Inorganica Chimica Acta, 211 (1993) 121-123

Note

Synthesis, characterization and X-ray crystal structure of *cis*-tetrakis(isothiocyanato)(triphenylphosphine)(triphenylphosphine oxide)rhenium(IV), [Re(NCS)$_4$(Ph$_3$P)(Ph$_3$PO)]

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(Received April 16, 1993)

Abstract

cis-Tetrakis(isothiocyanato)(triphenylphosphine)(triphenylphosphine oxide)rhenium(IV), [Re(NCS)$_4$(Ph$_3$P)(Ph$_3$PO)], is formed during the reaction of [ReOCl$_3$(Ph$_3$P)$_2$] and trimethylsilylisothiocyanate, Me$_3$SiNCS. The compound crystallizes monoclinic in the space group $P2_1/n$, $a=9.981(3)$, $b=37.447(6)$, $c=11.761(4)$ Å, $\beta=111.21(1)°$ and $Z=4$. Structure refinement converged at $R=0.037$. Ph$_3$P and Ph$_3$PO are *cis*-coordinated with Re–P and Re–O distances of 2.511(3) and 2.018(7) Å, respectively. The NCS ligands are coordinated via nitrogen.

Introduction

Trichlorobis(triphenylphosphine)oxorhenium(V), [ReOCl$_3$(Ph$_3$P)$_2$], is a common starting material for the preparation of new coordination compounds with the metal in its higher oxidation states [1]. In most of the reactions, the rhenium–oxygen double bond remains and rhenium(V) oxo complexes are formed [1–5]. This has also been reported for the reaction with potassium thiocyanate where [ReO(NCS)$_3$(Ph$_3$P)$_2$] is discussed as product [6].

In this paper, we describe the reaction of [ReOCl$_3$(Ph$_3$P)$_2$] with Me$_3$SiNCS which leads to a new type of rhenium complex with two *cis*-coordinated phosphine and phosphine oxide ligands.

Experimental

Synthesis

[ReOCl$_3$(Ph$_3$P)$_2$] was prepared by a literature procedure [1]. Me$_3$SiNCS was purchased commercially (Aldrich) and used without further purification.

[Re(NCS)$_4$(Ph$_3$P)(Ph$_3$PO)]. 415 mg (0.5 mmol) of [ReOCl$_3$(Ph$_3$P)$_2$] were suspended in about 100 ml CHCl$_3$ and excess (1 ml) Me$_3$SiNCS was added. The mixture was stirred for 3 h at room temperature. During this time the yellow–green, only slightly soluble, starting compound dissolved to form a red–brown solution. The solvent was removed in vacuum leaving a red–brown oily residue. This was dissolved in about 20 ml CHCl$_3$ and 30 ml isopropanol were added. A red–brown crystalline solid precipitated upon standing overnight. It was filtered off and washed with isopropanol and ether. Yield 570 mg (60% based on Re). *Anal.* Found: C, 51.8; H, 3.5; N, 5.5; S, 13.1. Calc. for C$_{40}$H$_{30}$N$_4$S$_4$OP$_2$Re: C, 50.1; H, 3.2; N, 5.8; S, 13.4%. IR: ν(NCS) 2062 and 2000, ν(P=O) 1116 cm^{-1}. Magnetic moment: $\mu_{\text{eff}}=3.09$ BM. FAB$^+$-MS: $m/z=959$ [Re(NCS)$_4$(Ph$_3$P)(Ph$_3$PO)]$^+$, $m/z=901$ [Re(NCS)$_3$(Ph$_3$P)(Ph$_3$PO)]$^+$, $m/z=843$ [Re(NCS)$_2$(Ph$_3$P)(Ph$_3$PO)]$^+$, $m/z=727$ [Re(Ph$_3$P)(Ph$_3$PO)]$^+$.

Physical measurements

IR spectra were recorded for KBr pellets on a Specord 75 IR. The magnetic moment was determined on a Squid magnetometer in the temperature range $70 \leqslant T \leqslant 300$ K. Measurement of the mass spectra was performed on a MAT 701 A spectrometer (Finnigan) with nitrobenzyl alcohol as matrix. Xenon was used as primary beam gas. The ion gun was operated at 8 kV, probe temperature: 30 °C.

X-ray diffraction

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CHCl$_3$/isopropanol solution of the complex. Data collection was obtained using a red–brown crystal of dimensions $0.35 \times 0.2 \times 0.2$ mm at 20 °C on an automatic CAD 4 diffractometer (Enraf-Nonius, Delft). Mo Kα radiation ($\lambda=0.7093$ Å) was used throughout the experiment. Cell parameters were determined from 25 high angle settings: $a=9.981(3)$, $b=37.447(6)$, $c=11.761(4)$ Å, $\beta=111.21(1)°$, $V=4058.1$ Å^3, $Z=4$. 8645 reflections were measured with the ω scan from which 4397 were observed ($I \geqslant 3\sigma(I)$). The

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space group was evident from systematic absences. The Patterson method was applied for the structure solution. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were calculated at idealized positions and introduced into the structure-factor calculations. Empirical absorption correction (DIFABS) and extinction correction (extinction coefficient 1.48008×10^{-8}) were applied. Refinement converged at $R = 0.037$ ($R_w = 0.041$) with a final shift to error ratio of 0.003. The most intense peak in the final Fourier map was 0.812 e/Å^3. Programs used: VAX-SDP [7], SCHAKAL [8]. See also 'Supplementary material'.

Results and discussion

$[Re(NCS)_4(Ph_3P)(Ph_3PO)]$ is formed by the reaction of the well-known $[ReOCl_3(Ph_3P)_2]$ with Me_3SiNCS. In contrast to the reactions with alkali or ammonium halides or pseudohalides [2, 6] not only a ligand exchange of the chloro ligands occurs but the oxo ligand is removed and the rhenium is reduced to the +4 oxidation state. Surprisingly, one Ph_3P ligand is oxidized and coordinates as triphenylphosphine oxide. However, a similar reaction has also been observed during the interaction of the neutral technetium(V) complex $[TcNCl_2(Me_2PhP)_3]$ with disulfur dichloride which gives the thionitrosyl technetium(II) compound $[Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)]$ [9].

The title compound is readily soluble in organic solvents such as acetone, $CHCl_3$ or acetonitrile. Susceptibility measurements confirm the Re^{4+} state giving a value of $\mu_{eff} = 3.09$ BM. IR studies show the ν(NCS) stretching vibration for the N-bound isothiocyanate ligands at 2062 and 2000 cm^{-1}. The ν(P=O) frequency is found at 1116 cm^{-1} which is close to the values of the coordinated phosphine oxide in the Tc(II) thionitrosyl compound $[Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)]$ [9] and the ν(P=O) frequency in $[ReO(et_2tcb)_2](BPh_4) \cdot Ph_3PO$ [5] ($et_2tcb^- = N$-(N,N-diethylaminothiocarbonyl)benzamidinate) where Ph_3PO only co-crystallizes in the crystal lattice. No evidence was found for an Re=O stretch which is expected in the 900–1000 cm^{-1} range.

Fast atom bombardment mass spectra of $[Re(NCS)_4(Ph_3P)(Ph_3PO)]$ show evidence for the molecular ion peak at $m/z = 959$. Fragmentation mainly occurs by the loss of complete ligands as is evident by the peaks at $m/z = 901$, $m/z = 843$ and $m/z = 727$ which correspond to the abstraction of the thiocyanate ligands.

$[Re(NCS)_4(Ph_3P)(Ph_3PO)]$ crystallizes monoclinic in the space group $P2_1/n$. The atomic positions and the thermal parameters are given in Table 1. A SCHAKAL diagram of the complex molecule is shown in Fig. 1.

TABLE 1. Fractional positional parameters[a] for the atoms in $[Re(NCS)_4(Ph_3P)(Ph_3PO)]$ with e.s.d.s in parentheses; for numbering see Fig. 1

Atom	*x/a*	*y/b*	*z/c*	*B*
Re	0.12939(4)	0.12912(1)	0.29023(3)	3.700(7)
S1	0.1552(4)	0.24069(9)	0.1070(3)	7.20(9)
S2	0.5617(4)	0.1494(1)	0.6220(3)	8.0(1)
S3	0.3687(5)	0.0786(2)	0.0530(4)	12.3(1)
S4	−0.2682(4)	0.1031(1)	−0.0665(3)	8.4(1)
P1	0.0847(3)	0.07189(7)	0.3819(2)	4.15(6)
P2	−0.0409(3)	0.18525(7)	0.4265(2)	3.95(6)
O	0.0269(6)	0.1530(2)	0.3894(5)	4.1(1)
N1	0.1423(8)	0.1763(2)	0.2135(7)	4.6(2)
N2	0.3110(8)	0.1374(2)	0.4296(7)	4.6(2)
N3	0.2336(8)	0.1057(2)	0.2002(7)	5.0(2)
N4	−0.0522(8)	0.1186(2)	0.1481(7)	4.7(2)
C1	0.1445(9)	0.2038(3)	0.1682(8)	4.6(2)
C2	0.418(1)	0.1426(3)	0.5104(9)	4.6(2)
C3	0.290(1)	0.0945(3)	0.1355(9)	5.7(3)
C4	−0.141(1)	0.1112(3)	0.0558(8)	4.7(2)
C11	−0.076(1)	0.0731(3)	0.4164(9)	4.4(2)
C12	−0.202(1)	0.0889(3)	0.336(1)	5.0(3)
C13	−0.326(1)	0.0899(3)	0.363(1)	6.1(3)
C14	−0.329(1)	0.0752(3)	0.471(1)	6.5(3)
C15	−0.205(1)	0.0595(3)	0.551(1)	6.4(3)
C16	−0.080(1)	0.0578(3)	0.5255(9)	5.3(3)
C21	0.226(1)	0.0612(3)	0.5272(9)	4.8(3)
C22	0.258(1)	0.0867(3)	0.6200(9)	5.6(3)
C23	0.359(1)	0.0789(3)	0.7332(9)	6.6(3)
C24	0.426(1)	0.0462(4)	0.755(1)	7.9(4)
C25	0.398(1)	0.0210(4)	0.663(1)	8.0(4)
C26	0.294(1)	0.0281(3)	0.545(1)	6.3(3)
C31	0.066(1)	0.0336(3)	0.2825(9)	4.9(3)
C32	0.182(1)	0.0241(3)	0.247(1)	6.2(3)
C33	0.164(1)	−0.0050(3)	0.168(1)	6.9(3)
C34	0.035(2)	−0.0248(3)	0.129(1)	7.7(4)
C35	−0.078(2)	−0.0152(3)	0.163(1)	7.1(4)
C36	−0.064(1)	0.0146(3)	0.242(1)	5.6(3)
C41	−0.229(1)	0.1864(2)	0.3353(9)	4.2(2)
C42	−0.267(1)	0.1788(3)	0.2108(9)	5.4(3)
C43	−0.412(1)	0.1771(4)	0.137(1)	6.6(3)
C44	−0.514(1)	0.1838(3)	0.187(1)	6.7(3)
C45	−0.477(1)	0.1921(3)	0.309(1)	6.3(3)
C46	−0.332(1)	0.1929(3)	0.3848(9)	5.0(3)
C51	−0.019(1)	0.1808(3)	0.5820(9)	4.6(2)
C52	−0.048(1)	0.1480(3)	0.6236(9)	6.0(3)
C53	−0.030(1)	0.1436(3)	0.745(1)	7.3(4)
C54	0.017(2)	0.1716(4)	0.826(1)	7.7(4)
C55	0.042(2)	0.2044(4)	0.784(1)	8.2(4)
C56	0.024(1)	0.2099(4)	0.662(1)	7.0(3)
C61	0.039(1)	0.2267(3)	0.4087(9)	4.7(2)
C62	0.188(1)	0.2296(3)	0.460(1)	5.7(3)
C63	0.249(1)	0.2620(4)	0.446(1)	7.1(3)
C64	0.164(1)	0.2902(3)	0.384(1)	7.3(3)
C65	0.018(1)	0.2872(3)	0.333(1)	7.6(4)
C66	−0.047(1)	0.2543(3)	0.345(1)	6.0(3)

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

The rhenium atom is six-coordinate in a distorted octahedral coordination sphere. The four NCS^- ligands are nitrogen-bonded as has been found for all structurally characterized Re–NCS complexes [1, 10, 11]. The triphenylphosphine and triphenylphosphine oxide

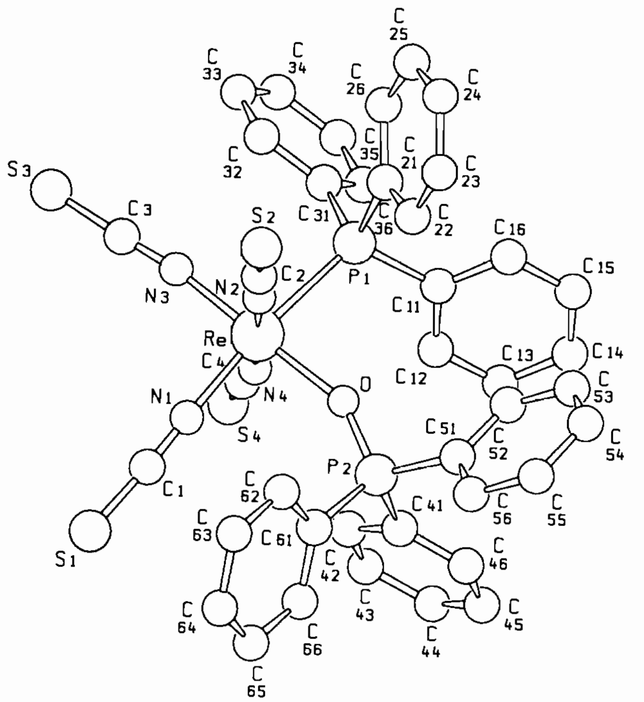

Fig. 1. Molecular structure of [Re(NCS)$_4$(Ph$_3$P)(Ph$_3$PO)] along with the atomic numbering scheme.

TABLE 2. Selected bond lengths and angles in [Re(NCS)$_4$(Ph$_3$P)(Ph$_3$PO)] with e.s.d.s in parentheses

Bond lengths (Å)					
Re–N1	2.009(8)	Re–P1	2.511(3)	N4–C4	1.16(2)
Re–N2	1.980(6)	O–P2	1.522(8)	C1–S1	1.58(1)
Re–N3	1.941(9)	N1–C1	1.16(1)	C2–S2	1.57(1)
Re–N4	2.011(7)	N2–C2	1.16(2)	C3–S3	1.57(1)
Re–O	2.018(7)	N3–C3	1.18(2)	C4–S4	1.57(1)

Bond angles (°)			
P1–Re–O	85.7(2)	O–Re–N4	94.3(4)
P1–Re–N1	173.6(2)	N1–Re–N2	92.7(3)
P1–Re–N2	91.7(2)	N1–Re–N3	91.1(4)
P1–Re–N3	93.6(3)	N1–Re–N4	89.1(4)
P1–Re–N4	86.7(2)	N2–Re–N3	90.7(3)
O–Re–N1	89.8(3)	N2–Re–N4	177.6(3)
O–Re–N2	87.4(3)	N3–Re–N4	87.6(3)
O–Re–N3	177.9(2)	Re–O–P2	152.6(4)

ligands are in *cis*-arrangement to each other. Selected bond lengths and angles of the compounds are summarized in Table 2. The Re–N bonds are found in the range 1.941(9)–2.011(7) Å. From this, a structural *trans*-effect can be discussed to increase in the order Ph$_3$PO < NCS ⩽ Ph$_3$P. The value of 2.018(7) Å for the Re–O bond distance is similar in length to those found for other rhenium–oxygen single bonds [1]. Despite the coordination of the three different ligands only a slight deviation from octahedral geometry is observed. The O atom is coplanar with the atoms N2, N3, N4 and Re within 0.01 Å, however, P1 deviates from the least-squares plane of the atoms N1–N2–N4–Re by 0.25 Å. The thiocyanate ligands are almost linear (N–C–S angles between 176(2) and 179(1)°) and do not show unusual bond distances.

Supplementary material

Further information on the structure solution as well as full lists of atomic positions, anisotropic temperature factors, interatomic bond lengths and angles and the F_oF_c list are deposited with the Fachinformationszentrum Karlsruhe m.b.H., Eggenstein-Leopoldshafen, D-76344, as Supplementary Publication No. CSD 56764.

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 hospitality and for providing us with facilities.

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