Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1278). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Chakravarty, A. R., Cotton, F. A. & Shamshoum, E. S. (1984). *Inorg. Chem.* **23**, 4216–4221.

Clark, G. R., Nielson, A. J. & Richard, C. E. F. (1988). *Polyhedron*, **7**, 117–128.

Cotton, F. A., Niswander, R. H. & Sekutowski, J. C. (1978). *Inorg. Chem.* **17**, 3541–3545.

Dietz, S., Allured, V. & Dubois, M. R. (1993). *Inorg. Chem.* **32**, 5418–5420.

Edema, J. J. H, Gambarotta, S., Meetsma, A., Spek, A. L. & Veldman, N. (1991). *Inorg. Chem.* **30**, 2062–2066.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881

Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.

Molecular Structure Corporation (1993*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993*b*). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T, Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Obaidi, N. A., Hamor, T. A., Jones, J. C., McCleverty, J. A. & Paxton, K. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1063–1069.

Schaaf, P. A. van der, Boersma, J., Kooijman, H., Spek, A. L. & van Koten, G. (1993). *Organometallics*, **12**, 4334–4341.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2982–2984

Ruthenium(II) Complex Containing a New Hybrid Bidentate Phosphine–Thioether Ligand: [(*p*-Cymene)RuCl($Me_2PCH_2CH_2SMe$)][BPh_4].0.5CH_2Cl_2

TAKAYOSHI SUZUKI,[a] NORIHIKO TAGUCHI[b] AND KAZUO KASHIWABARA[b]

[a]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560, Japan, and* [b]*Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan. E-mail: suzuki@chem.sci.osaka-u.ac.jp*

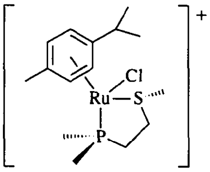
(*Received 5 July 1996; accepted 1 August 1996*)

Abstract

In the title compound, chloro(η^6-*p*-cymene)[1-(dimethylphosphino-*P*)-2-(methylthio-*S*)ethane]ruthenium(II) tetraphenylborate hemidichloromethane solvate, [$RuCl(C_{10}H_{14})(C_5H_{13}PS)$][$B(C_6H_5)_4$].0.5$CH_2Cl_2$, the hybrid $Me_2PCH_2CH_2SMe$ ligand is bidentate (κ^2P,S), forming a five-membered chelate ring. The complex cation has two chiral centres, *i.e.* on the Ru and S atoms, and the relative configuration is *R**(Ru)*S**(S).

Comment

In the course of our research on transition-metal complexes containing hybrid bidentate or polydentate phosphine ligands, we prepared a new phosphine–thioether ligand, *i.e.* $Me_2PCH_2CH_2SMe$ (Suzuki, Morikawa & Kashiwabara, 1996). The most intriguing properties of this ligand are related to the presence on the P atom of sterically undemanding but strongly electron-donating methyl substituents and the potential it has to act as both a monodentate P-atom donor and as a bidentate chelating ligand (Kashiwabara & Taguchi, 1996). In order to reveal the molecular structure of a transition metal complex containing such a novel ligand, we prepared the title complex and carried out a diffraction analysis. The asymmetric unit contains a discrete complex cation, [(*p*-cymene)RuCl($Me_2PCH_2CH_2SMe$)]$^+$, (I), a BPh_4^- anion and half a CH_2Cl_2 molecule. The CH_2Cl_2 solvate molecule lies close to a crystallographic inversion centre and the C atom (C51) is positionally disordered.



(I)

In the complex cation, (I), $Me_2PCH_2CH_2SMe$ acts as a bidentate ligand to form a five-membered chelate ring with a bite angle of 83.86 (6)°, which is comparable to that found for $Me_2PCH_2CH_2PMe_2$ in ruthenium(II) complexes (Field, Hambley & Yau, 1994). It has a piano-stool structure with the *p*-cymene and Cl ligands completing the coordination sphere of the metal. There are two chiral centres, *i.e.* on the Ru and S atoms, and the absolute configuration at these centers is *R*(Ru)*S*(S) or *S*(Ru)*R*(S). This configuration is more sterically advantageous than the diastereomeric alternative of *R*(Ru)*R*(S) or *S*(Ru)*S*(S), which would give rise to severe steric repulsion between the *p*-cymene and S—Me groups. The Ru—P bond [2.312 (2) Å] is slightly shorter than that in the structurally related complex [(*p*-cymene)RuCl{PPh(2-O-C_6H_3-6-OMe)[$C_6H_3(OMe)_2$-2,6]}] [(II), 2.342 (3) Å; Yamamoto, Sato, Matsuo, Sudoh & Igoshi, 1996], which may reflect the steric demand and greater electron-donating power of the methyl substituents in (I). The Ru—Cl bond length [2.389 (2) Å] is comparable to those found in the related (II) and [(*p*-cymene)RuCl-

(taz)]PF_6 complexes (where taz is 2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine) (Garcia, Solano, Sanchez, Santana, Lopez, Casabo, Molins & Miravitlles, 1994). The Ru—S bond length is 2.358 (2) Å. The Ru—C bond lengths vary from 2.198 (5) to 2.267 (6) Å and this variation may be related to the strong *trans* influence of the PMe_2 group; the longest Ru—C bond (Ru—C15) is *trans* with respect to the P atom.

The title complex is, to the best of our knowledge, the first structural example of a transition metal complex containing the $Me_2PCH_2CH_2SMe$ ligand. There is only one structural report of a ruthenium(II) complex containing a *P*,*S*-type hybrid ligand, namely, *cis*-[$RuCl_2\{(p\text{-tol})_2P(4\text{-DBT})\}_2$] [where $(p\text{-tol})_2P(4\text{-DBT})$ is 4-(di-*p*-tolylphosphino)dibenzothiophene] (Bucknor, Draganjac, Rauchfuss, Ruffing, Fultz & Rheingold, 1984). There is only one other reported structure of a transition metal complex containing a bidentate dialkylphosphine–alkylthioether ligand, namely, [$PdCl_2(R_2PCH_2CH_2SEt)$] (R = Et, ^{i}Pr) (Zhang, Yang, Huang & Li, 1993).

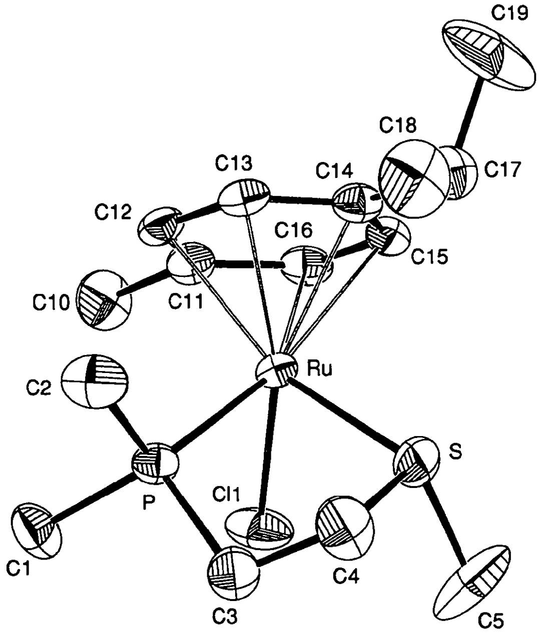


Fig. 1. A perspective view of the complex cation (I) in [(*p*-cymene)RuCl($Me_2PCH_2CH_2SMe$)][BPh_4].$0.5CH_2Cl_2$. H atoms have been omitted for clarity and ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was prepared by reaction of [(*p*-cymene)$RuCl_2$]$_2$ and $Me_2PCH_2CH_2SMe$ (molar ratio 1:3) in EtOH at room temperature, followed by precipitation with $NaBPh_4$. Recrystallization was from a mixture of CH_2Cl_2 and Et_2O.

Crystal data

$[RuCl(C_{10}H_{14})(C_5H_{13}PS)]$-$(C_{24}H_{20}B).0.5CH_2Cl_2$
$M_r = 768.63$
Monoclinic
$P2_1/c$
$a = 9.821\ (4)$ Å
$b = 11.855\ (5)$ Å
$c = 32.703\ (5)$ Å
$\beta = 93.97\ (3)°$
$V = 3798\ (2)$ Å^3
$Z = 4$
$D_x = 1.344$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.0$–$12.5°$
$\mu = 0.68$ mm^{-1}
$T = 293$ K
Prism
$0.50 \times 0.45 \times 0.24$ mm
Orange

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.762$, $T_{\max} = 0.852$
11 666 measured reflections
11 078 independent reflections

5927 observed reflections $[F_o > 3\sigma(F_o)]$
$R_{\rm int} = 0.039$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = -46 \rightarrow 45$
3 standard reflections monitored every 150 reflections intensity decay: 1.6%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.056$
$S = 1.62$
5927 reflections
603 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\max} = 0.0271$
$\Delta\rho_{\max} = 0.96$ e Å^{-3}
$\Delta\rho_{\min} = -0.75$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ru	0.12508 (4)	0.27199 (3)	0.34518 (1)	0.0380 (2)
Cl1	−0.0390 (2)	0.3374 (1)	0.29318 (5)	0.078 (1)
S	0.0600 (2)	0.4143 (1)	0.39026 (5)	0.078 (1)
P	0.2661 (1)	0.4105 (1)	0.32179 (4)	0.0475 (8)
C1	0.2702 (9)	0.4265 (8)	0.2669 (2)	0.072 (5)
C2	0.4459 (7)	0.4028 (8)	0.3401 (3)	0.080 (5)
C3	0.208 (1)	0.5449 (6)	0.3400 (3)	0.074 (5)
C4	0.175 (1)	0.5316 (7)	0.3838 (3)	0.097 (6)
C5	−0.099 (1)	0.479 (1)	0.3734 (6)	0.15 (1)
C10	0.118 (1)	0.0882 (7)	0.2671 (2)	0.075 (5)
C11	0.1398 (5)	0.1092 (4)	0.3127 (2)	0.048 (3)
C12	0.2656 (6)	0.1355 (4)	0.3309 (2)	0.048 (3)
C13	0.2835 (6)	0.1602 (4)	0.3734 (2)	0.050 (3)
C14	0.1747 (6)	0.1561 (4)	0.3984 (2)	0.051 (3)
C15	0.0446 (6)	0.1234 (4)	0.3799 (2)	0.050 (3)
C16	0.0282 (6)	0.1008 (4)	0.3382 (2)	0.050 (3)
C17	0.1870 (8)	0.1809 (6)	0.4440 (2)	0.076 (5)
C18	0.311 (1)	0.254 (1)	0.4579 (3)	0.117 (8)
C19	0.193 (3)	0.069 (1)	0.4664 (3)	0.17 (1)
C21	0.6444 (5)	−0.0253 (4)	0.3834 (2)	0.047 (3)
C22	0.6617 (6)	0.0575 (5)	0.3540 (2)	0.054 (3)
C23	0.6787 (6)	0.1712 (6)	0.3634 (2)	0.067 (4)

C24	0.6775 (7)	0.2075 (6)	0.4030 (3)	0.076 (5)
C25	0.6597 (7)	0.1285 (6)	0.4331 (2)	0.077 (5)
C26	0.6432 (6)	0.0150 (6)	0.4232 (2)	0.062 (4)
C27	0.5829 (5)	−0.2399 (5)	0.4069 (2)	0.052 (3)
C28	0.4638 (6)	−0.2119 (6)	0.4242 (2)	0.062 (4)
C29	0.4004 (7)	−0.2820 (7)	0.4514 (2)	0.074 (4)
C30	0.4524 (8)	−0.3874 (7)	0.4599 (2)	0.081 (5)
C31	0.5665 (9)	−0.4202 (7)	0.4426 (2)	0.083 (5)
C32	0.6316 (8)	−0.3475 (6)	0.4171 (2)	0.073 (5)
C33	0.5646 (5)	−0.1946 (4)	0.3294 (1)	0.042 (3)
C34	0.4535 (5)	−0.1341 (5)	0.3129 (2)	0.057 (4)
C35	0.3762 (6)	−0.1688 (6)	0.2778 (2)	0.068 (4)
C36	0.4085 (7)	−0.2664 (7)	0.2588 (2)	0.073 (4)
C37	0.5159 (6)	−0.3300 (6)	0.2736 (2)	0.059 (4)
C38	0.5922 (6)	−0.2950 (5)	0.3087 (2)	0.051 (3)
C39	0.8171 (5)	−0.1808 (4)	0.3708 (2)	0.047 (3)
C40	0.9018 (6)	−0.1801 (5)	0.4068 (2)	0.065 (4)
C41	1.0454 (7)	−0.1811 (6)	0.4060 (3)	0.076 (5)
C42	1.1054 (7)	−0.1840 (5)	0.3699 (3)	0.070 (4)
C43	1.0258 (6)	−0.1850 (5)	0.3337 (2)	0.061 (4)
C44	0.8844 (5)	−0.1836 (5)	0.3351 (2)	0.049 (3)
B	0.6503 (6)	−0.1606 (5)	0.3726 (2)	0.046 (3)
Cl2	0.0878 (5)	−0.4060 (5)	0.5003 (1)	0.258 (5)
C51†	−0.060 (2)	−0.441 (2)	0.4880 (5)	0.12 (1)

† Disordered atom; site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Ru—Cl1	2.389 (2)	Ru—C13	2.198 (5)
Ru—S	2.358 (2)	Ru—C14	2.245 (5)
Ru—P	2.312 (2)	Ru—C15	2.267 (6)
Ru—C11	2.212 (5)	Ru—C16	2.246 (5)
Ru—C12	2.198 (5)		
Cl1—Ru—S	90.81 (6)	S—Ru—P	83.86 (6)
Cl1—Ru—P	85.63 (6)	S—Ru—C11	162.6 (1)
Cl1—Ru—C13	156.6 (1)	P—Ru—C15	162.7 (1)

The C51 atom of the CH_2Cl_2 solvate molecule has a site-occupation factor of 0.5. All H atoms were included in the structural refinement, except for those of the CH_2Cl_2 solvate molecule. The structure solution and refinement used *Xtal*3.2 (Hall, Flack & Stewart, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *Xtal*3.2 *DIFDAT ABSORB ADDREF SORTRF*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2.

The authors wish to thank the Institute for Molecular Science (Okazaki, Japan) for the use of its X-ray and computation facilities. This work was supported by Grant-in-Aid for Scientific Research No. 08640709, Developmental Scientific Research No. 07554061 and Scientific Research on Priority Areas No. 08220230 from the Ministry of Education, Science, Sports and Culture, Japan.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1286). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bucknor, S. M., Draganjac, M., Rauchfuss, T. B., Ruffing, C. J., Fultz, W. C. & Rheingold, A. L. (1984). *J. Am. Chem. Soc.* **106**, 5379–5381.

Field, L. D., Hambley, T. W. & Yau, B. C. K. (1994). *Inorg. Chem.* **33**, 2009–2017.

Garcia, G., Solano, I., Sanchez, G., Santana, M. D., Lopez, G., Casabo, J., Molins, E. & Miravitlles, C. (1994). *J. Organomet. Chem.* **467**, 119–126.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Kashiwabara, K. & Taguchi, N. (1996). In preparation.

Molecular Structure Corporation (1989). *MSC/AFC Diffractometer Control Program*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Suzuki, T., Morikawa, A. & Kashiwabara, K. (1996). *Bull. Chem. Soc. Jpn*, **69**, 2539–2549.

Yamamoto, Y., Sato, R., Matsuo, F., Sudoh, C. & Igoshi, T. (1996). *Inorg. Chem.* **35**, 2329–2336.

Zhang, L.-F., Yang, J., Huang, D.-J. & Li, G.-N. (1993). *Sci. China Ser. B*, **36**, 513–525.

Acta Cryst. (1996). C**52**, 2984–2987

cis-Diaquabis(2,2′-bipyrimidine-*N*,*N*′)-cobalt(II) Diperchlorate Dihydrate, $[Co(C_8H_6N_4)_2(H_2O)_2](ClO_4)_2.2H_2O$

JOSEPH BRUNZELLE, ALANAH FITCH, YUNLONG WANG AND STEPHEN F. PAVKOVIC

Department of Chemistry, Loyola University Chicago,
6525 N. Sheridan Road, Chicago, IL 60626, USA. E-mail:
spavkov@luccpua.it.luc.edu

(*Received 13 March 1996; accepted 5 August 1996*)

Abstract

The complex cation in the title structure has a distorted octahedral coordination geometry with cobalt bonded to two bidentate bipyrimidine (bpm) ligands and two water molecules in *cis* positions. The structure has crystallographically imposed twofold symmetry.

Comment

Our interest in complexes of bipyridine-type ligands stems from studies of their diffusion behavior in clays. In our case, diffusion properties are measured electrochemically using prepared clay electrodes (Lee & Fitch, 1990). Earlier, an anomalous diffusion behavior was noted for $[Cr(bipy)_3]^{3+}$ (bipy is bipyridine; Edens, Fitch & Lavy-Feder, 1991) and this led to the preparation and testing of complexes with similar ligands.

The ligand 2,2′-bipyrimidine (bpm) has four N donor atoms so it can coordinate as a bidentate ligand to a single metal atom or as a bis-bidentate bridging

Acta Crystallographica Section C
ISSN 0108-2701 © 1996