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Note

Isothiocyanato complexes of rhenium
III. Synthesis and characterization of $[ReN(NCS)_2(Ph_3P)_2]$ and $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]$. X-ray crystal structure of $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$[☆]

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Abstract

Novel rhenium isothiocyanato complexes have been prepared by ligand exchange procedures starting from $[ReNCl_2(Ph_3P)_2]$ and KSCN. The reaction with KSCN yields the rhenium(V) nitrido complex $[ReN(NCS)_2(Ph_3P)_2]$. $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$ has been prepared by the reaction of $[ReN(NCS)_2(Ph_3P)_2]$ with CH_3CN. Both complexes are air-stable. They have been characterized spectroscopically. The crystal and molecular structure of $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$ has been determined by single-crystal X-ray diffraction. $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$ crystallizes in the monoclinic space group $P2_1/n$ ($a=9.242(3)$, $b=18.506(3)$, $c=21.773(6)$ Å, $\beta=93.84(2)°$ with $Z=4$. The final R value is 0.042. The compound consists of discrete $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]$ molecules with an additional CH_3CN solvent molecule per complex in the crystal lattice. The coordination sphere of the rhenium atom is a distorted octahedron, with a Re≡N bond length of 1.66(1) Å. The strong *trans* influence of the nitrido group is evident in the exceptionally long Re–N bond distance (2.42(1) Å) to the CH_3CN ligand.

Keywords: Crystal structures; Rhenium complexes; Nitrido complexes; Isothiocyanato complexes

1. Introduction

The synthesis, structural characterization and reactions of rhenium nitrido compounds have been described in numerous papers [2–10]. The 'N^{3-}' ligand which is one of the strongest π-donor ligands preferably stabilizes the 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. The usual starting materials for this approach are phosphine complexes of rhenium(V).

In this paper, we describe the synthesis and characterization of new isothiocyanate complexes of rhenium with the metal in the formal oxidation state +V which were prepared from $[ReNCl_2(Ph_3P)_2]$ and KSCN.

2. Experimental

2.1. Syntheses

$[ReNCl_2(Ph_3P)_2]$ was prepared by a literature procedure [10a]. KSCN was purchased commercially (Aldrich) and used without further purification.

2.1.1. $[ReN(NCS)_2(Ph_3P)_2]$

240 mg (0.3 mmol) $[ReNCl_2(Ph_3P)_2]$ were suspended in about 30 ml CH_2Cl_2, and 98 mg (1 mmol) KSCN dissolved in about 10 ml MeOH were added. The mixture was heated under reflux for 3 h. The brown solution was cooled and filtered to remove KCl. Then the volume was reduced to about 20 ml and upon standing overnight a yellow crystalline powder deposited which was collected.

Yield 91 mg (36% based Re). *Anal.* Found: C, 54.1; H, 3.6; N, 4.7. Calc. for $C_{38}H_{30}N_3P_2S_2Re$; C, 54.3; H, 3.4; N, 5.0%. IR: ν(Re≡N) 1097, ν(NCS) 2060 cm^{-1}. FAB-MS: $m/z=841$ (100% B) $[ReN(NCS)_2(Ph_3P)_2]^+$

[☆] For Part I and Part II see Refs. [1] and [2].

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Table 1
Crystal data collection and structure refinement parameters

	$[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$
Formula	$C_{42}H_{36}N_5P_2S_2Re$
Molecular weight	923.06
Space group	monoclinic $P2_1/n$
Lattice dimensions	
a (Å)	9.242(3)
b (Å)	18.506(3)
c (Å)	21.773(6)
β (°)	93.84(2)
Formula units	$Z=4$
V (Å^3)	3715.4
Measuring temperature (°C)	-60
D_c (g cm^{-3})	1.65
Radiation used, λ (Å)	Mo Kα, 0.7093
Scan type	ω
Absorption coefficient (cm^{-1})	35.45
Absorption correction	DIFABS
T_{min}	0.692
T_{max}	1.207
Range of h, k, l	$\overline{12}\rightarrow12$, $\bar{1}\rightarrow24$, $0\rightarrow28$
Weighting scheme	$1/\sigma^2(F)$
Total unique data	9016
Observed data ($I>3\sigma(I)$)	4701
No. parameters	461
R	0.042
R_w	0.046

(M^+), $m/z=783$ (16% B) $[ReN(NCS)(Ph_3P)_2]^+$, $m/z=725$ (8% B) $[ReN(Ph_3P)_2]^+$, $m/z=579$ (77% B) $[ReN(NCS)_2(Ph_3P)]^+$, $m/z=521$ (38% B) $[ReN(NCS)(Ph_3P)]^+$.

2.1.2. $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$

A solution of 253 mg (0.3 mmol) $[ReN(NCS)_2(Ph_3P)_2]$ in 30 ml acetonitrile was heated under reflux for 30 min to give a clear solution. Upon cooling and standing for two days, red crystals deposited which were collected by filtration.

Yield 263 mg (95% based Re). *Anal.* Found: C, 55.1; H, 3.9; N, 7.1. Calc. for $C_{42}H_{36}N_5P_2S_2Re$: C, 54.7; H, 3.9; N, 7.6%. IR: $\nu(Re\equiv N)$ 1074, $\nu(NCS)$ 2085, 2055 cm^{-1}.

2.2. Physical measurements

IR spectra were recorded as KBr discs on a Bruker IFS 25 spectrometer. Mass spectra were recorded on a MAT TSQ70 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.

2.3. X-ray diffraction

$[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$ crystallizes as red lozenge-shaped crystals. A crystal with the approximate dimension $0.1\times0.2\times0.2$ mm was selected. The X-ray experiment was carried out on a single crystal diffractometer CAD4 (ENRAF NONIUS) with Mo Kα radiation at a temperature of -60 °C. The lattice parameters of the monoclinic compound with the space group $P2_1/n$ (Table 1) were refined using 25 reflections in the range of θ between 9 and 13°. The data collection between $\theta=3$ and 28° resulted in 9789 reflections. During the measurements a decay of intensity could be detected (9%) and was corrected in the final data set. The space group $P2_1/n$ was derived from systematic absences. The structure was solved by the heavy-atom Patterson method.

An acetonitrile solvent molecule was located close to the special position ($\frac{1}{2}$, 0, 0), precluding the possibility of two solvent molecules at this position since this would place two centrosymmetrically related acetonitrile molecules at a short distance from each other. The solvent molecule was assumed disordered being between its two centrosymmetrically related positions. The relative peak heights of these atoms in the electron-density maps also suggest disorder.

After merging, 4701 unique intensity values with $I>3\sigma(I)$ remained and could be used for the structure determination and refinement. Refinement with isotropic temperature parameters converged at $R=0.107$. An empirical absorption correction [11] was applied and further refinement improved R to 0.077. With anisotropic temperature parameters for the non-

Table 2
Fractional positional parameters[a] for $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$

Atom	*x/a*	*y/b*	*z/c*	*B*
Re	0.00838(4)	0.24181(2)	0.07995(2)	2.582(5)
S1	−0.3823(4)	0.0951(2)	0.1455(2)	5.56(7)
S2	0.2417(3)	0.4713(1)	0.0590(1)	4.52(6)
P1	−0.1044(2)	0.2386(1)	−0.0274(1)	2.74(4)
P2	0.0998(2)	0.2529(1)	0.18889(9)	2.66(4)
N1	−0.1543(9)	0.1759(4)	0.1048(3)	3.5(2)
N2	0.1225(8)	0.3334(4)	0.0641(3)	3.0(1)
N3	−0.1688(8)	0.3372(4)	0.0912(4)	3.4(2)
N4	0.1347(8)	0.1806(4)	0.0665(4)	3.4(2)
N5	0.610(3)	0.929(2)	0.028(1)	8.8(8)
C1	−0.249(1)	0.1413(5)	0.1211(4)	3.6(2)
C2	0.174(1)	0.3907(5)	0.0618(4)	3.2(2)
C3	−0.254(1)	0.3817(6)	0.0860(4)	3.4(2)
C4	−0.365(1)	0.4379(6)	0.0806(6)	4.9(3)
C5	0.552(2)	0.9710(8)	0.0088(7)	8.3(4)
C6	0.448(2)	1.0290(8)	−0.0088(7)	8.3(4)
C11	−0.109(1)	0.1477(5)	−0.0602(4)	3.1(2)
C12	0.015(1)	0.1056(6)	−0.0531(5)	4.4(2)
C13	0.015(1)	0.0358(6)	−0.0787(6)	5.4(3)
C14	−0.109(1)	0.0098(6)	−0.1097(6)	5.0(3)
C15	−0.231(1)	0.0520(6)	−0.1179(5)	4.8(3)
C16	−0.228(1)	0.1224(6)	−0.0935(5)	4.0(2)
C21	−0.2931(9)	0.2695(5)	−0.0368(4)	3.1(2)
C22	−0.395(1)	0.2327(5)	−0.0048(4)	3.6(2)
C23	−0.539(1)	0.2547(7)	−0.0103(4)	4.2(2)
C24	−0.583(1)	0.3142(6)	−0.0454(5)	4.0(2)
C25	−0.481(1)	0.3500(6)	−0.0767(5)	4.1(2)
C26	−0.336(1)	0.3282(6)	−0.0735(4)	3.5(2)
C31	−0.013(1)	0.2950(4)	−0.0802(4)	2.9(2)
C32	0.0490(9)	0.2661(5)	−0.1323(5)	3.1(2)
C33	0.118(1)	0.3116(6)	−0.1723(5)	3.9(2)
C34	0.132(1)	0.3830(6)	−0.1600(5)	4.0(2)
C35	0.075(1)	0.4127(60	−0.1087(5)	3.7(2)
C36	0.002(1)	0.3682(5)	−0.0689(4)	3.4(2)
C41	0.0018(9)	0.3122(5)	0.2382(4)	2.7(2)
C42	−0.015(1)	0.3846(5)	0.2202(4)	3.1(2)
C43	−0.082(1)	0.4333(5)	0.2580(5)	3.3(2)
C44	−0.134(1)	0.4097(6)	0.3127(5)	3.9(2)
C45	−0.117(1)	0.3379(6)	0.3308(5)	4.0(2)
C46	−0.048(1)	0.2895(5)	0.2936(4)	3.1(2)
C51	0.2850(9)	0.2877(5)	0.1968(4)	2.9(2)
C52	0.3844(9)	0.2641(5)	0.1581(4)	3.4(2)
C53	0.528(1)	0.2841(6)	0.1649(5)	4.0(2)
C54	0.571(1)	0.3322(6)	0.2116(5)	3.8(2)
C55	0.472(1)	0.3569(5)	0.2514(5)	3.5(2)
C56	0.329(1)	0.3345(5)	0.2440(4)	3.2(2)
C61	0.114(1)	0.1661(4)	0.2281(4)	2.7(2)
C62	0.243(1)	0.1375(6)	0.2506(5)	3.8(2)
C63	0.248(1)	0.0700(5)	0.2790(5)	4.1(2)
C64	0.125(1)	0.0309(5)	0.2857(5)	3.9(2)
C65	−0.005(1)	0.0592(5)	0.2636(4)	3.4(2)
C66	−0.011(1)	0.1268(5)	0.2360(4)	3.2(2)

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

hydrogen atoms an *R* value of 0.049 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 [12] the final *R* value of 0.042 was obtained.

Crystal data and more details of the refinements are summarized in Table 1. See also Section 4. Positional parameters are given in Table 2. Programs used: VAX-SDP [13], SHELXS-86 [14], SCHAKAL [15].

3. Results and discussion

$[ReN(NCS)_2(Ph_3P)_2]$ is formed by the reaction of the well-known $[ReNCl_2(Ph_3P)_2]$ [10a] with KSCN. The air-stable compound is only slightly soluble in organic solvents such as acetone and $CHCl_3$. IR studies show the ν(NCS) stretching vibration for the N-bound isothiocyanate ligands at 2060 cm^{-1}; the ν(Re≡N) vibration is found at 1097 cm^{-1}. Fast atom bombardment mass spectrometric studies confirm the composition of $[ReN(NCS)_2(Ph_3P)_2]$ and show evidence for the molecular ion peak at $m/z=841$. 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 [2,8,9,16–18] and confirms the extraordinary stability of the Re≡N or Tc≡N bonds. In contrast, Re=O bonds are included in the fragmentation of comparable oxorhenium complexes [19,20].

$[Re(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$ is formed by the reaction of $[ReN(NCS)_2(Ph_3P)_2]$ with CH_3CN. The ν(NCS) stretching vibration for the N-bound isothiocyanate ligands can be detected in the IR spectrum at 2085 and 2055 cm^{-1}, the ν(Re≡N) vibration is found at 1074 cm^{-1}. Only two weak vibrations at 2266 and 2299 cm^{-1} were found which can be assigned to the ν(C≡N) bond of the acetonitrile molecules. This is in accordance with the spectroscopic behaviour of related compounds [4,21–23]. The FAB$^+$ mass spectrum of $[Re(NCS)_2(CH_3CN)(Ph_3P)_2]$ is exactly the same as that of $[ReN(NCS)_2(Ph_3P)_2]$. This can be understood by an immediate loss of the CH_3CN ligand during the dissolution of the complex in the FAB matrix nitrobenzylalcohol. Electron impact mass spectra could not be obtained.

$[Re(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$ forms large red crystals when crystallized from hot acetonitrile. They are indefinitely stable in air. An X-ray diffraction study shows that the compound consists of discrete monomeric molecules which are co-crystallized with one molecule of solvent acetonitrile.

A SCHAKAL plot [15] together with the molecular numbering scheme is given in Fig. 1. Table 3 contains selected interatomic distances and angles. The rhenium atom is six-coordinate; the two *trans* triphenylphosphine ligands are bonded to rhenium in an approximately

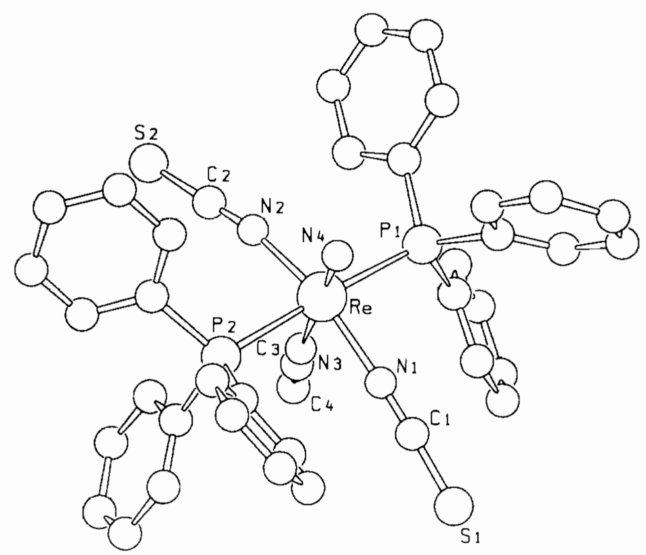

Fig. 1. SCHAKAL plot of $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]$.

Table 3
Selected bond lengths and angles in $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]$ with e.s.d.s in parentheses

Bond lengths (Å)							
Re–N1	2.023(8)	S1–C1	1.61(2)	N3–C3	1.13(1)		
Re–N2	2.024(7)	S2–C2	1.61(1)	C3–C4	1.45(1)		
Re–N3	2.415(8)	N1–C1	1.15(1)	Re–P1	2.477(3)		
Re–N4	1.655(8)	N2–C2	1.16(1)	Re–P2	2.454(2)		

Bond angles (°)			
N1–Re–N2	160.5(4)	P2–Re–N1	90.5(2)
N1–Re–N3	83.9(3)	P2–Re–N2	86.8(3)
N1–Re–N4	100.3(3)	P2–Re–N3	92.0(2)
N2–Re–N3	76.9(3)	P2–Re–N4	91.3(3)
N2–Re–N4	99.2(3)	Re–N1–C1	176.3(8)
N3–Re–N4	174.7(3)	Re–N2–C2	169.2(7)
P1–Re–P2	174.3(1)	Re–N3–C3	168.6(7)
P1–Re–N1	87.8(2)	S1–C1–N1	178.1(9)
P1–Re–N2	93.0(3)	S2–C2–N2	178.4(9)
P1–Re–N3	82.4(2)	N3–C3–C4	179.0(9)
P1–Re–N4	94.3(3)		

linear fashion with a P–Re–P angle of 174.3(1)°. The Re–P bond distances, 2.477(3) and 2.454(2) Å, fall in the normal range of Re–P distances observed in six-coordinate tertiary phosphine complexes (2.45–2.51 Å) [24,25]. The two NCS^- ligands are nitrogen-bonded as has been found for all structurally characterized complexes with this ligand [1–5,26,27]. The isothiocyanate ligands are almost linear (N–C–S angles between 178(1) and 179(1)°). The Re–N4 distance is 1.66 Å which is in the typical range of metal–nitrogen triple bonds [3,5]. The long Re–N3 bond distance of 2.415(8) Å of the coordinated acetonitrile group is a result of the strong *trans* influence of the nitrido ligand which is one of the strongest known π-electron donors [3]. The Re–N bond distance in six-coordinate acetonitrile complexes of rhenium varies widely as a consequence of the influence of the *trans* group. In $[ReCl_3(NO)_2(CH_3CN)]$ [25] and $[ReCl_3(CH_3CN)(Ph_3P)_2]$ [28] where the acetonitrile ligand is *trans* to chlorine, the Re–N bond distances are 1.95(6) and 2.05(5) Å, respectively. The Re–N bond distance increases to 2.15(1) Å in *trans*-$[Re(NO)Br_4(CH_3CN)](Et_4N)$ [29] and 2.31(6) Å in *trans*-$[ReOBr_4(CH_3CN)](Ph_4As)$ [30].

The long $Re{-}NCCH_3$ bond distance in $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]$ is manifested by the ease with which the coordinated acetonitrile molecule may be displaced. Dissolution of crystalline $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]$ in chloroform or other organic solvents at room temperature resulted in the complete loss of the coordinated acetonitrile and the formation of $[ReN(NCS)_2(Ph_3P)_2]$. With this, the structural feature and the reactivity are close to those of $[TcN(NCS)_2(CH_3CN)(Ph_3P)_2]$ [21].

4. Supplementary material

Further details of the crystal structure determination (F_o and F_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, as Supplementary Publication No CSD 57692 $[ReN(NCS)_2(CH_3CN)(Ph_3P)_2]\cdot CH_3CN$.

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