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Isothiocyanato complexes of rhenium
II. Synthesis, characterization and structures of $ReN(NCS)_2(Me_2PhP)_3$ and $Re(NS)(NCS)_2(Me_2PhP)_3$*

Rainer Hübener**, Ulrich Abram and Joachim Strähle
Institute of Inorganic Chemistry, University of Tubingen, Auf der Morgenstelle 18, D-72076 Tubingen (Germany)

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Abstract

Novel rhenium isothiocyanato complexes have been prepared by ligand exchange procedures starting from $[ReNCl_2(Me_2PhP)_3]$ and KSCN or trimethylsilylisothiocyanate, Me_3Si–NCS The reaction with KSCN yields the rhenium(V) nitrido complex $[ReN(NCS)_2(Me_2PhP)_3]$, whereas with Me_3Si–NCS the rhenium(I) thionitrosyl compound $[Re(NS)(NCS)_2(Me_2PhP)_3]$ is formed. Both complexes are air-stable. They have been characterized spectroscopically and studied by X-ray diffraction. $[ReN(NCS)_2(Me_2PhP)_3]$ crystallizes in the triclinic space group $P\bar{1}$ ($a=9.986(9)$, $b=12.49(1)$, $c=13.21(1)$ Å, $\alpha=95.23(5)$, $\beta=101\ 61(5)$, $\gamma=110.80(4)°$) with $Z=2$ The final R value is 0.049. The coordination sphere of the rhenium atom is a distorted octahedron, with an Re≡N bond length of 1.66(1) Å. $[Re(NS)(NCS)_2(Me_2PhP)_3]$ crystallizes in the monoclinic space group $P2_1$ ($a=11.442(4)$, $b=11.005(1)$, $c=12.770(4)$ Å, $\beta=91.96(2)°$) with $Z=2$. The final R value is 0 041. The coordination geometry about the rhenium atom is a distorted octahedron. The Re=NS bond distance is 1.85(3) Å.

Key words: Crystal structures, Rhenium complexes; Isothiocyanato complexes

Introduction

Synthesis, structural characterization and reactions of rhenium nitrido compounds have been described in numerous papers [2–9]. 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 reactions. Usual starting materials for this approach are phosphine complexes of rhenium(V).

In this paper, we describe the synthesis, characterization and X-ray crystal structures of new isothiocyanate complexes of rhenium with the metal in the formal oxidation states 'I' and 'V' which were prepared from $[ReNCl_2(Me_2PhP)_3]$ and KSCN or Me_3Si–NCS. The reaction of trimethylsilyl isothiocyanate with $[ReNCl_2(Me_2PhP)_3]$ is a new approach to thionitrosyl complexes of rhenium.

Experimental

Syntheses

$[ReNCl_2(Me_2PhP)_3]$ was prepared by a literature procedure [9]. KSCN and Me_3SiNCS were purchased commercially (Aldrich) and used without further purification.

$[ReN(NCS)_2(Me_2PhP)_3]$

1 g (1.45 mmol) $[ReNCl_2(Me_2PhP)_3]$ was dissolved in about 200 ml $CHCl_3$, and 291 mg (3 mmol) KSCN dissolved in about 100 ml MeOH were added. The mixture was stirred for 24 h at room temperature and filtered to remove KCl. Then the volume was reduced to about 50 ml and upon standing overnight yellow crystals deposited which were collected. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of $CHCl_3$/MeOH solutions.

Yield 1.045 g (98% based Re). *Anal.* Found: C, 42.6; H, 4.7; N, 5.7; S, 9.4. Calc. for $C_{26}H_{33}N_3P_3S_2Re$: C, 42.7; H, 4.6; N, 5.7; S, 8.8%. IR: ν(Re≡N) 1055, ν(NCS) 2088, 2052 cm^{-1}. FAB-MS: $m/z=731$ (8% B) $[ReN(NCS)_2(Me_2PhP)_3]^+$ (M^+), $m/z=673$ (89% B) $[ReN(NCS)(Me_2PhP)_3]^+$, $m/z=641$ (8% B) $[ReN(NC)(Me_2Ph)_3]^+$, $m/z=593$ (84% B) $[ReN(NCS)_2(Me_2$-

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*For Part I see ref. 1.

**Author to whom correspondence should be addressed

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$PhP)_2]^+$, $m/z = 535$ (68% B) $[ReN(NCS)(Me_2PhP)_2]^+$, $m/z = 455$ (16% B) $[ReN(NCS)_2(Me_2PhP)]^+$, $m/z = 396$ (10% B) $[ReN(NCS)(Me_2PhP)]^+$, $m/z = 338$ (18% B) $[ReN(Me_2PhP)]^+$. ^1H NMR: 7.58–6.97m (relative intensity 2.5H, phenyl), 2.03m (1H, methyl), 1.77m (1H, methyl), 1.38m (1H, methyl). ^{13}C NMR: 11.1m (methyl), 17.1m (methyl), 18.1m (methyl), 127.9–137.4m (phenyl), 142.0 and 148.2s (NCS).

[Re(NS)(NCS)$_2$(Me$_2$PhP)$_3$]

(a) 1 g (1.45 mmol) $[ReNCl_2(Me_2PhP)_3]$ was dissolved in about 250 ml $CHCl_3$, and excess (13 mmol) Me_3Si–NCS was added. The mixture was stirred for 3 h at room temperature. Upon standing for several days, brownish red crystals deposited which were collected and recrystallized from $CHCl_3$/iso-propanol. Yield 578 mg (53% based Re).

(b) 73 mg (0.1 mmol) $[ReN(NCS)_2(Me_2PhP)_3]$ were dissolved in about 10 ml CH_2Cl_2 and excess (13 mmol) Me_3Si–NCS was added. The mixture was stirred for 2 days at room temperature. During this time the colour changed to brownish red. After removing the solvent in vacuum, the oily residue was dissolved in a minimum amount of $CHCl_3$ and iso-propanol was added. Upon standing brownish red crystals of $[Re(NS)(NCS)_2(Me_2PhP)_3]$ deposited. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of $CHCl_3$/iso-propanol solutions.

Yield 12 mg (16% based Re). *Anal.* Found: C, 40.7; H, 4.4; N, 5.5; S, 14.8. Calc. for $C_{26}H_{33}N_3P_3S_3Re$. C, 40.9; H, 4.4; N, 5.5; S, 12.6%. IR: ν(N–S) 1176, ν(NCS) 2092, 2056 cm^{-1}. FAB-MS: $m/z = 763$ (26% B) $[Re(NS)(NCS)_2(Me_2PhP)_3]^+$ (M^+), $m/z = 705$ (61% B) $[Re(NS)(NCS)(Me_2PhP)_3]^+$, $m/z = 673$ (27% B) $[ReN(NCS)(Me_2PhP)_3]^+$, $m/z = 625$ (28% B) $[Re(NS)(NCS)_2(Me_2PhP)_2]^+$, $m/z = 593$ (28% B) $[ReN(NCS)_2(Me_2PhP)_2]^+$, $m/z = 567$ (44% B) $[Re(NS)(NCS)(Me_2PhP)_2]^+$, $m/z = 535$ (32% B) $[ReN(NCS)(Me_2PhP)_2]^+$. ^1H NMR: 7.4–6.9 (relative intensity 2.5H, phenyl), 1.82m (1H, methyl), 1.69m (1H, methyl), 1.22m (1H, methyl). ^{13}C NMR: 12.3m (methyl), 13.2m (methyl), 13.5m (methyl), 128.7–136.4m (phenyl), NCS signals could not be detected unambiguously.

Physical measurements

IR spectra were recorded as KBr discs on a Bruker IFS 25 spectrometer. ^1H NMR 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: 50 °C); nitrobenzylalcohol was used as matrix.

X-ray diffraction

$[ReN(NCS)_2(Me_2PhP)_3]$ crystallizes as yellow columns. From the air-stable crystals one with approximate dimensions $0.15 \times 0.15 \times 0.15$ mm was selected. All X-ray experiments were carried out on a single crystal diffractometer CAD4 (Enraf-Nonius) with Mo Kα radiation at a temperature of -50 °C. The lattice parameters of the triclinic compound with the space group $P\bar{1}$ (Table 1) were refined using 25 reflections in the range of θ between 6 and 14°. The data collection between $\theta = 3$ and 32° resulted in 10 783 reflections. During the measurements no loss of intensity could be detected. The structure was solved by the heavy-atom Patterson method. 6053 unique intensity values with $I > 3\sigma(I)$ remained after merging, and could be used for the structure determination and refinement. Refinement with isotropic temperature parameters converged at $R = 0.084$. An empirical absorption correction [10] was applied and further refinement improved R to 0.065. With anisotropic temperature parameters for the non-hydrogen atoms an R value of 0.053 was obtained. With the calculated positions of the H atoms taken into account during the structure factor calculation and after refinement of the extinction coefficient [11] the final R value of 0.049 was obtained.

A brownish red rhombus of $[Re(NS)(NCS)_2(Me_2PhP)_3]$ with the approximate dimensions $0.1 \times 0.1 \times 0.1$ mm was used for the data collection. The data collection at room temperature between $\theta = 3$ and 31° resulted in 7976 reflections. The space group $P2_1$ was derived from systematic absences and the structure refinement. The positions of most atoms were obtained from a Patterson synthesis. Subsequent difference Fourier syntheses then showed the remaining C atoms of the dimethylphenylphosphine ligands Anisotropic temperature parameters were assigned to all non-hydrogen atoms with the exception of C1 and N3. A refinement with anisotropic temperature parameters for the C1 and N3 atoms did not result in satisfactory values. They were therefore assigned with isotropic temperature parameters. With the calculated positions of the H atoms taken into account during the structure factor calculation and after refinement of the extinction coefficient [11] the final R value of 0.041 was obtained.

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. Program used: VAX-SDP [12], SHELXS-86 [13], SCHAKAL [14].

Results and discussion

The nitrido ligand is one of the most powerful π-donor ligands [2, 4] and stabilizes metals preferably in

TABLE 1. Crystal data collection and structure refinement parameters

	$[ReN(NCS)_2(Me_2PhP)_3]$	$[Re(NS)(NCS)_2(Me_2PhP)_3]$
Formula	$C_{26}H_{33}N_3P_3S_2Re$	$C_{26}H_{33}N_3P_3S_3Re$
Molecular weight	730.82	726.89
Space group	triclinic $P\bar{1}$	monoclinic $P2_1$
Lattice dimensions		
a (Å)	9.986(9)	11.442(4)
b (Å)	12.49(1)	11.005(1)
c (Å)	13.21(1)	12.570(4)
α (°)	95.23(5)	90
β (°)	101.61(5)	91.96(2)
γ (°)	110.80(4)	90
Formula units, Z	2	2
V (Å^3)	1484.6	1581.9
Measuring temperature (°C)	−50	20
D_c (g cm^{-3})	1.635	1.602
Radiation used (λ, (Å))	Mo Kα (0.7093)	Mo Kα (0.7093)
Scan type	ω	ω
Absorption coefficient (cm^{-1})	44.62	42.53
Absorption correction	DIFABS	DIFABS
T_{min}	0.595	0.361
T_{max}	1.164	1.126
Range of h, k, l	$0 \rightarrow 14$, $\overline{18} \rightarrow 18$, $\overline{19} \rightarrow 19$	$\overline{16} \rightarrow 16$, $0 \rightarrow 15$, $\overline{18} \rightarrow 18$
Weighting scheme	$1/\sigma_F{}^2$	$1/\sigma_F{}^2$
Total unique data	10268	4108
Observed data ($I > 3\sigma(I)$)	6053	2061
No. parameters	317	315
R	0.049	0.041
R_w	0.056	0.050

their high formal oxidation states. The rhenium–nitrogen triple bond is very stable [3, 4] and thus, numerous ligand exchange reactions can be performed with ReN complexes remaining the Re≡N unit. $[ReN(NCS)_2(Me_2PhP)_3]$ is formed in high yields by the reaction of the well-known $[ReNCl_2(Me_2PhP)_3]$ with KSCN.

The air-stable compound is readily soluble in organic solvents such as acetone or $CHCl_3$. IR studies show the ν(NCS) stretching vibration for the N-bound isothiocyanate ligands at 2088 and 2052 cm^{-1}; the ν(Re≡N) vibration is found at 1055 cm^{-1}. FAB mass spectrometric studies confirm the composition of $[ReN(NCS)_2(Me_2PhP)_3]$ and show evidence for the molecular ion peak at $m/z = 731$. 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 [7, 8, 15–17] and confirms the extraordinary stability of the Re(Tc)≡N bonds. In contrast, Re=O bonds are included in the fragmentation of comparable oxorhenium complexes [18, 19].

The ^{1}H NMR spectrum of $[ReN(NCS)_2(Me_2PhP)_3]$ consists of a typical high order pattern in the aromatic region between 6.97 and 7.58 ppm and of three well-separated signals due to the methyl protons (1.38, 1.77 and 2.03 ppm). The high order splitting patterns of the two downfield methyl signals caused by ^{31}P couplings are identical, but differ from those of the high field signals. The structure includes two equivalent and one different Me_2PhP ligands. The two methyl groups of the two equivalent ligands are diastereotopic, and different chemical shifts are expected. ^{1}H NMR studies on the diamagnetic Re(I) thionitrosyl complex $[Re(NS)(NCS)_2(Me_2PhP)_3]$ resulted in spectra with exactly the same patterns.

A SCHAKAL plot [14] together with the molecular numbering scheme is given in Fig. 1. Table 4 contains selected interatomic distances and angles. The rhenium atom is six-coordinate, with the three phosphine ligands coordinated meridionally *cis* to the nitrido ligand. The complex is distorted from the octahedral geometry, as the equatorial NCS ligand is bent out of the equatorial plane away from the nitrogen. The N3–Re–N2 angle is found to be 103.9(3)°, the N3–Re–P angles are between 90.7(2) and 94.5(3)°. With this, the structural feature is close to that of $[ReNCl_2(Me_2PhP)_3]$ [20]. The two NCS^- ligands are nitrogen bonded as has been found for all structurally characterized Re–NCS complexes [1–4, 21, 22]. The isothiocyanate ligands are almost linear (N–C–S angles between 178(1) and 179(1)°). The Re–N3 distance is 1.66 Å which is in the typical range of metal–nitrogen triple bonds [2, 4]. The *trans* effect

TABLE 2 Fractional positional parameters[a] for $[ReN(NCS)_2(Me_2PhP)_3]$

Atom	x/a	y/b	z/c	B
Re	0.24373(3)	0.34278(3)	0.28950(3)	2.304(5)
S1	−0.1935(3)	0.2317(3)	−0.0200(2)	5.53(7)
S2	−0.0300(3)	0.1810(3)	0.5376(2)	5.95(7)
P1	0.3495(2)	0.4220(2)	0.1500(2)	3.12(4)
P2	0.2018(2)	0.5163(2)	0.3515(2)	3.15(4)
P3	0.2360(2)	0.1470(2)	0.2363(2)	2.85(4)
N1	0.0345(7)	0.2930(6)	0.1608(6)	3.5(2)
N2	0.1027(8)	0.2662(6)	0.3811(6)	3.6(2)
N3	0.4110(7)	0.3896(6)	0.3709(5)	3.0(1)
C1	−0.0623(8)	0.2668(7)	0.0866(7)	3.3(2)
C2	0.0465(9)	0.2311(7)	0.4469(7)	3.7(2)
C11	0.3141(9)	0.3251(7)	0.0267(6)	3.1(2)
C12	0.186(1)	0.302(1)	−0.0519(7)	4.5(2)
C13	0.162(1)	0.231(1)	−0.1453(8)	5.1(3)
C14	0.256(1)	0.186(1)	−0.1639(9)	5.9(3)
C15	0.384(1)	0.2064(9)	−0.0870(8)	5.1(2)
C16	0.413(1)	0.2770(8)	0.0091(7)	4.0(2)
C21	0.550(1)	0.488(1)	0.1923(8)	5.0(3)
C31	0.294(1)	0.5350(8)	0.1014(8)	5.0(2)
C41	0.3426(8)	0.6563(6)	0.3558(7)	3.2(2)
C42	0.4905(9)	0.6734(7)	0.3953(7)	3.5(2)
C43	0.602(1)	0.7796(8)	0.4041(7)	4.0(2)
C44	0.570(1)	0.8717(9)	0.3759(9)	5.1(3)
C45	0.424(1)	0.8564(8)	0.335(1)	6.0(3)
C46	0.312(1)	0.7508(8)	0.325(1)	5.0(3)
C51	0.0290(9)	0.5229(8)	0.2848(9)	4.9(2)
C61	0.195(1)	0.5254(8)	0.4883(7)	4.2(2)
C71	0.4137(8)	0.1408(6)	0.2339(6)	3.0(2)
C72	0.436(1)	0.0808(8)	0.1488(8)	4.0(2)
C73	0.572(1)	0.0770(9)	0.1519(9)	4.9(2)
C74	0.687(1)	0.1291(9)	0.240(1)	5.4(3)
C75	0.667(1)	0.1864(9)	0.326(1)	5.7(3)
C76	0.5293(9)	0.1922(8)	0.3225(8)	4.3(2)
C81	0.112(1)	0.0684(8)	0.1119(8)	4.1(2)
C91	0.175(1)	0.0481(8)	0.3248(8)	4.1(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)

TABLE 3 Fractional positional parameters[a] for $[Re(NS)(NCS)_2(Me_2PhP)_3]$

Atom	x/a	y/b	z/c	B
Re	0.14064(5)	0.000	0.21483(6)	2.87(1)
S1	−0.2711(4)	0.0322(8)	0.1146(5)	6.7(2)
S2	0.1539(8)	0.4299(7)	0.2944(7)	7.1(2)
S3	0.1821(6)	−0.2843(7)	0.1307(6)	5.9(2)
P1	0.3404(3)	0.0269(5)	0.2779(4)	3.0(1)
P2	0.1708(4)	0.0696(6)	0.0312(4)	3.4(1)
P3	0.0684(5)	−0.0603(6)	0.3881(5)	3.7(1)
N1	−0.034(1)	0.022(2)	0.1702(9)	3.0(3)
N2	0.123(2)	0.181(1)	0.259(1)	4.8(4)
N3	0.168(2)	−0.157(2)	0.168(1)	4.6(4)[b]
C1	−0.133(1)	0.025(2)	0.148(1)	3.3(3)[b]
C2	0.131(2)	0.285(2)	0.276(2)	5.5(6)
C11	0.431(2)	−0.094(3)	0.249(2)	5.6(6)
C21	0.415(2)	0.154(2)	0.227(1)	4.4(4)
C31	0.370(2)	0.046(2)	0.416(1)	3.7(5)
C32	0.337(2)	0.154(3)	0.462(2)	6.5(7)
C33	0.355(3)	0.177(4)	0.575(2)	9.4(9)
C34	0.411(3)	0.089(3)	0.636(2)	8.8(9)
C35	0.445(2)	−0.023(3)	0.593(2)	7.4(7)
C36	0.423(2)	−0.035(2)	0.480(2)	5.8(8)
C41	0.070(2)	−0.015(2)	−0.063(1)	4.5(5)
C51	0.138(2)	0.227(2)	0.005(2)	6.3(6)
C61	0.307(2)	0.039(2)	−0.027(2)	5.0(7)
C62	0.382(2)	0.132(2)	−0.048(2)	4.7(5)
C63	0.494(2)	0.115(3)	−0.081(2)	5.7(6)
C64	0.532(2)	0.005(6)	−0.104(1)	6.8(6)
C65	0.454(2)	−0.096(2)	−0.085(2)	7.1(6)
C66	0.337(2)	−0.068(2)	−0.045(2)	5.1(6)
C71	−0.064(2)	−0.143(3)	0.379(2)	6.8(7)
C81	0.030(2)	0.065(2)	0.469(2)	5.5(6)
C91	0.153(2)	−0.157(2)	0.473(2)	4.2(5)
C92	0.155(2)	−0.147(2)	0.585(2)	5.2(6)
C93	0.221(3)	−0.233(3)	0.647(2)	7.2(8)
C94	0.280(2)	−0.327(3)	0.602(2)	6.8(7)
C95	0.278(2)	−0.342(2)	0.494(2)	5.6(6)
C96	0.213(2)	−0.255(2)	0.431(2)	4.5(5)

[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] Isotropically refined atoms.

of the nitrido ligand can be detected in the long Re–N1 bond distance of 2.257(6) Å, which is longer by 0.18 Å than the comparable Re–N2 bond (*trans* to Me_2PhP).

$[Re(NS)(NCS)_2(Me_2PhP)_3]$ is formed by the reaction of $[ReNCl_2(Me_2PhP)_3]$ with Me_3Si–NCS. In contrast to the reaction with alkali or ammonium halides or pseudohalides, not only a ligand exchange of the chloro ligands occurs, but also the nitrido ligand is converted into a thionitrosyl group due to the interaction with excess Me_3Si–NCS.

Transition metal thionitrosyl complexes are commonly prepared (i) from nitrido complexes by the reaction with S_2Cl_2, $SOCl_2$, propylene sulfide or elemental sulfur, (ii) from metal complexes and $(NSCl)_3$, (iii) by reactions of N_4S_4 with metal halides or nitrides, (iv) by halide abstraction from coordinated NSF or NSCl, or (v) by reactions of NS^+ salts with transition metal complexes [23].

To our knowledge, there is only one report on the formation of a thionitrosyl group from nitride complexes and KSCN [24]. The use of trimethylsilyl isothiocyanate as sulfur donor is a new and facile approach to NS^+ complexes. The metal undergoes a four-electron reduction upon addition of the sulfur atom to the nitrido ligand. Simultaneously, a ligand exchange Cl^- versus NCS^- occurs. Interestingly, the reaction of $[ReN(NCS)_2(Me_2PhP)_3]$ with Me_3Si–NCS proceeds very slowly at room temperature. The product of this reaction, however, could also be identified as $[Re(NS)(NCS)_2(Me_2PhP)_3]$.

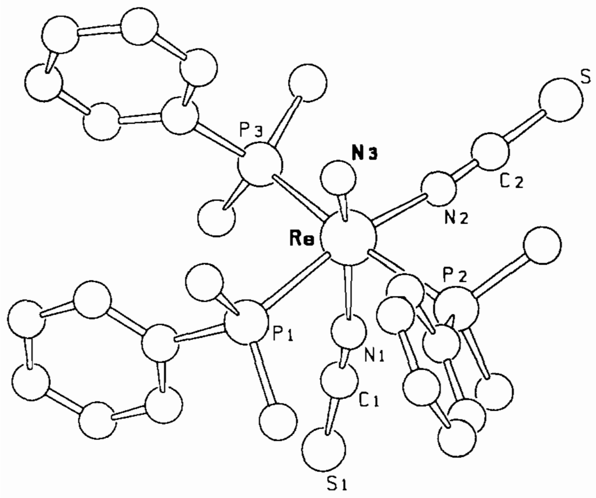

Fig. 1 SCHAKAL plot of [ReN(NCS)$_2$(Me$_2$PhP)$_3$].

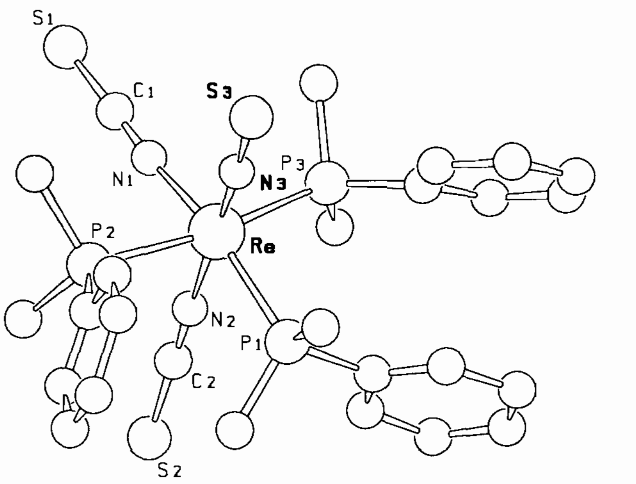

Fig. 2. SCHAKAL plot of [Re(NS)(NCS)$_2$(Me$_2$PhP)$_3$].

TABLE 4 Selected bond lengths and angles in [ReN(NCS)$_2$-(Me$_2$PhP)$_3$] with e.s.d.s in parentheses

Bond lengths (Å)					
Re–N1	2.257(6)	S2–C2	1.60(2)	Re–P1	2.421(2)
Re–N2	2.074(8)	N1–C1	1.16(1)	Re–P2	2.451(3)
Re–N3	1.660(6)	N2–C2	1.16(1)	Re–P3	2.452(2)
S1–C1	1.622(8)				
Bond angles (°)					
N1–Re–N2	85.0(3)	P2–Re–N2	83.0(2)		
N1–Re–N3	171.1(4)	P2–Re–N3	92.7(3)		
N2–Re–N3	103.9(3)	P3–Re–N1	86.8(3)		
P1–Re–P2	94.9(1)	P3–Re–N2	85.8(2)		
P1–Re–P3	94.7(1)	P3–Re–N3	94.5(3)		
P2–Re–P3	167.9(1)	Re–N1–C1	171.8(8)		
P1–Re–N1	80.4(3)	Re–N2–C2	167.8(7)		
P1–Re–N2	165.3(2)	S1–C1–N1	177.9(9)		
P1–Re–N3	90.7(2)	S2–C2–N2	179.0(9)		
P2–Re–N1	87.6(2)				

TABLE 5. Selected bond lengths and angles in [Re(NS)(NCS)$_2$-(Me$_2$PhP)$_3$] with e.s.d.s in parentheses

Bond lengths (Å)					
Re–N1	2.07(1)	Re–P1	2.411(4)	S2–C2	1.64(3)
Re–N2	2.08(2)	Re–P2	2.468(5)	N1–C1	1.16(2)
Re–N3	1.85(3)	Re–P3	2.447(6)	N2–C2	1.16(4)
S3–N3	1.49(2)	S1–C1	1.62(2)		
Bond angles (°)					
N1–Re–N2	81.9(7)	P2–Re–N2	88.3(5)		
N1–Re–N3	101.2(7)	P2–Re–N3	87.6(6)		
N2–Re–N3	101.2(7)	P3–Re–N1	85.4(4)		
P1–Re–P2	96.2(2)	P3–Re–N2	89.1(5)		
P1–Re–P3	94.9(2)	P3–Re–N3	95.7(6)		
P1–Re–N1	165.9(6)	Re–N1–C1	175(2)		
P1–Re–N2	84.0(6)	Re–N2–C2	168(2)		
P1–Re–N3	92.7(6)	Re–N3–S3	177(1)		
P2–Re–P3	168.3(2)	S1–C1–N1	178(1)		
P2–Re–N1	82.9(4)	S2–C2–N2	175(2)		

[Re(NS)(NCS)$_2$(Me$_2$PhP)$_3$] is readily soluble in organic solvents such as acetone or CHCl$_3$. IR studies show the ν(NCS) stretching vibration for the N-bound isothiocyanate ligands at 2092 and 2056 cm^{-1}; the ν(N–S) vibration of the thionitrosyl moiety is found at 1176 cm^{-1}.

In the FAB mass spectra of [Re(NS)(NCS)$_2$-(Me$_2$PhP)$_3$] the molecular ion can be detected at $m/z = 763$. Main fragments result from the abstraction of complete ligands. The sulfur atom of the thionitrosyl ligand is involved in the mass spectrometric fragmentation which is evident, for example, from the intense peaks at $m/z = 673$ or $m/z = 593$ which can be assigned to the fragments [ReN(NCS)(Me$_2$PhP)$_3$]$^+$ and [ReN-(NCS)$_2$(Me$_2$PhP)$_2$]$^+$, respectively.

A SCHAKAL plot [14] together with the molecular numbering scheme is given in Fig. 2. Table 5 contains selected distances and angles. The rhenium atom is six-coordinate, with the three phosphine ligands coordinated meridionally *cis* to the thionitrosyl group. The complex is slightly distorted from the octahedral geometry. Three ligands are bent out of the equatorial plane away from the thionitrosyl group. The NCS$^-$ ligands are N-bonded with Re–N distances of 2.07(2) Å. A significantly shorter Re–N bond length was found for the metal–thionitrosyl bond. The value of 1.85(3) Å falls in the region which is typical for thionitrosyl complexes [16, 23, 25, 26].

The resulting ReNS core is nearly linear with a bond angle of 177(1)° and thus, the bonding mode of the thionitrosyl group has to be discussed as NS$^+$ with extensive backbonding from the Re(I) centre. The N=S bond length of 1.49(2) Å in *mer*-[Re(NS)(NCS)$_2$-(Me$_2$PhP)$_3$] is comparable to the averaged value of 1.508 Å which can be derived from other thionitrosyl complexes [23].

A comparison of the general structural features of the title compounds shows a wide correspondence of the bond distances and angles. The most significant difference is the structural *trans* effect of the nitrido ligand which leads to a lengthening of the Re–N1 bond to 2.257(6) Å. In contrast to that, the corresponding bond distance in $[\mathrm{Re(NS)(NCS)_2(Me_2PhP)_3}]$ is 2.07(1) Å (the same value was found for the Re–N bond *trans* to $\mathrm{Me_2PhP}$). These results agree with the situation in other thionitrosyl complexes of rhenium and technetium [16, 23, 25–27].

Supplementary material

Further details of the crystal structure determination (F_oF_c lists, full lists of bond lengths and angles and isotropic thermal parameters) have been deposited with the Fachinformationszentrum, Gesellschaft fur wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, as Supplementary Publication No.s CSD 57066 $[\mathrm{ReN(NCS)_2(Me_2PhP)_3}]$ and CSD 56975 $[\mathrm{Re(NS)(NCS)_2(Me_2PhP)_3}]$.

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