Experimental

The title compound was prepared by refluxing 0.12 g (0.5 mmol) $CpCrCl_2(CH_3CN)$ (Scheer, Nam, Schenzel *et al.*, 1990) and 0.3 g (0.52 mmol) [PPN]Cl for 2 h in 30 ml CH_3CN. The solvent volume was reduced to 10 ml and 5 ml diethyl ether added. Storage at 278 K gave 0.25 g (63%) blue crystals. Analysis: $C_{41}H_{35}Cl_3CrNP_2$, calculated C 64.62, H 4.63, N 1.84%; found C 64.24, H 4.52, N 1.51%.

Crystal data

$(C_{36}H_{30}NP_2)[CrCl_3(C_5H_5)]$
$M_r = 761.99$
Triclinic
$P\overline{1}$
$a = 10.307\,(5)$ Å
$b = 16.161\,(10)$ Å
$c = 22.496\,(10)$ Å
$\alpha = 91.57\,(4)°$
$\beta = 89.81\,(4)°$
$\gamma = 101.10\,(4)°$
$V = 3676\,(3)$ Å^3
$Z = 4$
$D_x = 1.377$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10.0–11.5°$
$\mu = 0.647$ mm^{-1}
$T = 178\,(2)$ K
Irregular fragment
0.50 × 0.45 × 0.40 mm
Blue

Data collection

Siemens $R3$ diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Nicolet, 1987)
$T_{\min} = 0.689$, $T_{\max} = 0.772$
24 201 measured reflections
12 995 independent reflections

8181 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 25.05°$
$h = -12 \rightarrow 8$
$k = -19 \rightarrow 19$
$l = -26 \rightarrow 26$
3 standard reflections every 147 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.164$
$S = 0.950$
12 995 reflections
865 parameters
H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.497$ e Å^{-3}
$\Delta\rho_{\min} = -0.623$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cr1—Cent1	1.907	Cr2—Cent2	1.901
Cr1—Cl3	2.291 (2)	Cr2—Cl5	2.294 (2)
Cr1—Cl2	2.300 (2)	Cr2—Cl6	2.306 (2)
Cr1—Cl1	2.312 (2)	Cr2—Cl4	2.318 (2)
Cl3—Cr1—Cl2	96.27 (6)	Cl5—Cr2—Cl6	98.12 (7)
Cl3—Cr1—Cl1	93.18 (6)	Cl5—Cr2—Cl4	96.95 (6)
Cl2—Cr1—Cl1	100.05 (6)	Cl6—Cr2—Cl4	96.15 (6)
Cl1—Cr1—Cent1	121.0	Cl4—Cr2—Cent2	119.4
Cl2—Cr1—Cent1	118.5	Cl5—Cr2—Cent2	120.1
Cl3—Cr1—Cent1	122.1	Cl6—Cr2—Cent2	120.8

Data collection: *P*3 *Program System* (Nicolet, 1987). Cell refinement: *P*3 *Program System*. Data reduction: *XDISK* in *P*3 *Program System*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1314). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1039–1041

Triphenyl[2-(triphenylsilyl)phenylthio]phosphonium Tetraoxorhenate(1−)–Dichloromethane (1/1)

John R. Miller, Canzhong Lu and Yifan Zheng

Department of Biological and Chemical Sciences, Central Campus, University of Essex, Colchester CO4 3SQ, England. E-mail: john@essex.ac.uk

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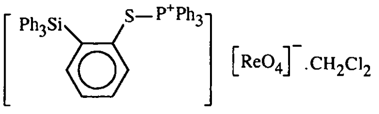
Abstract

The cation of the title compound, $C_{42}H_{34}PSSi^+.ReO_4^-.$-$CH_2Cl_2$, is formed by a bond between the S atom of the 2-(triphenylsilyl)benzenethiol and the P atom of the

triphenylphosphine. The perrhenate $[ReO_4]^-$ anion is tetrahedral.

Comment

As part of a study (Ahmet *et al.*, 1995) of coordination complexes of sterically hindered thiolate ligands, the title compound, (I), was obtained unexpectedly from the reaction of $[ReOCl_3(Ph_3P)_2]$ with $[Ph_3SiC_6H_4SH$-2] (TPSTH); the structural analysis shows it to contain the perrhenate ion, $[ReO_4]^-$, and the unusual cation, $[Ph_3SiC_6H_4SPPh_3]^+$. It is remarkable that, during the course of the reaction, the triphenylphosphine should detach from the rhenium and bind to sulfur, and that the oxidation state of the rhenium should increase from V to VII. The crystal also contains one molecule of dichloromethane acquired during recrystallization.



(I)

The bond distances and angles are consistent with atomic radii. A search of the Cambridge Structural Database (Allen & Kennard, 1993) for the fragment $[C_3PSC]$ revealed reports of only three comparable cations. The first of these (Blower, Dilworth, Hutchinson, Nicholson & Zubieta, 1984) arose from the reaction of $[ReCl_3(Ph_3P)_2(MeCN)]$ with 2,6-diisopropylbenzenethiol; it has a P—S distance of 2.11 (2) Å and a P—S—C angle of 100.0 (1)°. The cation $[Me_3PSMe]^+$ has been structurally characterized as its iodide and the similar cation $[MeCl_2PSMe]^+$ as the hexachloroantimonate (Minkwitz, Medger, Greth & Preut, 1992); the P—S bond lengths in these salts were 2.063 (2) and 2.007 (2) Å, and the C—S—C angles 100.7 (2) and 99.3 (2)°, respectively. All these data are entirely consistent with those in the title compound. A further search of the database for fragments $[X_3PSC]$, where X is any atom, showed a total of 42 fragments, many of them containing phosphorus co-ordinated to a transition metal, with a mean P—S distance and a mean P—S—C angle of 2.097 (5) Å and 103.2 (6)°, respectively. The disposition of the P atom relative to the triphenylsilylphenyl unit has been compared elsewhere with the dispositions of transition metal atoms in complexes of TPST (Ahmet *et al.*, 1995).

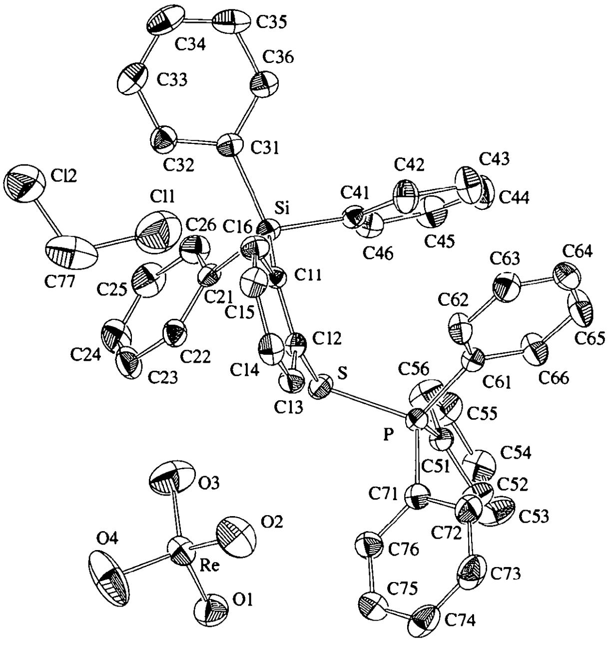


Fig. 1. The molecular structures (*ZORTEP*; Zsolnai, 1994) of the cation, the perrhenate anion and the dichloromethane molecule showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The proligand 2-(triphenylsilyl)benzenethiol (TPSTH) was synthesized according to the method of Zheng (1993). 0.1 mmol $[ReOCl_3(Ph_3P)_2]$ and 0.1 mmol $[Pb(TPST)_2]$ were refluxed in methanol for 4 h. 0.1 g of a brown solid was recrystallized by layering a solution in CH_2Cl_2 with hexane. Pale brown crystals formed after 2 d, which were suitable for X-ray structure analysis. Analysis: C 53.2 (calculated 53.5%), H 3.5 (calculated 3.7%). ^{31}P NMR (ref. 85% H_3PO_4): 41.6 (*s*).

Crystal data

$C_{42}H_{34}PSSi^+.ReO_4^-.CH_2Cl_2$
$M_r = 964.94$
Monoclinic
$P2_1/c$
$a = 10.055$ (3) Å
$b = 22.575$ (4) Å
$c = 18.227$ (5) Å
$\beta = 99.359$ (12)°
$V = 4082.5$ (17) Å^3
$Z = 4$
$D_x = 1.570$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18$–20°
$\mu = 3.268$ mm^{-1}
$T = 291$ (1) K
Prism
0.40 × 0.20 × 0.20 mm
Pale brown

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (Fair, 1990)
$T_{min} = 0.285$, $T_{max} = 0.520$
7595 measured reflections
7144 independent reflections
4969 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 26$
$l = -21 \rightarrow 21$
3 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0308$
$wR(F^2) = 0.0892$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.102$ e Å^{-3}
$\Delta\rho_{min} = -0.429$ e Å^{-3}

$S = 1.030$
7144 reflections
614 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 3.3805P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Re—O4	1.688 (5)	P—C51	1.800 (5)
Re—O2	1.697 (4)	Si—C21	1.877 (4)
Re—O3	1.699 (5)	Si—C41	1.878 (4)
Re—O1	1.709 (4)	Si—C31	1.879 (4)
S—P	2.074 (2)	Si—C11	1.887 (4)
S—C12	1.797 (5)	C77—Cl2	1.692 (9)
P—C61	1.787 (4)	C77—Cl1	1.726 (10)
P—C71	1.788 (5)		
O4—Re—O2	109.6 (3)	C41—Si—C11	109.8 (2)
O4—Re—O3	111.4 (4)	C31—Si—C11	108.8 (2)
O2—Re—O3	108.8 (3)	C61—P—C71	109.5 (2)
O4—Re—O1	109.0 (2)	C61—P—C51	110.4 (2)
O2—Re—O1	110.8 (2)	C71—P—C51	109.1 (2)
O3—Re—O1	107.1 (3)	C61—P—S	116.3 (2)
C12—S—P	105.98 (14)	C71—P—S	110.8 (2)
C21—Si—C41	114.2 (2)	C51—P—S	100.3 (2)
C21—Si—C31	105.9 (2)	C22—C21—Si	123.3 (4)
C41—Si—C31	108.6 (2)	C26—C21—Si	120.3 (4)
C21—Si—C11	109.3 (2)	Cl2—C77—Cl1	114.4 (5)

All non-H atoms were refined with anisotropic displacement parameters. Phenyl H atoms were refined isotropically. The two H atoms of the dichloromethane solvate molecule did not refine to reasonable positions and therefore were included in calculated positions and not refined. One peak of height 1.1 e Å^{-3} was found in the final Fourier difference map, at a distance of 0.956 Å from the Re atom. This peak was assigned to an accumulation of errors arising from series termination, non-quadratic thermal movements and imprecision in the rhenium scattering factor. No other difference peaks were of absolute height greater than 0.6 e Å^{-3}.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

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A Bioctahedral Nb^{IV} Cluster with Bridging Sulfides: [$Nb_2(\mu\text{-}S)_2Cl_4(thf)_4$]

Myungok Yoon,† Victor Young Jr‡ and Gordon J. Miller

Department of Chemistry, Iowa State University, Ames, IA 50011, USA. E-mail: gmiller@iastate.edu

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Abstract

The title compound, tetrachloro-$1\kappa^2Cl,2\kappa^2Cl$-tetrakis(tetrahydrofuran-*O*)-$1\kappa^2O,2\kappa^2O$-di-μ-thioxo-$1{:}2\kappa^4S$-diniobium(IV)(*Nb*—*Nb*), [$Nb_2Cl_4S_2(C_4H_8O)_4$], was obtained by the reaction of $NbCl_4(thf)_2$ (thf is tetrahydrofuran) with $S(SiMe_3)_2$ (hexamethyldisilathiane) in tetrahydrofuran. The compound forms edge-sharing bioctahedral clusters with bridging sulfide ligands and terminal chloride and thf ligands. All thf ligands coordinate in the equatorial plane formed by the Nb—S—Nb—S cycle. Two independent half dimers are found in the asymmetric unit about independent inversion centers located at the midpoints of the Nb—Nb bonds. Distance ranges are: Nb—Nb 2.865 (1)–2.869 (1), Nb—Cl 2.370 (2)–2.388 (2) and Nb—S 2.324 (2)–2.336 (2) Å.

Comment

Metal–metal bonded edge-sharing bioctahedral complexes, $M_2(\mu\text{-}X)_2Y_4L_4$, are interesting structural systems to investigate in order to study the interactions between two adjacent metal atoms by changing the types of metal atoms *M*, bridging ligands *X*, and terminal ligands *Y* and *L* (Cotton, 1987). Several group V transition metal

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† Current address: Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, USA.

‡ Current address: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA.