Haiduc, I. & Popa, V. (1977). *Adv. Organomet. Chem.* **15**, 113–146.
Hwu, H. R. & Wang, N. (1989). *Chem. Rev.* **89**, 1599–1615.
Ittel, S. D. & Ibers, J. A. (1976). *Adv. Organomet. Chem.* **14**, 33–61.
Johnson, C. K. (1976). *ORTEP*II. Oak Ridge National Laboratory, Tennessee, USA.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.
Panek, J. S. (1991). *Comprehensive Organic Synthesis*, Vol. 1, Part 1, edited by B. M. Trost. New York: Pergamon.
Rettig, M. F., Wing, R. M. & Weiger, G. R. (1981). *J. Am. Chem. Soc.* **103**, 2980–2986.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for Crystal Structure Solution.* Univ. of Göttingen, Germany.
Weber, W. P. (1983). *Silicon Reagents for Organic Synthesis.* Berlin: Springer.

Acta Cryst. (1994). C**50**, 1231–1233

Cyclopentadienyl(thioacetamide-*S*)-bis(triphenylphosphine-*P*)ruthenium(II) Tetrafluoroborate

C. D. Bryan and A. W. Cordes

Department of Chemistry and Biochemistry,
University of Arkansas, Fayetteville, AR 72701, USA

M. Draganjac

Department of Chemistry and Biochemistry,
Arkansas State University, AR 72467, USA

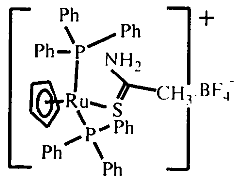
(*Received* 21 *December* 1993; *accepted* 30 *March* 1994)

Abstract

The title compound $[\mathrm{Ru(C_5H_5)(C_2H_5NS)(C_{18}H_{15}P)_2}]\mathrm{BF_4}$ crystallizes in the space group $P2_1/c$. The Ru atom has pseudotetrahedral coordination geometry formed by the cyclopentadienyl centroid, the two $\mathrm{PPh_3}$ ligands and the S atom of the neutral thioacetamide molecule. The Ru—S and C=S distances are 2.3820 (13) and 1.671 (5) Å, respectively, and the Ru—S=C angle is 116.3 (2)°. The Ru atom is at a distance of 0.405 (9) Å from the plane formed by the atoms of the thioacetamide group.

Comment

Structural parameters of transition-metal sulfides are of interest because these complexes are employed in model studies of desulfurization catalysts. The structure determination of the title compound (1) was undertaken in order to compare the structural parameters of the small S=CR_2 ligand with those of previously reported complexes, namely, two complexes of dithiooxamide, a bridging Ru′–dtoxa–Ru′ unit (I) and a chelating dtoxa–Ru′ complex (II), where Ru′ is $\mathrm{CpRu(PPh_3)_2^+}$ and dtoxa is $\mathrm{NH_2C(S)C(S)NH_2}$ (Draganjac, Minick & Cordes, 1993), an Ru complex of thiobenzaldehyde (III) (Schenk, Stur & Dombrowski, 1992) and an Ru′ complex of 1-propanethiol (IV) (Amarasekera & Rauchfuss, 1989). The small thioacetamide molecule as a fourth unit in a tetrahedral complex with three other large ligands might be considered to show Ru—S parameters which are very nearly free of any steric perturbations.



(1)

The Ru—S distance [2.3820 (13) Å] in the title complex is comparable to both the average Ru—S distance involving the bridging unit of (I) and the Ru—S distance involving the mercapto unit of (IV) [2.372 (6) and

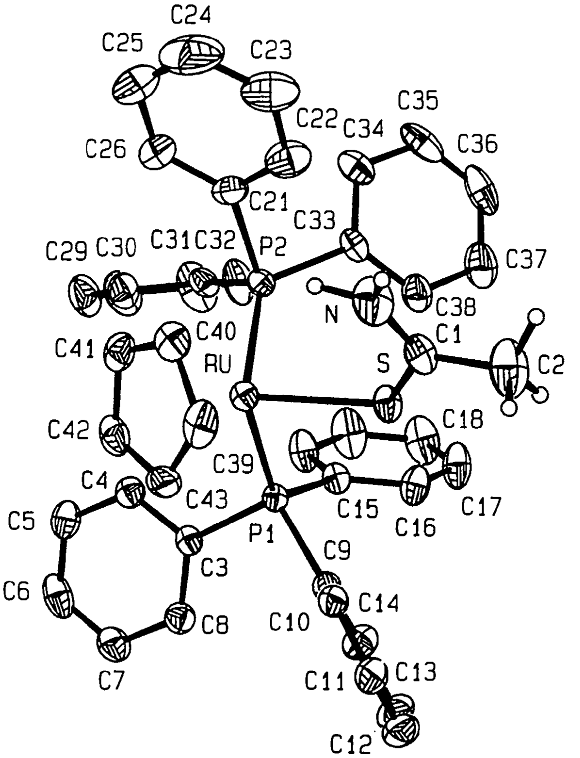


Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the cation with 30% probability ellipsoids showing the numbering scheme. H atoms have been omitted for clarity.

2.377 (2) Å for (I) and (IV), respectively], but is longer than both the distance involving the chelate of structure (II) and that involving the thioaldehyde of (III) [2.297 (10) and 2.314 (1) Å, respectively]. The Ru—S═C angle [116.3 (2)°] of the unstrained thioacetamide complex is 3–8° larger than the analogous angles found for structures (II), (III) and (IV).

Experimental

The compound was prepared from the reaction of CpRu(PPh$_3$)$_2$Cl with MeC(S)NH$_2$ and AgBF$_4$.

Crystal data

[Ru(C$_5$H$_5$)(C$_2$H$_5$NS)(C$_{18}$H$_{15}$P)$_2$]BF$_4$
$M_r = 852.67$
Monoclinic
$P2_1/c$
$a = 13.600$ (2) Å
$b = 14.8693$ (13) Å
$c = 19.444$ (3) Å
$\beta = 91.600$ (10)°
$V = 3930.6$ (9) Å^3
$Z = 4$
$D_x = 1.441$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11.50$–12.00°
$\mu = 0.57$ mm^{-1}
$T = 293$ K
Block
0.44 × 0.48 × 0.60 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.7930$, $T_{\max} = 0.9995$
5372 measured reflections
5119 independent reflections

4097 observed reflections [$I > 3.0\sigma(I)$]
$R_{\text{int}} = 0.019$
$\theta_{\max} = 22.43°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity variation: 0.8%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.059$
$S = 1.09$
4097 reflections
478 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0025F^2]$
$\Delta\rho_{\max} = 5.90$ e Å^{-3}
$\Delta\rho_{\min} = -5.40$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	U_{eq}
Ru	0.22609 (2)	0.08903 (2)	0.255376 (17)	0.0356 (2)
S	0.23431 (9)	−0.04331 (8)	0.18675 (6)	0.0449 (6)
P1	0.39187 (8)	0.05870 (8)	0.28278 (6)	0.0335 (6)
P2	0.14829 (9)	0.01594 (8)	0.34637 (6)	0.0359 (6)
F1	−0.1425 (4)	−0.0103 (3)	0.0686 (3)	0.115 (3)
F2	−0.2381 (3)	−0.0920 (3)	−0.0031 (2)	0.103 (3)
F3	−0.0843 (3)	−0.1304 (4)	0.0157 (3)	0.158 (5)
F4	−0.1903 (5)	−0.1430 (3)	0.0967 (2)	0.146 (5)
N	0.0612 (4)	−0.0117 (4)	0.1278 (3)	0.075 (3)
C1	0.1419 (4)	−0.0592 (3)	0.1295 (3)	0.050 (3)
C2	0.1497 (5)	−0.1293 (5)	0.0768 (3)	0.086 (4)
C3	0.4555 (3)	0.1506 (3)	0.3294 (2)	0.038 (2)
C4	0.4069 (3)	0.1944 (3)	0.3818 (3)	0.048 (3)
C5	0.4487 (4)	0.2652 (4)	0.4173 (3)	0.057 (3)
C6	0.5417 (5)	0.2940 (4)	0.4008 (3)	0.068 (4)
C7	0.5919 (4)	0.2516 (4)	0.3527 (3)	0.058 (3)
C8	0.5498 (4)	0.1795 (3)	0.3160 (3)	0.051 (3)
C9	0.4695 (3)	0.0430 (3)	0.2068 (2)	0.042 (3)
C10	0.4347 (4)	0.0654 (3)	0.1417 (2)	0.045 (3)
C11	0.4954 (4)	0.0569 (4)	0.0852 (3)	0.056 (3)
C12	0.5885 (5)	0.0266 (4)	0.0937 (3)	0.070 (4)
C13	0.6246 (4)	0.0009 (5)	0.1581 (4)	0.075 (4)
C14	0.5657 (4)	0.0084 (4)	0.2135 (3)	0.058 (3)
C15	0.4287 (3)	−0.0390 (3)	0.3341 (2)	0.040 (2)
C16	0.4450 (4)	−0.1223 (4)	0.3037 (3)	0.057 (3)
C17	0.4657 (5)	−0.1975 (4)	0.3427 (3)	0.073 (4)
C18	0.4710 (5)	−0.1910 (4)	0.4132 (3)	0.081 (4)
C19	0.4561 (6)	−0.1110 (5)	0.4446 (3)	0.083 (5)
C20	0.4338 (5)	−0.0342 (4)	0.4057 (3)	0.060 (3)
C21	0.0160 (4)	0.0414 (4)	0.3368 (3)	0.052 (3)
C22	−0.0350 (4)	−0.0074 (5)	0.2847 (3)	0.070 (4)
C23	−0.1299 (5)	0.0104 (6)	0.2673 (4)	0.099 (6)
C24	−0.1771 (6)	0.0785 (8)	0.3011 (6)	0.126 (8)
C25	−0.1308 (6)	0.1254 (6)	0.3536 (6)	0.122 (8)
C26	−0.0331 (5)	0.1050 (5)	0.3728 (4)	0.086 (5)
C27	0.1851 (4)	0.0498 (3)	0.4338 (2)	0.043 (2)
C28	0.1813 (4)	0.1411 (4)	0.4538 (2)	0.057 (3)
C29	0.2157 (6)	0.1679 (4)	0.5181 (3)	0.081 (4)
C30	0.2545 (6)	0.1063 (5)	0.5641 (3)	0.087 (5)
C31	0.2601 (6)	0.0185 (5)	0.5449 (3)	0.095 (5)
C32	0.2258 (5)	−0.0101 (4)	0.4794 (3)	0.071 (4)
C33	0.1392 (4)	−0.1062 (3)	0.3596 (2)	0.041 (3)
C34	0.0651 (4)	−0.1392 (4)	0.4015 (3)	0.059 (3)
C35	0.0632 (5)	−0.2314 (5)	0.4164 (3)	0.076 (4)
C36	0.1310 (6)	−0.2879 (4)	0.3922 (4)	0.082 (5)
C37	0.2031 (5)	−0.2561 (4)	0.3495 (4)	0.079 (5)
C38	0.2066 (4)	−0.1643 (3)	0.3340 (3)	0.059 (3)
C39	0.1815 (5)	0.1754 (4)	0.1667 (3)	0.062 (3)
C40	0.1054 (4)	0.1757 (3)	0.2142 (3)	0.054 (3)
C41	0.1423 (4)	0.2150 (3)	0.2751 (3)	0.054 (3)
C42	0.2395 (4)	0.2377 (3)	0.2670 (3)	0.057 (3)
C43	0.2644 (4)	0.2135 (3)	0.1990 (3)	0.059 (3)
B	−0.1629 (5)	−0.0949 (4)	0.0444 (4)	0.057 (4)

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

Ru—S	2.3820 (13)	P1—C15	1.825 (5)
Ru—P1	2.3460 (12)	P2—C21	1.842 (5)
Ru—P2	2.3527 (12)	P2—C27	1.830 (5)
Ru—Cp	1.8783 (5)	P2—C33	1.839 (5)
Ru—C39	2.221 (5)	N—C1	1.304 (8)
Ru—C40	2.219 (5)	C1—C2	1.468 (8)
Ru—C41	2.232 (5)	C39—C40	1.405 (8)
Ru—C42	2.229 (5)	C39—C43	1.397 (9)
Ru—C43	2.221 (5)	C40—C41	1.401 (8)
S—C1	1.671 (5)	C41—C42	1.378 (8)
P1—C3	1.842 (5)	C42—C43	1.421 (9)
P1—C9	1.854 (5)		
S—Ru—P1	84.75 (4)	S—C1—C2	119.8 (4)
S—Ru—P2	93.94 (4)	N—C1—C2	116.3 (5)
P1—Ru—P2	100.95 (4)	C40—C39—C43	107.6 (5)
P1—Ru—Cp	120.74 (3)	C39—C40—C41	107.8 (5)
P2—Ru—Cp	121.95 (3)	C40—C41—C42	109.1 (5)
S—Ru—Cp	125.90 (3)	C41—C42—C43	107.4 (5)
Ru—S—C1	116.3 (2)	C39—C43—C42	108.1 (5)
S—C1—N	123.9 (4)		

The data crystal was mounted on a glass fiber with epoxy glue. The intensity scan widths were $(1.0 + 0.35\tan\theta)°$, with scan speeds of 4–16° min^{-1}. The total exposure time for data collection was 54.7 h. *CAD-4 Software* (Enraf–Nonius, 1989) was used for data collection and cell refinement. Data reduction was performed using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The structure was solved by direct methods (*NRCVAX*). In the final least-squares refinement (*NRCVAX*), the phenyl and methyl H atoms were constrained to idealized (C—H = 0.95 Å) positions (the orientation of the methyl group had been shown previously by a difference map), and the amide H atoms were fixed at difference-map positions. All H atoms were assigned isotropic *U* values of 0.01 plus the *U* value of the attached N or C atom.

MD acknowledges the support of an ASU Faculty Research Grant and an ASU Basic Research Grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Amarasekera, J. & Rauchfuss, T. B. (1989). *Inorg. Chem.* **28**, 3875–3883.
Draganjac, M., Minick, D. & Cordes, A. W. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 265–271.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., Charland,. J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Schenk, W. A., Stur, T. & Dombrowski, E. (1992). *Inorg. Chem.* **31**, 723–724.

Acta Cryst. (1994). C**50**, 1233–1235

A Redetermination of the X-ray Structure of the Hexanuclear Mixed-Metal Cluster $[Ru_5Rh(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\eta^5\text{-}C_{10}H_{15})]$

TRUSHAR ADATIA,* MARY MCPARTLIN
AND JILL MORRIS

School of Chemistry, University of North London, Holloway Road, London N7 8DB, England

HILARY CURTIS AND JACK LEWIS

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received* 3 *September* 1993; *accepted* 24 *January* 1994)

Abstract

The X-ray structure analysis shows that the octahedral hexanuclear mixed-metal cluster μ_6-carbido-μ-carbonyl-4:5κ^2C-tridecacarbonyl-1κ^3C,2κ^3C,3κ^3C,4κ^2C,5κ^2C-[6(η^5)-pentamethylcyclopentadienyl]-*octahedro*-pentarutheniumrhodium(4 *Rh—Ru*)(8 *Ru—Ru*) $[Ru_5Rh(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\eta^5\text{-}C_{10}H_{15})]$, encapsulating a C atom, has Ru—Ru bond lengths in the range 2.813 (1)–2.959 (1) and Ru—Rh bond lengths of 2.825 (1)–2.895 (1) Å. The pentamethylcyclopentadienyl ligand is bound in a terminal fashion to the Rh atom. Of the fourteen carbonyl groups, one is bridging, two semi-bridging and 11 adopt essentially terminal positions.

Comment

A recent report has shown that treatment of the salt $[N(PPh_3)_2][Ru_5C(CO)_{14}]$ with an equivalent amount of $[Rh(C_5Me_5)(NCMe)_3][BF_4]_2$, under ambient conditions, affords the compound $[Ru_5Rh(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\eta^5\text{-}C_{10}H_{15})]$, (1), in *ca* 60% yield. X-ray analysis on the only available crystals of this cluster has established the overall structure, but as a result of poor diffraction the e.s.d.'s assigned to all parameters are relatively high, limiting detailed discussion of the cluster geometry (Bailey *et al.*, 1993). In our recent investigations of the reactivity of cluster (1), we have been able to synthesize this compound in *ca* 75% yield by reacting the carbonylate ion with the rhodium salt $[Rh(C_5Me_5)(NCMe)_3][SbF_6]_2$ (Adatia *et al.*, 1993). Excellent crystals were obtained for the hexanuclear cluster (1) and this allowed the redetermination of its solid-state structure to be carried out with greater precision.

The overall molecular geometry established for the mixed-metal cluster (1) is shown in Fig. 1 and is similar to that reported by Bailey *et al.* (1993). The metal-core geometry established for (1) may be compared with the metal frameworks in the homonuclear analogue $[Ru_6C(CO)_{16}]^{2-}$ (Johnson *et al.*, 1980) and the arene derivatives $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$ (arene $= C_6H_3Me_3$ and C_6H_5Me) (Mason & Robinson, 1968; Farrugia, 1988). The Ru—Ru distances in (1) [2.813 (1)–2.959 (1) Å] are similar in range to those attained from the previous X-ray study [2.815 (5)–2.957 (5) Å], but the mean Ru—Ru bond length of 2.899 (1) Å obtained from the current study is 0.012 (2) Å shorter than that obtained earlier (Bailey *et al.*, 1993). Interestingly, the mean Ru—Ru distance in (1) closely resembles that in the homonuclear analogue $[Ru_6C(CO)_{16}]^{2-}$ [2.891 (3) Å (Johnson *et al.*, 1980)]. The shortest Ru—Ru bond length of 2.813 (1) Å in (1) is that assigned to Ru(3)—Ru(5), the metal–metal vector asymmetrically bridged by the carbonyl group CO(35), (Fig. 1). Similar shortening of Ru—Ru bonds bridged by CO ligands is also a structural feature present in the carbido dianion $[Ru_6C(CO)_{16}]^{2-}$, where the four Ru—Ru edges of the metal octahedron bridged by carbonyl groups are notably shorter than unbridged bonds.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994