

C4	0.4757 (11)	-0.0136 (7)	0.4297 (11)	0.065 (3)
C5	0.6224 (12)	0.0161 (7)	0.5025 (14)	0.084 (4)
C6	0.4095 (15)	-0.0230 (9)	0.5381 (13)	0.091 (4)
C11	-0.0685 (8)	0.2516 (7)	0.3817 (9)	0.050 (2)
C12	-0.0689 (9)	0.2558 (7)	0.2425 (9)	0.061 (3)
C13	-0.1863 (11)	0.2761 (7)	0.1253 (11)	0.080 (4)
C14	-0.3079 (12)	0.2889 (8)	0.1411 (15)	0.096 (4)
C15	-0.3090 (11)	0.2870 (10)	0.2757 (16)	0.113 (6)
C16	-0.1898 (10)	0.2657 (9)	0.3975 (12)	0.092 (4)
C21	0.0590 (9)	0.1420 (6)	0.6266 (10)	0.059 (3)
C22	-0.0262 (13)	0.1422 (8)	0.7017 (14)	0.099 (5)
C23	-0.0470 (15)	0.0760 (10)	0.7669 (16)	0.112 (6)
C24	0.0210 (18)	0.0121 (9)	0.7657 (16)	0.113 (6)
C25	0.1083 (19)	0.0126 (8)	0.698 (2)	0.131 (6)
C26	0.1260 (13)	0.0762 (6)	0.6245 (15)	0.085 (4)
C31	0.1939 (9)	0.0136 (5)	0.2106 (9)	0.044 (2)
C32	0.1630 (9)	-0.0621 (6)	0.1680 (11)	0.060 (3)
C33	0.0273 (12)	-0.0853 (6)	0.1111 (12)	0.073 (3)
C34	-0.0766 (12)	-0.0365 (8)	0.0985 (14)	0.085 (4)
C35	-0.0458 (11)	0.0360 (7)	0.1453 (14)	0.079 (4)
C36	0.0878 (10)	0.0623 (6)	0.1964 (12)	0.066 (3)
C41	0.4377 (9)	0.0455 (5)	0.1427 (9)	0.047 (2)
C42	0.4613 (13)	0.1114 (6)	0.0827 (12)	0.080 (4)
C43	0.5156 (14)	0.1105 (8)	-0.0221 (13)	0.094 (4)
C44	0.5452 (13)	0.0448 (8)	-0.0707 (13)	0.080 (4)
C45	0.5188 (12)	-0.0215 (8)	-0.0178 (13)	0.081 (4)
C46	0.4685 (12)	-0.0229 (6)	0.0910 (12)	0.069 (3)

Table 2. Selected geometric parameters (Å, °)

I1—Co	2.558 (1)	P2—O2	1.475 (7)
I2—Co	2.593 (2)	P2—C4	1.791 (11)
Co—O2	1.946 (6)	P2—C41	1.802 (9)
Co—O1	1.958 (6)	P2—C31	1.814 (9)
P1—O1	1.491 (6)	C1—C3	1.52 (2)
P1—C1	1.800 (11)	C1—C2	1.52 (2)
P1—C11	1.805 (8)	C4—C6	1.50 (2)
P1—C21	1.814 (9)	C4—C5	1.51 (2)
O2—Co—O1	102.7 (3)	C41—P2—C31	109.1 (4)
O2—Co—I1	105.8 (2)	P1—O1—Co	157.9 (4)
O1—Co—I1	108.6 (2)	P2—O2—Co	169.4 (5)
O2—Co—I2	110.4 (2)	C3—C1—C2	113.6 (11)
O1—Co—I2	111.1 (2)	C3—C1—P1	110.2 (8)
I1—Co—I2	117.11 (5)	C2—C1—P1	109.8 (7)
O1—P1—C1	113.7 (4)	C6—C4—C5	111.8 (10)
O1—P1—C11	110.5 (4)	C6—C4—P2	109.3 (8)
C1—P1—C11	106.6 (5)	C5—C4—P2	110.9 (9)
O1—P1—C21	108.7 (4)	C16—C11—P1	122.6 (7)
C1—P1—C21	107.5 (5)	C12—C11—P1	119.2 (6)
C11—P1—C21	109.9 (4)	C26—C21—P1	118.6 (7)
O2—P2—C4	111.7 (5)	C22—C21—P1	123.6 (9)
O2—P2—C41	110.4 (4)	C36—C31—P2	119.6 (6)
C4—P2—C41	107.6 (5)	C32—C31—P2	121.6 (7)
O2—P2—C31	109.3 (4)	C42—C41—P2	120.3 (7)
C4—P2—C31	108.7 (5)	C46—C41—P2	122.3 (7)

Since the compound crystallizes in a polar space group, polar axis restraints were applied by the method of Flack & Schwarzenbach (1988). Refinement was on  $F^2$  for all reflections, omitting ( $\bar{1},1,1$ ), ( $0,\bar{1},2,1$ ) and ( $\bar{1},1,3,1$ ) due to large negative  $F^2$  values. All non-H atoms were assigned anisotropic displacement parameters. Restraints were used to impose planar twofold symmetry upon phenyl rings. Methyl H-atom positions (C—H 0.95 Å) were optimized by a difference Fourier process before each series of cycles, and phenyl H atoms were included in calculated positions (C—H 0.90 Å). A riding model was used for all H atoms, with isotropic Debye factors 110% of those of the attached C atoms. The absolute structure of the crystal was determined by the method of Flack (1983).

Data collection: CAD-4F diffractometer software (Enraf-Nonius, 1982). Cell refinement: CAD-4F diffractometer software. Data reduction: *SDP-Plus* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SDP-Plus*. Program(s) used

to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1993). Software used to prepare material for publication: *SHELXL93*.

This work was supported by NSERC Canada.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Alnaji, O., Dartigueanave, M., Dartigueanave, Y., Simard, M. & Beauchamp, A. L. (1991). *Inorg. Chim. Acta*, **187**, 31–38.
- Dias Rodrigues, A. M. G., Francisco, R. H. & Lechat, J. R. (1982). *Cryst. Struct. Commun.* **11**, 847–852.
- Enraf-Nonius (1982). *CAD-4F User's Manual*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Enraf-Nonius (1985). *Structure Determination Package. SDP-Plus*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* **A44**, 499–506.
- Mangion, M. M., Smith, R. & Shore, S. G. (1976). *Cryst. Struct. Commun.* **5**, 493–500.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pierrard, J.-C., Rimbault, J. & Hugel, R. P. (1976). *Bull. Soc. Chim. Fr.* pp. 11–12, 1711–1714.
- Pierrard, J.-C., Rimbault, J. & Hugel, R. P. (1982). *J. Chem. Res. Synop.* pp. 332–333.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Siemens (1993). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1995). **C51**, 588–591

## Dimethylacetonysulfonium Tetrachlorobis(dimethyl sulfoxide-S)rhodate(III)

MARIO CALLIGARIS AND PAOLO FALESCHINI

*Dipartimento di Scienze Chimiche,  
Università di Trieste, 34127 Trieste, Italy*

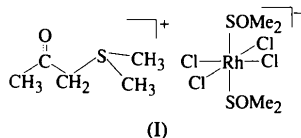
(Received 13 March 1994; accepted 12 September 1994)

### Abstract

The title compound, (C<sub>5</sub>H<sub>11</sub>OS)[RhCl<sub>4</sub>(C<sub>2</sub>H<sub>6</sub>OS)<sub>2</sub>], is built up of [(CH<sub>3</sub>)<sub>2</sub>SCH<sub>2</sub>C(O)CH<sub>3</sub>]<sup>+</sup> cations and [RhCl<sub>4</sub>{(CH<sub>3</sub>)<sub>2</sub>SO}<sub>2</sub>]<sup>-</sup> anions held together by van der Waals forces. The sulfonium cation is derived from an unprecedented deoxygenation reaction of dimethyl sulfoxide. The Rh<sup>III</sup> atom has a nearly octahedral environment, including two *trans* S-bonded sulfoxide ligands (dmsO-S).

### Comment

The title compound (I) was accidentally obtained in the course of an investigation of Rh<sup>III</sup>-chloride-dmsc complexes. During the preparation of [(dmsc)<sub>2</sub>H][RhCl<sub>4</sub>(dmsc-S)<sub>2</sub>], needle-like light orange crystals were obtained, which were shown by NMR (Alessio, Sessanta o Santi, Faleschini, Calligaris & Mestroni, 1994) and X-ray analysis (Faleschini, 1993) to contain both [*cis*-RhCl<sub>4</sub>(dmsc-S)<sub>2</sub>]<sup>-</sup> and [*trans*-RhCl<sub>4</sub>(dmsc-S)<sub>2</sub>]<sup>-</sup> anions in a non-stoichiometric ratio. Unfortunately, the crystals were affected by a severe static disorder due to the 'overlap' of the two isomers and, in part, to the presence of some acetone and dimethyl sulfoxide, as solvents of crystallization. The structure could not be refined well (*R* = 0.055, *S* = 7.73) and displayed some unreliable coordination bond lengths. A batch of selected crystals was left in a closed vessel exposed to light for one year; the crystals were eventually found to have become opaque with powdered surfaces, except for some small red prisms apparently formed from the original crystals.



The crystal structure determination of the red prisms showed the formation of a completely new compound containing the unexpected dimethylacetonylsulfonium cation, [Me<sub>2</sub>SCH<sub>2</sub>C(O)Me]<sup>+</sup>, and only the [*trans*-RhCl<sub>4</sub>(dmsc-S)<sub>2</sub>]<sup>-</sup> isomer as the anion. The NMR spectra of the few available crystals were consistent with the presence of the [Me<sub>2</sub>SCH<sub>2</sub>C(O)Me]<sup>+</sup> cation. However, the signals were rather low because of the high dilution of the available solution.

Even though it is known that sulfonium ions can be obtained from the reaction of protonated sulfoxides with nucleophiles (Lowe, 1981), this is, to our knowledge, the first report of the formation of such a species in the synthesis of transition metal sulfoxide complexes, where it is more usual for the deoxygenation of dimethyl sulfoxide to yield thioethers (Davies, 1981; Yapp, Jaswal, Rettig, James & Skov, 1990; Kukushkin, Belsky, Kononov, Aleksandrova, Pankova & Moiseev, 1992).

The S—CH<sub>3</sub> bond distances of the sulfonium ion in the two crystallographically independent molecules average 1.774(11) Å and are slightly shorter than the S—C(acetonyl) distances of 1.802(6) and 1.800(6) Å. These values are in agreement, within experimental error, with the average values of 1.786(7) and 1.823(16) Å reported, respectively, for the S<sup>+</sup>—CH<sub>3</sub> and S<sup>+</sup>—C (C ≠ CH<sub>3</sub>) species (*International Tables for Crystallography*, 1992, Vol. C). The C—C and C—O distances of the acetonyl moiety, with the exclusion of the C8—C9 bond length of molecule *B* [1.46(1) Å], average 1.517(3) and 1.203(4) Å, respectively, which are close

to the expected values for ketones of 1.511(15) and 1.210(8) Å, respectively. The trigonal nature of atom C8 is confirmed by the sum of the bond angles around it (360.0°), while the S<sup>+</sup> atom S3 has the expected pyramidal bonding structure with an average C—S—C bond angle of 101.8(9)°.

The average Rh—Cl bond distance of 2.340(7) Å compares well with that of 2.351(15) Å found in (NEt<sub>4</sub>)[*cis*-RhCl<sub>4</sub>(dmsc-S)<sub>2</sub>] (Alessio, Sessanta o Santi, Faleschini, Calligaris & Mestroni, 1994) and with that of 2.331(7) Å found in other complexes containing the *trans* Cl—Rh<sup>III</sup>—Cl group (Calligaris, Faleschini & Alessio, 1991).

The average Rh—S bond distance of 2.330(6) Å is comparable to that of 2.323(9) Å for mutually *trans* Rh—S bonds, while it is significantly longer than those *trans* to Cl, which range from 2.254(7) to 2.306(1) Å (Alessio, Sessanta o Santi, Faleschini, Calligaris & Mestroni, 1994). In agreement with the suggestion that dimethyl sulfoxide behaves essentially as a σ donor towards Rh<sup>III</sup> (Alessio, Faleschini, Sessanta o Santi, Mestroni & Calligaris, 1993), this lengthening is ascribable to the higher σ-*trans* influence of S compared to Cl. Correspondingly, the average S—O bond distance of 1.466(6) Å is equal to that of 1.466(2) Å found in other Rh—S complexes. Furthermore, these distances are very close to those found in analogous Ru<sup>III</sup> complexes [1.465(4)–1.467(3) Å; Calligaris, Bresciani-Pahor & Srivastava, 1993]. Interestingly, all these are shorter than the average value of 1.477(2) Å found for [*cis*-RuCl<sub>2</sub>(dmsc-S)<sub>2</sub>] fragments because of the increased π back-donation ability of Ru<sup>II</sup> associated with the π-accepting properties of the dmsc-S ligand (Davies, 1981).

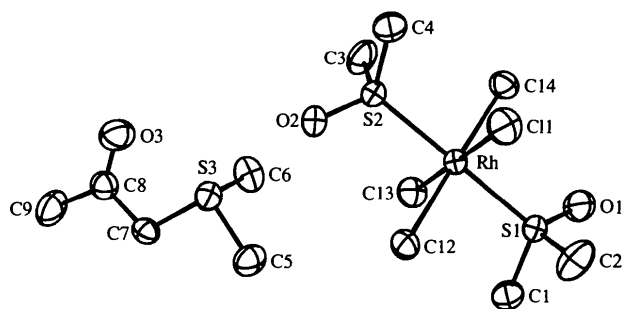


Fig. 1. ORTEP (Johnson, 1965) view of one of the two crystallographically independent molecules (*B*) of the title compound, shown with 50% probability ellipsoids.

### Experimental

#### Crystal data

(C<sub>5</sub>H<sub>11</sub>OS)[RhCl<sub>4</sub>-(C<sub>2</sub>H<sub>6</sub>OS)<sub>2</sub>]

Mo Kα radiation  
λ = 0.71069 Å

$M_r = 520.19$   
 Monoclinic  
 $P2_1/a$   
 $a = 16.031 (3) \text{ \AA}$   
 $b = 16.036 (2) \text{ \AA}$   
 $c = 16.821 (3) \text{ \AA}$   
 $\beta = 113.74 (1)^\circ$   
 $V = 3958 (1) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.75 \text{ Mg m}^{-3}$

Cell parameters from 25  
 reflections  
 $\theta = 14\text{--}18^\circ$   
 $\mu = 1.702 \text{ mm}^{-1}$   
 $T = 294 \text{ K}$   
 Prism  
 $0.5 \times 0.3 \times 0.3 \text{ mm}$   
 Red

O1B	0.4621 (3)	0.6457 (3)	0.5444 (2)	5.1 (1)
O2B	0.4844 (3)	0.5991 (3)	0.9341 (2)	4.19 (9)
O3B	0.2187 (3)	-0.1177 (3)	0.5439 (3)	4.9 (1)
C1B	0.5847 (5)	0.7518 (5)	0.6396 (4)	6.1 (2)
C2B	0.4064 (6)	0.7744 (5)	0.6047 (5)	6.6 (2)
C3B	0.6142 (5)	0.5013 (5)	0.9304 (5)	6.7 (2)
C4B	0.4366 (5)	0.4606 (4)	0.8475 (4)	5.1 (1)
C5B	0.3738 (4)	0.0383 (4)	0.4290 (4)	3.9 (1)
C6B	0.2487 (4)	-0.0892 (4)	0.3685 (4)	4.1 (1)
C7B	0.2509 (3)	0.0141 (3)	0.5030 (3)	2.9 (1)
C8B	0.2050 (4)	-0.0438 (4)	0.5443 (3)	3.3 (1)
C9B	0.1490 (4)	-0.0036 (5)	0.5830 (4)	5.0 (1)

## Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 empirical,  $\psi$  scans of  
 three reflections  
 $T_{\min} = 0.886$ ,  $T_{\max} =$   
 0.999  
 9231 measured reflections  
 8935 independent reflections

5058 observed reflections  
 $[F > 3\sigma(F)]$   
 $R_{\text{int}} = 0.017$   
 $\theta_{\text{max}} = 27^\circ$   
 $h = -20 \rightarrow 20$   
 $k = 0 \rightarrow 20$   
 $l = 0 \rightarrow 21$   
 3 standard reflections  
 frequency: 83.3 min  
 intensity decay: 1.7%

## Refinement

Refinement on  $F^2$   
 $R = 0.033$   
 $wR = 0.035$   
 $S = 0.389$   
 5058 reflections  
 361 parameters  
 H-atom parameters not  
 refined

$w = 1/[1 + \sigma(F_o) + (0.02|F_o|^2)^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.05$   
 $\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	$B_{\text{eq}}$
RhA	0.50157 (2)	0.12872 (2)	0.75218 (3)	2.164 (6)
Cl1A	0.34703 (8)	0.1645 (1)	0.69151 (9)	3.79 (3)
Cl2A	0.46764 (8)	0.00543 (8)	0.67032 (8)	3.18 (3)
Cl3A	0.65684 (8)	0.09251 (9)	0.81160 (9)	3.47 (3)
Cl4A	0.53107 (9)	0.25164 (8)	0.83312 (8)	3.29 (3)
S1A	0.48176 (8)	0.05354 (8)	0.86153 (8)	2.91 (3)
S2A	0.52847 (8)	0.20428 (8)	0.64613 (7)	2.64 (2)
S3A	0.67132 (8)	0.29968 (8)	1.03566 (8)	3.06 (3)
O1A	0.5044 (3)	0.0970 (3)	0.9440 (2)	5.0 (1)
O2A	0.5381 (2)	0.1545 (2)	0.5769 (2)	3.48 (8)
O3A	0.7755 (3)	0.3626 (3)	0.9487 (3)	5.6 (1)
Cl1A	0.5466 (5)	-0.0397 (4)	0.8861 (4)	5.0 (1)
C2A	0.3709 (4)	0.0123 (5)	0.8294 (5)	5.5 (2)
C3A	0.6258 (4)	0.2694 (4)	0.6912 (4)	4.5 (1)
C4A	0.4437 (4)	0.2812 (4)	0.5974 (4)	4.4 (1)
C5A	0.7506 (4)	0.3539 (5)	1.1278 (4)	4.6 (1)
C6A	0.6286 (4)	0.2242 (4)	1.0859 (4)	4.3 (1)
C7A	0.7440 (3)	0.2359 (4)	1.0022 (3)	3.0 (1)
C8A	0.7902 (3)	0.2891 (4)	0.9570 (3)	3.3 (1)
C9A	0.8524 (4)	0.2419 (4)	0.9242 (4)	4.5 (1)
RhB	0.50229 (2)	0.61953 (2)	0.74905 (2)	2.019 (6)
Cl1B	0.34504 (8)	0.63137 (9)	0.71041 (8)	3.41 (3)
Cl2B	0.52945 (8)	0.74756 (8)	0.82223 (8)	3.21 (3)
Cl3B	0.65891 (8)	0.6067 (1)	0.78908 (8)	3.67 (3)
Cl4B	0.48076 (8)	0.49251 (8)	0.67589 (8)	3.03 (2)
S1B	0.48693 (9)	0.69308 (8)	0.62495 (8)	3.13 (3)
S2B	0.50801 (8)	0.54931 (8)	0.87260 (7)	2.75 (2)
S3B	0.32590 (8)	-0.04327 (8)	0.46718 (8)	2.92 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

RhA—Cl1A	2.339 (1)	RhB—Cl1B	2.344 (1)
RhA—Cl2A	2.345 (1)	RhB—Cl2B	2.343 (1)
RhA—Cl3A	2.351 (1)	RhB—Cl3B	2.332 (1)
RhA—Cl4A	2.333 (1)	RhB—Cl4B	2.332 (1)
RhA—S1A	2.326 (1)	RhB—S1B	2.323 (1)
RhA—S2A	2.336 (1)	RhB—S2B	2.333 (1)
S1A—O1A	1.461 (4)	S1B—O1B	1.461 (4)
S1A—C1A	1.772 (6)	S1B—C1B	1.759 (8)
S1A—C2A	1.765 (7)	S1B—C2B	1.768 (8)
S2A—O2A	1.470 (4)	S2B—O2B	1.471 (5)
S2A—C3A	1.774 (6)	S2B—C3B	1.761 (7)
S2A—C4A	1.773 (6)	S2B—C4B	1.767 (7)
S3A—C5A	1.785 (6)	S3B—C5B	1.764 (7)
S3A—C6A	1.765 (7)	S3B—C6B	1.782 (5)
S3A—C7A	1.802 (6)	S3B—C7B	1.800 (6)
O3A—C8A	1.200 (7)	O3B—C8B	1.205 (7)
C7A—C8A	1.519 (9)	C7B—C8B	1.515 (8)
C8A—C9A	1.52 (1)	C8B—C9B	1.46 (1)
Cl1A—RhA—Cl2A	89.77 (5)	Cl1B—RhB—Cl2B	91.51 (5)
Cl1A—RhA—Cl3A	179.36 (6)	Cl1B—RhB—Cl3B	179.24 (5)
Cl1A—RhA—Cl4A	88.72 (5)	Cl1B—RhB—Cl4B	90.59 (5)
Cl1A—RhA—S1A	90.82 (5)	Cl1B—RhB—S1B	89.81 (5)
Cl1A—RhA—S2A	91.63 (5)	Cl1B—RhB—S2B	86.46 (5)
Cl2A—RhA—Cl3A	89.82 (5)	Cl2B—RhB—Cl3B	88.58 (5)
Cl2A—RhA—Cl4A	178.39 (5)	Cl2B—RhB—Cl4B	177.77 (5)
Cl2A—RhA—S1A	87.37 (5)	Cl2B—RhB—S1B	87.55 (5)
Cl2A—RhA—S2A	93.41 (5)	Cl2B—RhB—S2B	91.30 (5)
Cl3A—RhA—Cl4A	91.69 (5)	Cl3B—RhB—Cl4B	89.34 (5)
Cl3A—RhA—S1A	89.66 (5)	Cl3B—RhB—S1B	90.96 (5)
Cl3A—RhA—S2A	87.90 (5)	Cl3B—RhB—S2B	92.78 (5)
Cl4A—RhA—S1A	92.10 (5)	Cl4B—RhB—S1B	91.70 (5)
Cl4A—RhA—S2A	87.20 (5)	Cl4B—RhB—S2B	89.60 (5)
S1A—RhA—S2A	177.44 (4)	S1B—RhB—S2B	176.06 (5)
RhA—S1A—O1A	116.3 (2)	RhB—S1B—O1B	117.4 (2)
RhA—S1A—C1A	111.6 (3)	RhB—S1B—C1B	112.3 (2)
RhA—S1A—C2A	113.1 (2)	RhB—S1B—C2B	110.6 (3)
O1A—S1A—C1A	106.4 (3)	O1B—S1B—C1B	107.6 (3)
O1A—S1A—C2A	107.7 (3)	O1B—S1B—C2B	107.4 (3)
C1A—S1A—C2A	100.3 (3)	C1B—S1B—C2B	99.9 (4)
RhA—S2A—O2A	115.7 (2)	RhB—S2B—O2B	115.8 (2)
RhA—S2A—C3A	112.3 (2)	RhB—S2B—C3B	112.7 (3)
RhA—S2A—C4A	111.8 (3)	RhB—S2B—C4B	112.7 (2)
O2A—S2A—C3A	107.7 (3)	O2B—S2B—C3B	108.3 (3)
O2A—S2A—C4A	108.5 (2)	O2B—S2B—C4B	106.2 (3)
C3A—S2A—C4A	99.6 (3)	C3B—S2B—C4B	99.8 (3)
C5A—S3A—C6A	101.3 (3)	C5B—S3B—C6B	102.0 (3)
C5A—S3A—C7A	102.9 (3)	C5B—S3B—C7B	101.0 (3)
C6A—S3A—C7A	100.7 (3)	C6B—S3B—C7B	102.5 (3)
S3A—C7A—C8A	110.2 (4)	S3B—C7B—C8B	110.7 (4)
O3A—C8A—C7A	119.8 (6)	O3B—C8B—C7B	118.5 (6)
O3A—C8A—C9A	125.0 (6)	O3B—C8B—C9B	125.8 (6)
C7A—C8A—C9A	115.2 (5)	C7B—C8B—C9B	115.7 (5)

Data collection: *CAD-4 Software* (Enraf-Nonius, 1988). Programs used to solve and refine structure: *MolEN* (Fair, 1990). Molecular graphics: *ORTEP* (Johnson, 1965).

Financial support from MURST (Rome) is gratefully acknowledged. Thanks are due to Dr E. Alessio for kind supply of the starting material and the NMR spectra.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Alessio, E., Faleschini, P., Sessanta o Santi, A., Mestroni, G. & Calligaris, M. (1993). *Inorg. Chem.* **32**, 5756–5761.
- Alessio, E., Sessanta o Santi, A., Faleschini, P., Calligaris, M. & Mestroni, G. (1994). *J. Chem. Soc. Dalton Trans.* In the press.
- Calligaris, M., Bresciani-Pahor, N. & Srivastava, R. S. (1993). *Acta Cryst.* **C49**, 448–451.
- Calligaris, M., Faleschini, P. & Alessio, E. (1991). *Acta Cryst.* **C47**, 747–750.
- Davies, J. A. (1981). *Adv. Inorg. Chem. Rev.* **24**, 115–187.
- Enraf–Nonius (1988). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Faleschini, P. (1993). PhD thesis, Univ. of Trieste, Italy.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Kukushkin, V. Yu., Belsky, V. K., Kononov, V. E., Aleksandrova, E. A., Pankova, E. Yu. & Moiseev, A. I. (1992). *Phosphorus Sulfur Silicon*, **69**, 103–117.
- Lowe, P. A. (1981). *The Chemistry of the Sulphonium Group*, edited by C. J. M. Stirling, pp. 286–288. New York: Wiley.
- Yapp, D. T. T., Jaswal, J., Rettig, S. J., James, B. R. & Skov, K. A. (1990). *Inorg. Chim. Acta*, **177**, 199–208.

*Acta Cryst.* (1995). **C51**, 591–593

## *trans*-[Ni(Me<sub>3</sub>Ph)(NHPH)(PMe<sub>3</sub>)<sub>2</sub>], a Monomeric Ni<sup>II</sup>–Amide Complex

DANIEL D. VANDERLENDE, JAMES M. BONCELLA AND KHALIL A. ABBOUD\*

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA

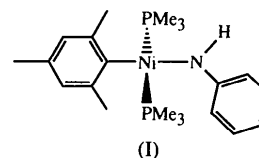
(Received 3 May 1994; accepted 12 October 1994)

### Abstract

*trans*-Phenylamido(2,4,6-trimethylphenyl)bis(trimethylphosphine)nickel(II), [Ni(C<sub>6</sub>H<sub>6</sub>N)(C<sub>9</sub>H<sub>11</sub>)(C<sub>3</sub>H<sub>9</sub>P)<sub>2</sub>], has been synthesized and its crystal structure determined as part of an ongoing study of the reactivity and stability of late transition metal–amide complexes. The geometry about the amide N atom is planar, with a relatively long interaction with the metal center. The Ni atom exhibits square-planar coordination geometry with the PMe<sub>3</sub> ligands *trans* with respect to each other.

### Comment

The chemistry of late transition metal–amide complexes (Groups 8–10) has been studied extensively over the past several years (Bryndza & Tam, 1988; Fryzuk & Montgomery, 1989; Boncella & Villanueva, 1994). In spite of the great interest in these compounds, few have been structurally characterized. The scarcity of these compounds can be attributed to the incompatibility between the electronically saturated metal center and the lone pair of electrons on the amide N atom (Lappert, Power, Sanger & Srivastava, 1980). Knowledge of the structural characteristics is essential for the understanding of the stability and reactivity of these compounds. Determining the geometry about the amide N atom is crucial, since the location of its lone electron pair should lend insight into the reactivity of the metal amide. From a search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983), we have established that there are no examples of primary amides (derived from a primary amine, forming *M*–NHR) of the Ni triad where the amide proton has been located and refined. Therefore, the exact geometry about the N atom is unknown. Here we report the structure of the title compound, (I).



A displacement ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the title molecule with the atom-labelling scheme is given in Fig. 1. The coordination geometry around the Ni atom is square planar with the phosphine ligands *trans* with respect to each other. The Ni atom lies in the coordination plane (the average deviation is 0.01 Å for the plane defined by atoms Ni, P1, N, P2 and C1). The mesityl ring is oriented perpendicular to the coordination plane, forming an angle of 89.7° with it. Since the amide proton was located in the difference Fourier map and refined without constraints at 0.82(3) Å from N, it was possible to determine the geometry about the N atom unambiguously. This atom lies 0.03 Å from the plane defined by atoms Ni, C7 and H. The planarity around the N atom favors delocalization of its lone pair of electrons.

Since the geometry about the N atom is planar, the lone pair of electrons from the N atom must be delocalized within the structure. There appears to be an interaction between the lone pair of electrons and the Ni metal center. The Ni–N bond length of 1.932(3) Å is consistent with the Ni–N bond length of 1.924(2) Å found in [NiClN(SiMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], (II) (Fryzuk, MacNeil, Rettig, Secco & Trotter, 1982). This interaction is not observed in the complexes *trans*-[Ni(Mes){N(Ph)C(O)CHPh<sub>2</sub>}(PMe<sub>3</sub>)<sub>2</sub>], (III) (Van-