReN(Cl)(Me$_2$PhP)$_2$(piptcb)]

The compound was prepared as outlined above for [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)]. Yield 45 mg (59% based

TABLE 1. Crystal data collection and structure refinement parameters

	$[ReN(Cl)(Me_2PhP)_2(Et_2tcb)]$	$[ReN(Me_2PhP)_2(Etdtp)]_2$
Crystal dimensions (mm)	0.3 × 0.2 × 0.2	0.3 × 0.15 × 0.15
Formula	$C_{28}H_{38}N_4P_2SClRe$	$C_{36}H_{54}N_2O_4P_6S_4Re_2$
Molecular weight	746.31	1265.34
Space group	triclinic $P\bar{1}$	triclinic $P\bar{1}$
Lattice dimensions		
a (Å)	9.774(3)	9.971(3)
b (Å)	11.993(3)	10.837(3)
c (Å)	13.707(4)	11.888(5)
α (°)	90.29(2)	89.18(2)
β (°)	91.00(2)	74.76(2)
γ (°)	98.03(2)	69.15(3)
V (Å^3)	1524.2	1153.8
D_c (g cm^{-3})	1.626	1.821
Radiation used (λ)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Scan type	ω	ω
Absorption coefficient (cm^{-1})	43.21	57.30
Absorption correction	DIFABS	DIFABS
T_{min}	0.9365	0.9533
T_{max}	1.0684	1.0435
T_{av}	0.9971	0.9955
Range of h, k, l	$0 \rightarrow 11, -15 \rightarrow 15, -17 \rightarrow 17$	$0 \rightarrow 15, -17 \rightarrow 17, -18 \rightarrow 18$
Weighting scheme	$1/\sigma_F^2$	$1/\sigma_F^2$
Total unique data	7014	8924
Observed data ($I > 3\sigma(I)$)	6532	7608
No. parameters	338	245
R	0.026	0.021
R_w	0.034	0.024
Programs used	SDP [8]	SDP [8]

on Re). *Anal.* Found: C, 45.9; H, 5.0; N, 7.4; S, 4.2; Cl 4.6. Calc. for $C_{29}H_{38}N_4ClP_2SRe$: C, 45.9; H, 5.0; N, 7.4; S, 4.2; Cl, 4.6% IR: ν(Re≡N) 1052, ν(N–H) 3330 cm^{-1}. ^{1}H NMR (ppm): CH_3 1.45–2.25 m (12H), CH_2 3.95 m (broad) (4H) and 4.22 m (broad) (6H), phenyl 6.9–7.9 m (15H). ^{13}C NMR (ppm): CH_3 13.4, 14.4, 19.3 and 20.5, CH_2 24.5, 26.1, 26.4, 47.2 and 50.3, phenyl 127.1–142.5, C(N)Ph 166.3, C=S 172.2. FAB-MS: $m/z = 758$ (1% B) $[ReN(Cl)(Me_2PhP)_2(piptcb)]^+$ (M^+), $m/z = 512$ (35% B) $[ReN(Cl)(Me_2PhP)_2]^+$, $m/z = 620$ (100% B) $[ReN(Cl)(Me_2PhP)(piptcb)]^+$, $m/z = 723$ (72% B) $[ReN(Me_2PhP)_2(piptcb)]^+$.

Physical measurements

Routine IR spectra were recorded as KBr discs on a Specord 75 IR. ^{1}H 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 (Finningan). 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. Field desorption spectra were recorded with $CHCl_3$ as solvent.

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 maximum peaks of 0.843 e/Å^3 for $[ReN(Me_2PhP)_2(Etdtp)]_2$ in the neighbourhood of Re and 2.81 e/Å^3 for $[ReN(Cl)(Me_2PhP)_2(Et_2tcb)]$ in the Re–Cl bond. Crystal data and more details of the refinements are summarized in Table 1. See also 'Supplementary material'. Positional parameters are given in Tables 2 and 3.

Results and discussion

Synthesis and characterization

Novel nitrido complexes of rhenium(V) have been prepared by ligand-exchange reactions starting from

TABLE 2. Fractional positional parameters[a] for $[ReN(Cl)(Me_2PhP)_2(Et_2tcb)]$

Atom	x/a	y/b	z/c	B
Re1	0.23581(2)	0.29759(1)	0.28363(1)	2.017(3)
Cl1	0.3446(1)	0.2283(1)	0.11650(8)	2.96(2)
S1	0.4055(1)	0.2035(1)	0.37175(9)	3.11(2)
P1	0.0949(1)	0.3862(1)	0.16499(8)	2.35(2)
P2	0.0942(1)	0.1128(1)	0.27337(8)	2.45(2)
N1	0.1357(4)	0.3385(4)	0.3751(3)	3.08(8)
N2	0.4021(4)	0.4327(3)	0.2764(3)	2.54(7)
N3	0.5773(4)	0.4094(3)	0.3994(3)	2.82(7)
N4	0.5966(5)	0.2791(4)	0.5109(3)	3.45(9)
C1	0.5313(5)	0.3073(4)	0.4289(3)	2.69(8)
C2	0.5258(5)	0.4605(4)	0.3246(3)	2.36(8)
C3	0.7042(6)	0.3620(5)	0.5625(4)	3.8(1)
C4	0.8524(7)	0.3643(6)	0.5235(5)	5.2(2)
C5	0.5739(8)	0.1656(6)	0.5497(5)	6.8(1)
C6	0.480	0.132	0.621	6.2
C11	0.6212(5)	0.5655(4)	0.2999(4)	2.56(8)
C12	0.7213(6)	0.6186(4)	0.3693(4)	3.6(1)
C13	0.8101(7)	0.7154(5)	0.3470(5)	5.3(1)
C14	0.8012(7)	0.7607(5)	0.2569(6)	5.6(2)
C15	0.7031(7)	0.7101(5)	0.1877(5)	4.3(1)
C16	0.6136(5)	0.6121(4)	0.2089(4)	3.06(9)
C20	−0.0632(5)	0.4355(5)	0.2166(4)	3.8(1)
C30	0.0221(5)	0.3082(4)	0.0555(4)	3.15(9)
C41	0.1943(5)	0.5139(4)	0.1174(3)	2.45(8)
C42	0.1948(5)	0.6174(4)	0.1653(4)	3.10(9)
C43	0.2754(6)	0.7137(4)	0.1310(4)	3.8(1)
C44	0.3557(6)	0.7073(4)	0.0483(4)	3.6(1)
C45	0.3555(6)	0.6056(4)	0.0009(4)	3.5(1)
C46	0.2764(5)	0.5090(4)	0.0344(4)	2.99(9)
C50	0.1898(6)	0.0000(4)	0.2310(5)	4.0(1)
C60	0.0418(6)	0.0708(5)	0.3942(4)	4.1(1)
C71	−0.0782(5)	0.0839(4)	0.2066(3)	2.48(8)
C72	−0.1931(6)	0.1351(5)	0.2415(4)	3.5(1)
C73	−0.3260(6)	0.1167(6)	0.1937(5)	4.7(1)
C74	−0.3459(7)	0.0487(6)	0.1126(5)	5.0(1)
C75	−0.2348(8)	−0.0029(5)	0.0767(4)	4.8(1)
C76	−0.0990(6)	0.0152(4)	0.1225(4)	3.3(1)

Atom C6 is disordered with 50% probability on the position 0.66047, 0.10947, 0.54385. [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].

TABLE 3. Fractional positional parameters[a] for $[ReN(Me_2PhP)_2(Etdtp)]_2$[b]

Atom	x/a	y/b	z/c	B
Re1	0.03493(1)	0.20551(1)	0.35839(1)	1.535(2)
S1	−0.17717(8)	0.13166(7)	0.38858(6)	2.23(1)
S2	−0.05515(8)	0.23525(7)	0.57143(6)	2.06(1)
P1	−0.19874(8)	0.14299(7)	0.56306(6)	1.81(1)
P2	0.14700(8)	0.08779(7)	0.16405(6)	1.87(1)
P3	0.25296(8)	0.24238(7)	0.37636(7)	1.92(1)
O1	−0.3657(3)	0.2321(2)	0.6344(2)	2.72(5)
O2	0.1721(2)	−0.0146(2)	0.3825(2)	2.16(4)
N1	−0.0319(3)	0.3574(2)	0.3174(2)	2.19(5)
C1	−0.4331(5)	0.3666(4)	0.6086(4)	4.5(1)
C2	−0.5743(6)	0.4327(5)	0.6969(5)	5.6(1)
C10	0.0734(4)	−0.0385(3)	0.1427(3)	2.86(7)
C20	0.3464(4)	−0.0062(3)	0.1281(3)	2.72(7)
C31	0.1214(3)	0.1832(3)	0.0387(3)	2.34(6)
C32	−0.0030(4)	0.2978(4)	0.0496(3)	3.28(8)
C33	−0.0266(5)	0.3649(4)	−0.0484(3)	4.23(9)
C34	0.0728(5)	0.3198(5)	−0.1569(3)	4.8(1)
C35	0.1951(6)	0.2073(5)	−0.1690(3)	5.0(1)
C36	0.2203(5)	0.1384(4)	−0.0723(3)	3.83(9)
C40	0.2039(4)	0.3898(3)	0.4717(3)	3.29(8)
C50	0.3714(4)	0.1135(3)	0.4438(3)	3.30(7)
C61	0.3791(3)	0.2717(3)	0.2461(3)	2.28(6)
C62	0.3207(4)	0.3383(3)	0.1590(3)	3.26(7)
C63	0.4155(5)	0.3616(4)	0.0593(4)	4.06(9)
C64	0.5667(5)	0.3213(4)	0.0468(4)	4.08(9)
C65	0.6235(4)	0.2568(4)	0.1323(4)	4.1(1)
C66	0.5315(4)	0.2312(4)	0.2320(4)	3.35(8)

[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]. [b]Parameters of the symmetry-related atoms can be generated by the symmetry operation $-x, y, 1-z$.

$[ReNCl_2(Me_2PhP)_3]$. In contrast to similar reactions with $[ReNCl_2(Ph_3P)_2]$, the equatorial coordination sphere is only partially substituted by the chelating ligands and two Me_2PhP molecules remain. The products are yellow, neutral complexes which are easily soluble in $CHCl_3$ or benzene, moderately soluble in alcohols and nearly insoluble in hydrocarbons.

The resulting mixed-ligand complexes have the general formula $[ReNCl_2(Me_2PhP)_2L]$ with L=*N*-(*N*,*N*-thiocarbamoyl)benzamidinates, diphenyldithiophosphinate and diethyldithiocarbamate. Bishop *et al.* [9] reported the synthesis of $[ReN(Me_2PhP)(R_2dtc)_2]$ complexes during similar reactions with acetone as solvent. Obviously, the nature of the products is strongly dependent on the solvents used, as was also observed during ligand exchange reactions with $[ReCl_3(Me_2PhP)_3]$ and dithiocarbamates [10].

$[ReNCl_2(Me_2PhP)_3]$ reacts with ammonium diethyldithiophosphate under formation of a binuclear nitrido complex. During this reaction the cleavage of an O–ethyl bond occurs and the monoethyldithiophosphato ligand, $EtO(OH)PS_2^-$ (**II**), is formed which acts as a tridentate, bridging ligand between the two rhenium centres. To our knowledge, up to now the metal-induced saponification of a dialkyldithiophosphoric acid ester has only been observed in one case: during the formation of the nickel(II) mixed-ligand complex $Bu_4N[Ni(mnt)(EtO(OH)PS_2)]$ (mnt=1,2-dicyanoethene-dithiolate), the crystal structure of which has been reported [11]. In this complex, however, the monoethyldithiophosphato ligand is only coordinated bidentately via the sulfur donor atoms.

The IR spectra of the new rhenium nitrido complexes show Re≡N vibrations in the typical range between 1000 and 1100 cm^{-1} [2]. The compounds are diamagnetic as expected for d^2-complexes with the 'N^{3-}' ligand, the

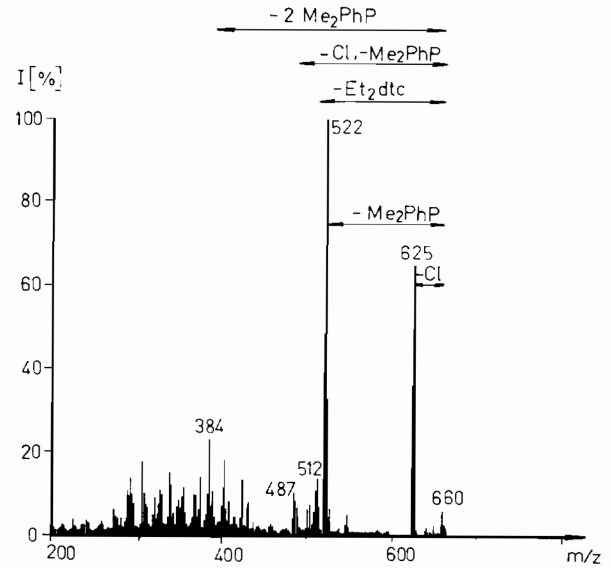


Fig. 1. FAB$^+$ mass spectrum of [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$dtc)] (matrix: 3-nitrobenzylalcohol).

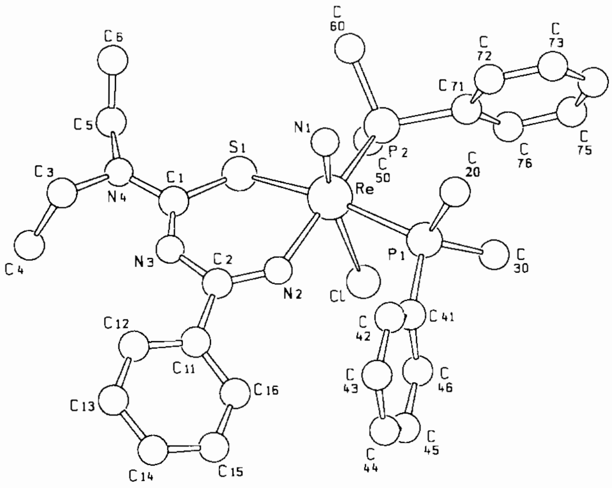


Fig. 2. SCHAKAL [15] plot of [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)] along with the atomic numbering scheme.

TABLE 4. Selected bond lengths and angles in [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)] with e.s.d.s

Bond lengths (Å)					
Re–N1	1.678(4)	Re–P1	2.444(1)	N3–C1	1.322(6)
Re–Cl	2.673(1)	Re–P2	2.416(1)	N3–C2	1.334(7)
Re–S	2.409(1)	S–C1	1.742(4)	N2–C2	1.319(5)
Re–N2	2.092(3)				

Bond angles (°)			
N1–Re–Cl	168.2(1)	S–Re–P2	83.74(4)
N1–Re–S	101.1(1)	S–Re–N2	86.6(1)
N1–Re–N2	103.2(2)	P1–Re–P2	97.42(2)
N1–Re–P1	90.9(1)	P1–Re–N2	89.6(2)
N1–Re–P2	91.1(1)	P2–Re–N2	164.1(1)
Cl–Re–S	88.96(4)	Re–S–C1	107.4(2)
Cl–Re–N2	83.5(2)	Re–N2–C2	133.3(3)
Cl–Re–P1	79.32(4)	S–C1–N3	128.2(4)
Cl–Re–P2	83.66(4)	C1–N3–C2	127.3(4)
S–Re–P1	168.00(4)	N2–C2–N3	128.1(4)

electrons of which strongly interact with the rhenium d_{xy} 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. This interpretation follows that which was given for diamagnetic rhenium(V) and technetium(V) complexes with the MO^{3+} moiety [12]. The ^{1}H and ^{13}C NMR spectra of the compounds are characterized by narrow lines and typical high order coupling patterns due to the ^{31}P nuclei of the phosphorus containing ligands and the formation of stereoisomers.

In the FAB$^+$ mass spectra of the [ReN(Cl)(Me$_2$PhP)$_2$L] complexes peaks due to the molecular ions are well established. Figure 1 shows that of [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$dtc)]; typical fragmentation pathways are indicated. Generally, fragmentations occur mainly by the loss of complete ligands. Obviously, the loss of one Me$_2$PhP or Cl$^-$ ligand is preferred. The FAB$^+$ spectrum of [ReN(Me$_2$PhP)$_2$(Etdtp)]$_2$ shows an intense (30% B) peak with $m/z = 634$ which corresponds to the protonated form of the monomeric complex. Peaks with higher m/z could not be observed. The field desorption mass spectrum of the compound, however, exhibits the molecular ion peak due to the dimeric unit at $m/z = 1266$.

The crystal structure of [ReN(Cl)(Me$_2$PhP)$_2$(Et$_2$tcb)] consists of discrete monomeric molecules. The molecular structure together with the atomic numbering scheme is given in Fig. 2. Selected interatomic distances and angles are summarized in Table 4.

The rhenium atom is six-coordinate with the chloro ligand coordinated *trans* to the nitrido nitrogen with an N1–Re–Cl bonding angle of 168.00(4)°. The complex is markedly distorted from octahedral geometry, as the donor atoms of the chelating ligand are bent out of the equatorial plane away from the nitrido ligand. This can be understood by the sterical requirements of the bulky ligands, but may also be a consequence of the significant π-bonding in the direction of the ReN bond. The Re≡N bond distance is 1.678(4) Å which falls in the typical region of metal–nitrogen triple bonds [1–3]. As a result of the strong *trans* labilizing influence of the nitrido ligand, the Re–Cl bond has the large value of 2.673(1) Å.

The *trans* effect of the phosphine ligands can be detected in the Re–S bond length of 2.409(1) Å which is longer by 0.09 Å than the mean value of 2.312(3) Å in the bis-chelate [ReO(Et$_2$tcb)$_2$]$^+$ [13]. In accordance with the bonding situation in the latter complex and its technetium analogue [TcO(Et$_2$tcb)$_2$]$^+$ [14], all C–N distances in the chelate ring of [ReN(Cl)(Me$_2$PhP)$_2$-

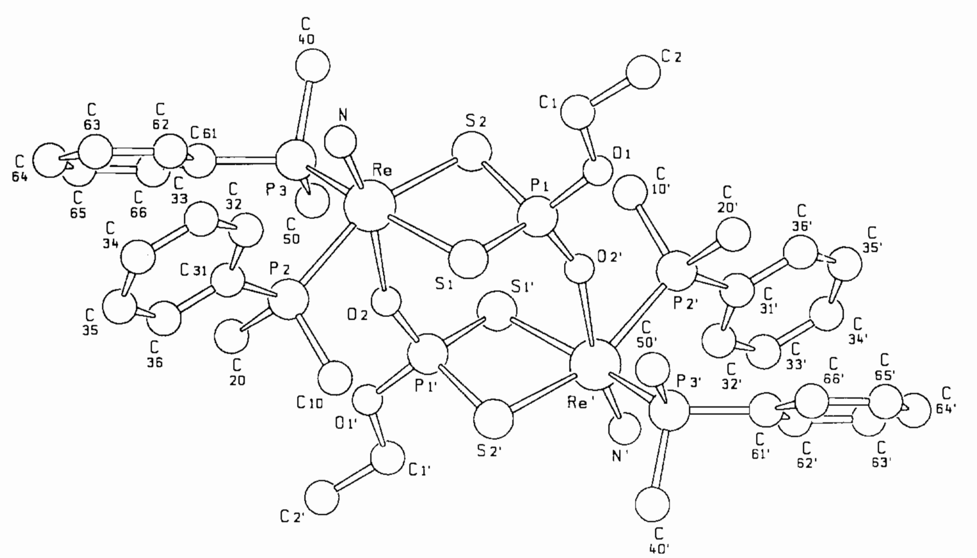


Fig. 3. SCHAKAL plot [15] of [ReN(Me$_2$PhP)$_2$(Etdtp)]$_2$ along with the atomic numbering scheme.

TABLE 5. Selected bond lengths and angles in [ReN(Me$_2$PhP)$_2$(Etdtp)]$_2$ with e.s.d.s

Bond lengths (Å)					
Re–N	1.661(2)	Re–P3	2.407(1)	S2–P1	2.039(1)
Re–S1	2.457(1)	Re–O2	2.347(2)	P1–O1	1.601(3)
Re–S2	2.439(1)	S1–P1	2.029(2)	P1–O2	1.493(2)
Re–P2	2.434(1)				

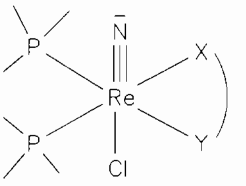
Bond angles (°)			
N–Re–S1	102.9(2)	S2–Re–P3	87.56(3)
N–Re–S2	104.0(1)	S2–Re–O2	85.94(5)
N–Re–P2	97.8(1)	P2–Re–P3	96.63(3)
N–Re–P3	90.4(1)	P2–Re–O2	73.03(5)
N–Re–O2	168.0(1)	P3–Re–O2	83.3(1)
S1–Re–S2	79.97(3)	Re–S1–P1	88.55(4)
S1–Re–P2	91.15(3)	Re–S2–P1	88.86(4)
S1–Re–P3	163.56(3)	S1–P1–S2	101.3(1)
S1–Re–O2	85.22(6)	Re–O2–P1	155.6(1)
S2–Re–P2	157.83(2)		

(Et$_2$tcb)] are almost equal indicating the presence of an extended conjugated π-system.

Crystals of [ReN(Me$_2$PhP)$_2$(Etdtp)]$_2$ which were suitable for X-ray diffraction are available by slow evaporation of CHCl$_3$/iso-propanol solutions of the compound. The complex crystallizes in dimeric units in which the monoethyldithiophosphato ligands connect the two [ReN(Me$_2$PhP)$_2$(Etdtp)] units via their oxygen donor functions. A plot of the compound along with the atomic numbering scheme is given in Fig. 3. Table 5 contains selected bond lengths and angles.

The rhenium atoms are six-coordinate with the typical, short metal–(nitrido)nitrogen bond length of 1.661(2) Å and a labilized, weak bond in *trans* position (Re–O2′ 2.347(2) Å). The donor atoms S1, S2 and P2 are bent out of the equatorial plane by 7–13° away from the nitrido bond. An S1–Re–S2 angle of 79.79(3)° is found which is a result of the restricting bite of the dithiophosphate. The atom P1 has an approximate tetrahedral environment as is expected for an sp^3 hybridized phosphorus atom. The bond distance P1–O1 is longer by about 0.1 Å than the P1–O2 distance indicating considerable double bond character for the latter bond.

With the mixed-ligand complexes discussed above, especially with the [ReN(Cl)(Me$_2$PhP)$_2$(L)] (**III**) compounds, a new class of rhenium compounds has been developed which has a considerable potential as starting material for further ligand-exchange reactions.



III

They are equipped with differently coordinated ligands (X$^-$, PR$_3$, L, N^{3-}) which should enable distinct ligand exchange experiments and/or reactions using the nucleophilic properties of the nitrido nitrogen to be performed.

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-7514 Eggenstein-Leopoldshafen 2, as Supplementary Publication Nos. CSD 56945 [ReN(Cl)$(Me_2PhP)_2(Et_2tcb)$] and CSD 56883 $[ReN(Me_2PhP)_2(Etdtp)]_2$.

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References

1 K. Dehnicke and J. Strähle, *Angew. Chem., 93* (1981) 451, and refs. therein.
2 K.A. Walton, in G. Wilkison, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 4, Pergamon, Oxford, 1st edn., 1987, pp. 125, and refs. therein.
3 K. Dehnicke and J. Strähle, *Angew. Chem., 104* (1992) 978, and refs. therein.
4 (a) J. Chatt, J.D. Garforth, N.P. Johnson and G.A. Rowe, *J. Chem. Soc. (London),* (1964) 1012; (b) J. Chatt, C.D. Falk, G.J. Leigh and R.J. Paske, *J. Chem. Soc. A,* (1969) 2288.
5 J.F. Rowbottom and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* (1972) 826.
6 L. Beyer and R. Widera, *Tetrahedron Lett., 23* (1982) 1881.
7 L. Beyer, J. Hartung and R. Widera, *Tetrahedron, 40* (1984) 405.
8 *VAX-SDP, structure determination package,* Version 3.0, Enraf-Nonius, Delft, Netherlands.
9 M.W. Bishop, J. Chatt, J.R. Dilworth, B.D. Neaves, P. Dahlstrom, J. Hyde and J. Zubieta, *J. Organometallic Chem., 213* (1981) 109.
10 U. Abram and B. Lorenz, *Z. Naturforsch., Teil B,* in press.
11 R. Kirmse, W. Dietzsch, J. Stach, L. Golic, R. Böttcher, W. Brunner, M.C.M. Gribnau and C.P. Keijzers, *J. Mol. Phys., 57* (1986) 1139.
12 A. Davison and A.G. Jones, *Int. J. Appl. Radiat. Isot., 33* (1982) 881.
13 U. Abram and R. Hübener, *Inorg. Chim. Acta, 206* (1993) 231.
14 U. Abram, R. Münze, J. Hartung, L. Beyer, R. Kirmse, K. Köhler, J. Stach, H. Behm and P.T. Beurskens, *Inorg. Chem., 28* (1989) 834.
15 E. Keller, *SCHAKAL Program,* University of Freiburg, Germany.