in CH_3CN (pzH = pyrazole),[22] $E^r_{1/2} = 2.76$ V vs. quasi Ag reference electrode for $[Ru^{II}(bpy)_3](ClO_4)_2$ in SO_2.[23]

In the present case the oxidation potentials of the deprotonated BiBzIm complexes are shifted to considerably more negative potentials compared with those of other complexes, which suggests stronger π-donation of deprotonated BiBzIm to metal stabilizes the higher oxidation states and the contribution of resonance form B becomes larger (Scheme I). The large shift towards a less positive potential enables the oxidation state IV complexes to be observed in aqueous media via oxidation at glassy-carbon electrodes. Recently, the deprotonation of coordinated amide, i.e. amidate nitrogens, has been reported to stabilize the high-valent Pd(IV),[24] Ni(III),[25] Os(VI),[26] and Co(IV).[27] Meyer et al. have reported that loss of protons from aquo ligands on oxidation in $[M(bpy)_2(OH_2)_2]^{2+}$ (M = Ru, Os) complexes results in the stabilization of higher oxidation states, i.e. M(IV), M(V) and M(VI).[21] Naturally, these higher oxidation state species are powerful oxidants. In the present case, reaction with water and/or electrolyte is moderately slow. Reactions of the kind

$$4[M^{IV}(bpy)_2(BiBzIm)]^{2+} + 2H_2O \rightarrow 4[M^{III}(bpy)_2(BiBzImH)]^{2+} + O_2 \quad (24)$$

would explain the catalytic response observed with long time domain voltammetric studies (see also eq 23). This class of reaction has been demonstrated to occur in studies of other Ru(IV) complexes.[28] Catalytic reactions with the sulfur dioxide as the solvent have also been reported.[23]

In this work we have used the formal notation of M(II), M(III), and M(IV) to describe the oxidation processes. However, Bard et al.[29] have suggested that for $[Ru(bpy)_3]^{2+}$ the second oxidation process is ligand based, whereas for $[Os(bpy)_3]^{2+}$ the second oxidation process is assumed to be metal based. In our case, the similarity in pH dependence for both metals leads us to suggest that both oxidation processes are essentially metal based, although of course the concept of formal oxidation states is notoriously treacherous in this area of chemistry.

Acknowledgment. The authors gratefully acknowledge financial support from the Ministry of Education, Japan, and the award of a Gordon Fellowship from the Deakin University Research Committee that made it possible for M.H. to spend a study leave period at Deakin University.

Registry No. $[Os^{II}(bpy)_2(BiBzImH_2)](ClO_4)_2$, 104642-28-6; $[Os^{II}(bpy)_2(BiBzImH_2)]^{2+}$, 104642-27-5; $[Os^{III}(bpy)_2(BiBzImH_2)]^{3+}$, 104642-29-7; $[Os^{II}(bpy)_2(BiBzImH)]^{+}$, 104642-30-0; $[Os^{II}(bpy)_2(BiBzIm)]$, 104642-31-1; $[Os^{III}(bpy)_2(BiBzImH)]^{2+}$, 104642-32-2; $[Os^{III}(bpy)_2(BiBzIm)]^{+}$, 104642-33-3; $[Os^{IV}(bpy)_2(BiBzIm)]^{2+}$, 104642-34-4; $[Ru^{II}(bpy)_2(BiBzImH_2)]^{2+}$, 88228-00-6; $[Ru^{II}(bpy)_2(BiBzImH)]^{+}$, 88437-65-4; $[Ru^{II}(bpy)_2(BiBzIm)]$, 88437-60-9; $[Ru^{III}(bpy)_2(BiBzImH_2)]^{3+}$, 88228-00-6; $[Ru^{III}(bpy)_2(BiBzImH)]^{2+}$, 104642-35-5; $[Ru^{III}(bpy)_2(BiBzIm)]^{+}$, 104642-36-6; $[Ru^{IV}(bpy)_2(BiBzIm)]^{2+}$, 104642-37-7; $Os(bpy)_2Cl_2$, 15702-72-4; $NOBF_4$, 14635-75-7.

---

(22) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *18*, 3369.

(23) Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373.

(24) Hamburg, A.; Ho, C.; Getek, T. A. *Inorg. Chem.* **1985**, *24*, 2593.

(25) Kirksey, S. T.; Neubecker, T. A.; Margerum, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 1631.

(26) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Kraft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460.

(27) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 5037.

(28) Baar, R. B.; Anson, F. C. *J. Electroanal. Chem.* **1985**, *187*, 265.

(29) Gaudiello, J. G.; Bradley, P. G.; Norton, K. A.; Woodruff, W. H.; Bard, A. J. *Inorg. Chem.* **1984**, *23*, 3.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Cluster Syntheses. 13. Chemistry of Sulfidoruthenium Carbonyl Clusters. Synthesis and Characterization of the New Unsaturated Clusters $Ru_4(CO)_{11-n}L_n(\mu_4\text{-}S)_2$ (n = 0–2, L = PMe_2Ph)

Richard D. Adams,* James E. Babin, and Miklos Tasi

Received July 17, 1986

The compound $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**) has been prepared by three methods: pyrolysis and photolysis of $Ru_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$, in 89% and 80% yields, respectively, and the reaction of $Ru_3(CO)_{12}$ and ethylene sulfide in 67% yield. The compound $Ru_3(CO)_9(\mu_3\text{-}S)_2$ (**3**) was prepared in 94% yield from the reaction of $Ru_3(CO)_{12}$ with an excess of ethylene sulfide. Compound **3** was also obtained from the reaction of **1** with ethylene sulfide in 97% yield. Compounds **1** and **3** react with hydrogen by loss of CO to form the compounds $Ru_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**) and $Ru_3(CO)_8(\mu_3\text{-}S)_2(\mu\text{-}H)_2$ (**4**) in 92% and 48% yields, respectively. Compound **4** can be converted back into **3** by reaction with CO under 50 atm pressure in 94% yield. Compound **3** reacts with $Ru(CO)_5$ in the presence of UV irradiation to form the tetraruthenium cluster $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$ (**5**) in 90% yield. The reaction of **4** with PMe_2Ph at 25 °C yields the substitution products $Ru_4(CO)_{11-n}(PMe_2Ph)_n(\mu_4\text{-}S)_2$ (**6**, n = 1; **7**, n = 2). The structure of **7** was established by a single-crystal X-ray diffraction analysis. Crystal data: space group, $P2_1/n$; a = 9.752 (2) Å; b = 20.471 (3) Å; c = 16.236 (2) Å; β = 93.04 (1)°; Z = 4; ρ_{calcd} = 2.07 g/cm^3. The structure was solved by direct methods and was refined (3843 reflections) to the final values of the residuals R = 0.027 and R_w = 0.031. The molecule consists of a square cluster of four ruthenium atoms with quadruply bridging sulfido ligands on the two square faces of the cluster. Two carbonyl ligands bridge adjacent edges of the square and produce a slight shortening of the two Ru–Ru bonds. The clusters of compounds **5** and **6** are believed to be structurally similar to **7**. Compounds **5**–**7** contain 62 valence electrons and are therefore electron deficient by two electrons. They do, however, conform to the requirements of the polyhedral skeletal electron pair theory.

Introduction

Sulfur has always played an important role in the chemistry of the transition elements. The sulfido ligand is probably one of the most versatile of all known ligands. It exhibits a wide variety of structural geometries and electron-donating capabilities.[1-4] We have recently synthesized a large number of new sulfidoosmium carbonyl cluster compounds.[5] Some of these possess unusually high reactivities that could have implications for catalysis.[6] The

---

(1) (a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322. (b) Müller, A. *Polyhedron* **1986**, *5*, 323. (c) Abel, E. W.; Crosse, B. C. *Organomet. Chem. Rev.* **1967**, *2*, 443. (d) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201.

(2) Adams, R. D.; Foust, D. F. *Organometallics* **1983**, *2*, 323, and references therein.

(3) Adams, R. D.; Hor, R. S. A. *Organometallics* **1984**, *3*, 1915.

(4) Adams, R. D.; Babin, J. E.; Natarajan, K. *J. Am. Chem. Soc.* **1986**, *108*, 3518.

(5) Adams, R. D. *Polyhedron* **1985**, *4*, 2003.

0020-1669/86/1325-4514$01.50/0 © 1986 American Chemical Society

catalytic properties of one has already been demonstrated.[7] To date, the chemistry of sulfidoruthenium carbonyl cluster compounds has been very underdeveloped.[8] In this and a series of papers that will follow we shall report our recent studies of the synthesis and characterization of sulfidoruthenium carbonyl cluster compounds.[9]

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. THF was freshly distilled from sodium diphenylketyl before use. $Ru_3(CO)_{12}$ was purchased from Strem Chemical Co. and was used as received. Thiophenol, ethylene sulfide, and PMe_2Ph were purchased from Aldrich Chemical Co. and were used without further purification.

Photolysis experiments were performed by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. High-pressure reactions were performed in an Autoclave Engineers, Model APB-300 300-mL magnedrive high-pressure autoclave, or a Parr Model 4713 high-pressure reaction vessel. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrometer. ^1H NMR spectra were run on a Bruker AM-300 spectrometer operating at 300 MHz. Mass spectra were run on a Finnigan Model 4521 mass spectrometer by using electron-impact ionization. Elemental analyses were performed by MicAnal, Tucson, AZ.

Preparation of $HRu_3(CO)_{10}(\mu\text{-SPh})$. A 100-mg (0.156-mmol) sample of $Ru_3(CO)_{12}$ was dissolved in 80 mL of hexane and was heated to reflux. At this temperature 30 μL (0.294 mmol) of thiophenol was added and the solution was refluxed for an additional 30 min while being purged slowly with CO gas. The solution was concentrated and chromatographed over a Florisil column by using hexane as eluent. This yielded 28 mg of unreacted $Ru_3(CO)_{12}$ and 61 mg of $Ru_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ (56%). This procedure is similar to that used for preparation of the analogous alkanethiolato derivatives.[10] IR (ν(CO)/cm^{-1} in hexane): 2106 (w), 2066 (s), 2058 (m), 2027 (vs), 2011 (w), 1997 (w). ^1H NMR (δ in $CDCl_3$): 7.40–7.20 (m, 5 H), −14.98 s, 1 H).

Preparation of $Ru_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-S})$ (1). (a) From $Ru_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$. A 32-mg (0.046-mmol) sample of $Ru_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ was dissolved in 50 mL of hexane and was heated to reflux for 35 min in the presence of a slow purge with CO. After cooling, the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and was chromatographed by TLC on silica gel plates with hexane solvent. A small amount of $Ru_3(CO)_{12}$ (1.2 mg) and $Ru_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ (3.3 mg) were separated from the yellow, major product $Ru_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-S})$ (1) (25.5 mg, 89%). IR (ν(CO) cm^{-1} in hexane): 2075 (vs), 2036 (s), 2022 (w), 1735 (w). Mass spectrum (20 eV, 90 °C), *m/e*: 615–28*x*, *x* = 0–6([M]$^+$ − *x*CO). Anal. Calcd for $Ru_3SO_{10}C_{10}$: C, 19.51; H, 0. Found: C, 19.63; H, 0.

(b) From $HRu_3(CO)_{10}(\mu\text{-SPh})$ by Photolysis. A 12-mg (0.017-mmol) sample of $HRu_3(CO)_{10}(\mu\text{-SPh})$ was dissolved in 60 mL of hexane and was irradiated with UV light while being purged slowly with CO for 75 min. The reaction solution was worked up as described above. Yield: 8.7 mg (81%).

(c) From $Ru_3(CO)_{12}$ and Ethylene Sulfide. A 200-mg (0.313-mmol) sample of $Ru_3(CO)_{12}$ was dissolved in 110 mL of hexane and was heated to reflux under a slow purge with CO. At this temperature 50 μL (0.821 mmol) of ethylene sulfide was added, and the reflux was continued for 30 min. During this time the dark orange color of the solution changed to yellow-orange. The reaction solution was concentrated and was chromatographed over a Florisil column. An orange band containing a mixture of $Ru_3(CO)_{12}$ and $Ru_3(CO)_9(\mu_3\text{-S})_2$ was separated with hexane eluent. With a hexane/CH_2Cl_2, 9/1 solvent mixture light yellow 1 was separated. Yield: 130 mg, 67%.

Preparation of $Ru_3(CO)_9(\mu_3\text{-S})_2$ (3). (a) From $Ru_3(CO)_{12}$ and Ethylene Sulfide. A 200-mg (0.313 mmol) sample of $Ru_3(CO)_{12}$ was dissolved in 120 mL of cyclohexane, and the mixture was heated to reflux in the presence of a slow purge with CO. At this temperature 95 μL (1.565 mmol) of ethylene sulfide was added via syringe, and the reflux was continued for 75 min. The solution was chromatographed over a Florisil column by using hexane as eluent. This yielded 182 mg of orange 3 (94%).

(b) From 1 and Ethylene Sulfide. A 10-mg (0.016-mmol) sample of **1** was dissolved in 30 mL of cyclohexane solvent and was heated to reflux under a slow purge with CO. A 10-μL (0.160-mmol) aliquot of ethylene sulfide was added, and the reaction was continued for 50 min and then worked up as described above. Yield of **3**: 9.76 mg (97%).

Reaction of 1 with Hydrogen. A 10-mg (0.016 mmol) sample of **1** was dissolved in 15 mL of octane and refluxed for 25 min under a slow purge with hydrogen. The only product, $Ru_3(CO)_9(\mu_3\text{-S})(\mu\text{-H})_2$ (**2**), was separated on silica gel TLC plates with hexane eluent. Yield: 8.8 mg (92%).

Reaction of 3 with Hydrogen. A 31-mg (0.005 mmol) sample of $Ru_3(CO)_9(\mu_3\text{-S})_2$ in 8 mL of octane was placed into the 45-mL Parr high-pressure reaction vessel. The reaction with H_2 was performed at 100 °C/70 atm of H_2 for 7 h. After cooling, the reaction solution was filtered, evaporated to dryness, dissolved in CH_2Cl_2, and concentrated. The product was crystallized by cooling to −20 °C. Yield: 14.4 mg (48%) $Ru_3(CO)_8(\mu_3\text{-S})_2(\mu\text{-H})_2$ (**4**) as air-stable orange crystals. IR (ν(CO) cm^{-1} in hexane): 2115 (vw), 2045 (vs), 2042 (s, sh), 1991 (m). ^1H NMR (δ in $CDCl_3$): −11.08 (s, 2 H). Mass spectrum (20 eV, 90 °C), *m/e*: 593–28*x*, *x* = 0–6([M]$^+$ − *x*CO). Anal. Calcd for $Ru_3S_2O_8C_8H_2$: C, 16.19; H, 0.34. Found: C, 16.16; H, 0.18. The mother liquor contained mainly $Ru_3(CO)_9(\mu_3\text{-S})(\mu\text{-H})_2$ (**2**), which was separated on TLC plates (hexane eluent). Yield: 6.8 mg (23%).

Carbonylation of 4. A 6.6-mg (0.011-mmol) sample of $Ru_3(CO)_8(\mu_3\text{-S})_2(\mu\text{-H})_2$, was dissolved in 10 mL of hexane and placed into the 45-mL Parr high-pressure reaction vessel. After evacuation, the reaction vessel was pressurized to 50 atm with CO and then heated to 85 °C for 3 h. The workup as described above yielded **3** (6.5 mg, 94%).

Preparation of $Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-S})_2$ (5). (a) From 3. A 10-mg (0.016-mmol) sample of **3** was dissolved in minimum amount of cyclohexane, and a cyclohexane solution of $Ru(CO)_5$ (0.08 mmol) was added. The solution was irradiated with UV light for 1 h under a slow purge with nitrogen. During this time the product was formed as an orange precipitate. It was filtered, washed with pentane, and dried in air. Yield: 11.3 mg (90%). IR (ν(CO) cm^{-1} in hexane): 2076 (vw), 2055 (vs), 2023 (w), 2010 (w), 1991 (w), 1858 (w), 1844 (w). Mass spectrum (70 eV, 90 °C), *m/e*: 776–28*x*, *x* = 0–10([M]$^+$ − *x*CO). Anal. Calcd for $Ru_4S_2O_{11}C_{11}$: C, 17.01; H, 0. Found: C, 17.05; H, 0. Mp: 156 °C dec.

(b) From 1. A 31-mg (0.05-mmol) sample of **1** in 5 mL of octane was placed into the 45-mL Parr high-pressure reaction vessel. The vessel was closed, pressurized with CO to 100 atm, and heated to 125 °C for 4 h. After the vessel was cooled to 25 °C, the solution was removed and cooled to −20 °C. Fine orange needle crystals of spectroscopically pure **5** were formed. Yield: 8.3 mg (20%).

(c) Thermolysis of $HRu_3(CO)_{10}(\mu\text{-SPh})$. A 110-mg (0.152-mmol) sample of $HRu_3(CO)_{10}(\mu\text{-SPh})$ was placed into the 300-mL autoclave in 75 mL of heptane solvent. The autoclave was pressurized to 30 atm with carbon monoxide, vented to atmospheric pressure twice, then pressurized to 100 atm of CO and heated to 125 °C for 4 h. An orange solution was obtained, which was concentrated and cooled to −20 °C. A 18-mg mass of orange crystals of $Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-S})_2$ formed (yield, 15%). The mother liquor was chromatographed on a Florisil column using hexane as eluent. The first orange-yellow band was a mixture, which was subsequently separated by TLC (hexane) to yield 5.9 mg of $Ru_3(CO)_{12}$ (6%) and 19.6 mg of $Ru_3(CO)_9(\mu_3\text{-S})(\mu\text{-H})_2$ (21%). The second dark yellow band eluted with hexane/CH_2Cl_2; a 4/1 solvent mixture yielded 22.4 mg of $[Ru(CO)_3SPh]_2$ (24%).

Reaction of 5 with PMe_2Ph. A 25-mg (0.032-mmol) sample of **5** was dissolved in 40 mL of THF. Then, 300 μL of a 0.13 M THF solution of PMe_2Ph (0.039 mmol) was added in 50-μL portions at 5 min intervals over 30 min at 25 °C. The light orange color of the solution turned to dark orange. The solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and was chromatographed on silica TLC plates by using a hexane/CH_2Cl_2 4/1 solvent mixture. The separation yielded two orange bands. Recrystallization of the second band from a hexane/CH_2Cl_2 9/1 solvent mixture at −20 °C resulted in 15.6 mg of $Ru_4(CO)_7(\mu\text{-CO})_2(PMe_2Ph)_2(\mu_4\text{-S})_2$ as dark red crystals (49%). IR(ν(CO) cm^{-1} in hexane): 2043 (vw), 2016 (vs), 2003 (w, sh), 1992 (m), 1970 (w, sh), 1964 (w), 1848 (w), 1811 (w). ^1H NMR (δ in $CDCl_3$): 7.40–7.20 (m, 10 H), 1.80 (s, 6 H), 1.76 (s, 6 H). Mp: 151–153 °C. Anal. Calcd for $Ru_4S_2P_2O_9C_{25}H_{22}$: C, 30.12; H, 2.21. Found: C, 30.20; H, 2.07. The first orange compound was found to be $Ru_4(CO)_8(\mu\text{-CO})_2(PMe_2Ph)(\mu_4\text{-S})_2$ (**6**) (4.1 mg, 14%). IR (ν(CO) cm^{-1} in hexane): 2075 (w, sh), 2072 (w), 2038 (vs), 2034 (vs), 2004 (s), 1983 (m), 1955 (vw), 1862 (vw), 1821 (vw). ^1H NMR (δ in $CDCl_3$): 7.41–7.22 (m, 5 H), 1.89 (s, 3 H), 1.86 (s, 3 H). Mass spectrum (13 eV, 125 °C), *m/e*: 886–28*x*, *x* = 1–9([M]$^+$ − CO).

Crystallographic Analyses. Red crystals of **7** were obtained by cooling CH_2Cl_2/hexane, 3/7 v/v, solutions to −20 °C. The data crystal was

---

(6) (a) Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 235. (b) Adams, R. D.; Wang, S. *Organometallics* **1985**, *5*, 1272. (c) Adams, R. D.; Wang, S. *Inorg. Chem.*, in press.

(7) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.

(8) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Chapter 32.

(9) Adams, R. D.; Babin, J. E.; Tasi, M., reports in preparation.

(10) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 797.

Table I. Crystallographic Data for X-ray Diffraction Analysis of Compound 7

(A) Crystal Data

formula	$Ru_4S_2P_2O_9C_{26}H_{22}$	β, deg	93.04 (1)
temp, °C	23 (±3)	V, Å^3	3237 (1)
space group	$P2_1/n$	M_r	1008.6
a, Å	9.752 (2)	Z	4
b, Å	20.471 (3)	ρ_{calcd}, g/cm^3	2.07
c, Å	16.236 (2)		

(B) Measurement of Intensity Data

radiation	Mo Kα (0.71073 Å)
monochromator	graphite
detector aperture, mm	
horiz	2.0
vert	2.0
crystal faces	010, 0$\bar{1}$0, 001 00$\bar{1}$, $\bar{1}$10, 100
crystal size, mm	0.08 × 0.13 × 0.41
crystal orientation: direction; deg from ϕ axis	a^*; 3.3
reflcns measd	$h,k,\pm l$
max 2θ, deg	moving cryst–stationary counter
ω-scan width (A + 0.347 tan θ), deg	1.10
bkgd (count time, at each end of scan), s	9.0
ω-scan rate,[a] deg/min	4.0
no. of reflcns measd	5603
no. of data used ($F^2 \geq 3.0\sigma(F^2)$)	3843

(C) Treatment of Data

abs cor	not applied
abs coeff, cm^{-1}	20.6
no. of variables (refined)	379
P factor	0.03
final residuals	
R_F	0.027
R_{wF}	0.031
esd of unit wt observn, value of final cycle	1.18
largest peak in final diff Fourier, e/Å^3	0.52

[a] Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to those of the first scan, etc. A maximum of three scans was permitted per reflection.

mounted in thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the automatic search, center, index, and least-squares routines. Crystal data, data collection, parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX I computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., College Station, TX. Neutral-atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[11b] Full-matrix least-squares refinements minimized the function

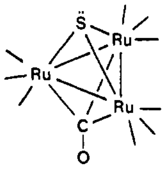
$$\sum_{hkl} w(|F_o| - |F_c|)^2 \qquad \sigma(F) = \sigma(F_o^2)/2F_o$$

$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$$

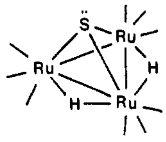
Compound 7 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified on the basis of the systematic absences observed during the collection of data. The coordinates of the heavy atoms were obtained by direct methods (MULTAN). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the phenyl rings were calculated by assuming planar 6-fold symmetry. The positions of the methyl hydrogen atoms were calculated by assuming idealized tetrahedral and staggered conformational geometries. The contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not refined. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement. See supplementary material for a table of the structure factor amplitudes and the values of the anisotropic thermal parameters.

Results

The new compound $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**) was prepared by three methods: (1) pyrolysis of $Ru_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ in refluxing hexane under a CO atmosphere resulted in the loss of a formula equivalent of C_6H_6 (not observed) and the formation of **1** in 89% yield; (2) UV irradiation of $Ru_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ under an atmosphere of CO also yields **1** (80%); (3) the reaction of $Ru_3(CO)_{12}$ with ethylene sulfide under an atmosphere of CO produced **1** in 67% yield. Compound **1** was characterized by IR spectroscopy, mass spectrometry, and C, H elemental analyses. The mass spectrum showed the parent ion m/e 615 for ^{101}Ru and ions corresponding to the loss of each of six carbonyl ligands. The IR spectrum shows an absorption at 1735 cm^{-1}, which can be attributed to a triply bridging carbonyl ligand. Compound **1** is believed to be structurally analogous to its iron[12] and osmium[13] homologues, both of which have been characterized by X-ray crystallographic methods. Thus **1** is believed to contain a triangular cluster of three ruthenium atoms bridged by a triply bridging sulfido ligand on one side of the cluster and a triply bridging carbonyl ligand on the other side. Each metal should have three terminal carbonyl ligands. When compound **1** was allowed to react with H_2 (1 atm) at 125 °C, it eliminated 1 mol of CO and added 1 mol of H_2 to form the known compound $Ru_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**) in 92% yield.[14]



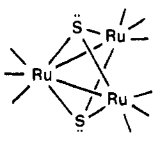
1



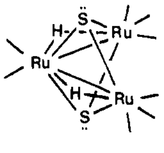
2

When $Ru_3(CO)_{12}$ was reacted with an excess of ethylene sulfide over a longer period of time (75 min), two sulfur atoms were introduced into the cluster and the compound $Ru_3(CO)_9(\mu_3\text{-}S)_2$ (**3**) was formed in 94% yield. Compound **3** was reported previously as a product of the reaction of $Ru_3(CO)_{12}$ with elemental sulfur.[15] It is believed to have a structure analogous to those of its iron[16] and osmium[17] homologues, consisting of an open triangular cluster of three metal atoms with triply bridging sulfido ligands on opposite sides of the cluster. It was suspected that compound **1** was an intermediate in the formation of **3**, and this was confirmed by an independent synthesis which gave **3** in 97% yield.

Compound **3** was found to react with hydrogen at 100 °C/70 atm to yield the new compound $Ru_3(CO)_8(\mu_3\text{-}S)_2(\mu\text{-}H)_2$ (**4**) in 48% yield and $Ru_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**) in 23% yield. Compound **4** was characterized by IR and ^1H NMR spectroscopies, mass spectrometry, and C, H elemental analysis. Its IR spectrum



3



4

---

[11] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

[12] Marko, L.; Madach, T.; Vahrenkamp, H. *J. Organomet. Chem.* **1980**, *190*, C67.

[13] Adams, R. D.; Horvath, I. T.; Kim, H. S. *Organometallics* **1984**, *3*, 548.

[14] Adams, R. D.; Katahira, D. *Organometallics* **1982**, *1*, 53.

[15] Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1979**, 719.

[16] Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 493.

[17] Adams, R. D.; Horvath, I. T.; Segmuller, B. E.; Yang, L.-W. *Organometallics* **1983**, *2*, 144.

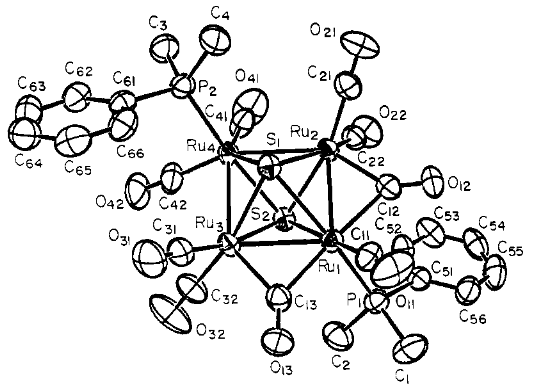


Figure 1. Perspective ORTEP diagram of the molecular structure of $Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)_2$ (7) showing 50% probability thermal ellipsoids.

is very similar to that of its osmium homologue, which has been characterized by crystallographic methods.[18] Accordingly, compound **4** is believed to possess a similar open triangular cluster of metal atoms with two equivalent bridging hydride ligands ($\delta = -11.08$) and two triply bridging sulfido ligands. In the mass spectrum the parent ion was observed in addition to ions corresponding to the loss of each of six carbonyl ligands. The addition of hydrogen to **3** is reversible. When compound **4** was heated to 85 °C for 3 h under CO (50 atm), compound **3** was regenerated in 94% yield. The formation of **2** from **3** was a result of the addition of 1 mol of H_2 and the loss of one sulfido ligand, presumably in the form of H_2S, but this was not observed.

Table II. Positional Parameters with Esd's for $Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)_2$ (7)

atom	*x*	*y*	*z*
Ru(1)	0.139 207 (42)	0.064 493 (19)	0.252 339 (25)
Ru(2)	−0.140 866 (42)	0.053 987 (19)	0.237 745 (26)
Ru(3)	0.154 449 (43)	−0.065 305 (20)	0.291 168 (27)
Ru(4)	−0.132 588 (43)	−0.079 146 (19)	0.271 652 (26)
S(1)	−0.011 42 (14)	0.005 218 (60)	0.355 143 (81)
S(2)	0.010 95 (14)	−0.024 264 (63)	0.171 571 (81)
P(1)	0.254 02 (15)	0.100 459 (72)	0.140 215 (89)
P(2)	−0.257 36 (15)	−0.112 018 (69)	0.381 048 (94)
O(11)	0.292 56 (48)	0.162 73 (24)	0.359 04 (29)
O(12)	−0.030 03 (44)	0.190 68 (19)	0.217 33 (28)
O(13)	0.426 08 (43)	0.004 43 (21)	0.284 89 (31)
O(21)	−0.353 10 (45)	0.118 53 (23)	0.339 37 (29)
O(22)	−0.317 67 (47)	0.075 30 (23)	0.081 94 (28)
O(31)	0.283 45 (49)	−0.110 91 (25)	0.453 46 (30)
O(32)	0.296 05 (58)	−0.174 55 (27)	0.204 74 (35)
O(41)	−0.379 61 (54)	−0.088 52 (28)	0.152 30 (34)
O(42)	−0.059 13 (61)	−0.220 56 (21)	0.250 09 (31)
C(1)	0.402 17 (65)	0.149 74 (34)	0.164 87 (42)
C(2)	0.320 17 (71)	0.034 34 (34)	0.080 18 (41)
C(3)	−0.413 75 (63)	−0.154 72 (31)	0.352 69 (42)
C(4)	−0.313 48 (70)	−0.046 57 (31)	0.446 91 (40)
C(11)	0.232 13 (60)	0.126 31 (28)	0.319 18 (36)
C(12)	−0.019 68 (56)	0.134 80 (28)	0.227 41 (34)
C(13)	0.305 21 (61)	0.002 09 (26)	0.278 09 (35)
C(21)	−0.272 98 (59)	0.094 62 (28)	0.300 31 (36)
C(22)	−0.251 64 (59)	0.068 88 (28)	0.141 47 (38)
C(31)	0.230 94 (60)	−0.095 57 (28)	0.391 20 (38)
C(32)	0.242 27 (65)	−0.133 60 (32)	0.236 33 (39)
C(41)	−0.288 96 (69)	−0.084 27 (30)	0.199 27 (41)
C(42)	−0.082 60 (74)	−0.166 17 (30)	0.258 95 (38)
C(51)	0.152 00 (55)	0.146 40 (26)	0.063 64 (31)
C(52)	0.036 53 (63)	0.117 23 (28)	0.026 43 (36)
C(53)	−0.047 52 (68)	0.149 63 (32)	−0.031 31 (38)
C(54)	−0.013 56 (75)	0.212 33 (32)	−0.052 97 (39)
C(55)	0.099 77 (83)	0.241 71 (31)	−0.018 06 (42)
C(56)	0.183 70 (64)	0.210 17 (29)	0.041 45 (38)
C(61)	−0.160 80 (55)	−0.166 71 (26)	0.450 51 (32)
C(62)	−0.191 25 (63)	−0.232 28 (28)	0.455 74 (36)
C(63)	−0.111 28 (74)	−0.272 23 (29)	0.509 07 (40)
C(64)	−0.004 60 (70)	−0.246 90 (35)	0.557 44 (41)
C(65)	0.025 42 (64)	−0.182 10 (35)	0.551 27 (37)
C(66)	−0.052 25 (65)	−0.141 71 (29)	0.499 03 (35)

Table III. Intramolecular Distances (Å) for $Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)_2$ (7)

Ru(1)–C(11)	1.870 (6)	P(1)–C(2)	1.807 (7)
Ru(1)–C(13)	2.087 (6)	P(1)–C(51)	1.814 (5)
Ru(1)–C(12)	2.138 (6)	P(2)–C(3)	1.797 (6)
Ru(1)–P(1)	2.308 (2)	P(2)–C(4)	1.817 (6)
Ru(1)–S(2)	2.532 (1)	P(2)–C(61)	1.817 (6)
Ru(1)–S(1)	2.584 (1)	O(11)–C(11)	1.132 (7)
Ru(1)–Ru(3)	2.7330 (7)	O(12)–C(12)	1.159 (6)
Ru(1)–Ru(2)	2.7376 (8)	O(13)–C(13)	1.179 (7)
Ru(2)–C(21)	1.877 (6)	O(21)–C(21)	1.142 (7)
Ru(2)–C(22)	1.877 (6)	O(22)–C(22)	1.140 (7)
Ru(2)–C(12)	2.045 (6)	O(31)–C(31)	1.152 (7)
Ru(2)–S(1)	2.443 (1)	O(32)–C(32)	1.127 (7)
Ru(2)–S(2)	2.466 (1)	O(41)–C(41)	1.140 (7)
Ru(2)–Ru(4)	2.7807 (7)	O(42)–C(42)	1.147 (7)
Ru(3)–C(31)	1.857 (6)	C(51)–C(52)	1.385 (8)
Ru(3)–C(32)	1.887 (7)	C(51)–C(56)	1.393 (8)
Ru(3)–C(13)	2.036 (6)	C(52)–C(53)	1.382 (8)
Ru(3)–S(1)	2.441 (1)	C(53)–C(54)	1.376 (9)
Ru(3)–S(2)	2.479 (1)	C(54)–C(55)	1.36 (1)
Ru(3)–Ru(4)	2.8147 (8)	C(55)–C(56)	1.392 (9)
Ru(4)–C(42)	1.861 (6)	C(61)–C(62)	1.378 (8)
Ru(4)–C(41)	1.878 (7)	C(61)–C(66)	1.384 (8)
Ru(4)–P(2)	2.306 (2)	C(62)–C(63)	1.398 (8)
Ru(4)–S(1)	2.459 (1)	C(63)–C(64)	1.372 (9)
Ru(4)–S(2)	2.470 (1)	C(64)–C(65)	1.363 (9)
P(1)–C(1)	1.790 (6)	C(65)–C(66)	1.382 (9)

When irradiated in the presence of $Ru(CO)_5$, compound **3** was observed to add a mononuclear ruthenium carbonyl fragment to form the tetraruthenium compound $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$ (**5**) in 90% yield. Compound **5** has been characterized by IR spectroscopy, mass spectrometry, and a single-crystal X-ray diffraction analysis of its disubstituted PMe_2Ph derivative. The mass spectrum of **5** shows the parent ion at *m*/*e* 776 for ^{101}Ru plus ions corresponding to the loss of each of 10 carbonyl ligands. The IR spectrum shows six absorptions in the region 1950–2050 cm^{-1} (see Experimental Section for exact values) that can be attributed to terminally coordinated carbonyl groups, but there are also two absorptions at 1858 and 1844 cm^{-1} that are due to two bridging carbonyl ligands. Compound **5** was also obtained by the pyrolysis of $Ru_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ under a CO atmosphere (125 °C/100 atm, 15% yield) and by the pyrolysis of **1** under a CO atmosphere (125 °C/100 atm, 20% yield). Compound **5** reacted readily with PMe_2Ph (25 °C/30 min) to yield the mono- and disubstituted PMe_2Ph derivatives $Ru_4(CO)_{9-n}(\mu\text{-}CO)_2(PMe_2Ph)_n(\mu_4\text{-}S)_2$ (**6**, $n = 1$; **7**, $n = 2$). The infrared spectra of compounds **6** and **7** both show two absorptions that can be attributed to bridging carbonyl ligands, 1862 and 1821 cm^{-1} for **6** and 1848 and 1811 cm^{-1} for **7**. Compound **7** was characterized by a single-crystal X-ray diffraction analysis. Final positional parameters are listed in Table II. Selected intramolecular bond distances and angles are listed in Tables III and IV, respectively. An ORTEP drawing of the molecular structure of **7** is shown in Figure 1. The molecule consists of a cluster of four ruthenium atoms arranged approximately in the form of a square. Quadruply bridging sulfido ligands lie on opposite sides of the square. The two ruthenium–ruthenium bonds that are bridged by carbonyl ligands, Ru(1)–Ru(2) = 2.7376 (8) Å and Ru(1)–Ru(3) = 2.7330 (7) Å, are both significantly shorter than the two other ruthenium–ruthenium bonds, Ru(2)–Ru(4) = 2.7807 (7) Å and Ru(3)–Ru(4) = 2.8147 (8) Å. This compound is believed to be the first structurally characterized ruthenium compound to contain quadruply bridging sulfido ligands bonded to a square of ruthenium atoms. As expected,[19] the ruthenium–sulfur distances in **7**, 2.441–2.584 Å are significantly longer than the ruthenium–sulfur distances to triply bridging sulfido ligands, 2.35–2.40 Å.[14] The metal–sulfur distances to Ru(1), 2.584 (1) and 2.532 (1) Å, are significantly longer than

---

(18) Adams, R. D.; Horvath, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 1869.

(19) Adams, R. D.; Horvath, I. T.; Yang, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 1533.

Table IV. Intramolecular Bond Angles (deg) for $Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)_2$ (7)

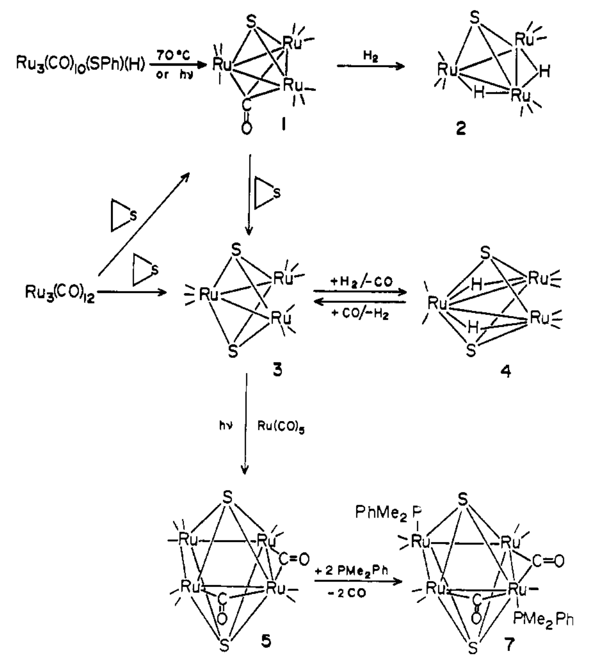
C(11)-Ru(1)-C(13)	87.2 (2)	C(22)-Ru(2)-S(2)	94.3 (2)	C(42)-Ru(4)-S(1)	127.7 (2)	C(51)-P(1)-Ru(1)	115.8 (2)
C(11)-Ru(1)-C(12)	88.8 (2)	C(22)-Ru(2)-Ru(1)	125.9 (2)	C(42)-Ru(4)-S(2)	101.6 (2)	C(3)-P(2)-C(4)	103.4 (3)
C(11)-Ru(1)-P(1)	90.1 (2)	C(22)-Ru(2)-Ru(4)	109.5 (2)	C(42)-Ru(4)-Ru(2)	157.1 (2)	C(3)-P(2)-C(61)	105.3 (3)
C(11)-Ru(1)-S(2)	175.7 (2)	C(12)-Ru(2)-S(1)	96.8 (2)	C(42)-Ru(4)-Ru(3)	81.0 (2)	C(3)-P(2)-Ru(4)	114.8 (2)
C(11)-Ru(1)-S(1)	102.6 (2)	C(12)-Ru(2)-S(2)	97.3 (2)	C(41)-Ru(4)-P(2)	91.2 (2)	C(4)-P(2)-C(61)	104.6 (3)
C(11)-Ru(1)-Ru(3)	120.4 (2)	C(12)-Ru(2)-Ru(1)	50.6 (2)	C(41)-Ru(4)-S(1)	137.3 (2)	C(4)-P(2)-Ru(4)	115.2 (2)
C(11)-Ru(1)-Ru(2)	123.6 (2)	C(12)-Ru(2)-Ru(4)	143.0 (2)	C(41)-Ru(4)-S(2)	94.8 (2)	C(61)-P(2)-Ru(4)	112.4 (2)
C(13)-Ru(1)-C(12)	175.4 (2)	S(1)-Ru(2)-S(2)	77.12 (5)	C(41)-Ru(4)-Ru(2)	85.2 (2)	O(11)-C(11)-Ru(1)	177.6 (6)
C(13)-Ru(1)-P(1)	87.1 (2)	S(1)-Ru(2)-Ru(1)	59.51 (4)	C(41)-Ru(4)-Ru(3)	147.7 (2)	O(12)-C(12)-Ru(2)	139.8 (5)
C(13)-Ru(1)-S(2)	91.2 (2)	S(1)-Ru(2)-Ru(4)	55.71 (3)	P(2)-Ru(4)-S(1)	92.18 (5)	O(12)-C(12)-Ru(1)	138.4 (5)
C(13)-Ru(1)-S(1)	92.6 (2)	S(2)-Ru(2)-Ru(1)	57.96 (3)	P(2)-Ru(4)-S(2)	168.48 (5)	Ru(2)-C(12)-Ru(1)	81.7 (2)
C(13)-Ru(1)-Ru(3)	47.7 (2)	S(2)-Ru(2)-Ru(4)	55.79 (3)	P(2)-Ru(4)-Ru(2)	115.31 (4)	O(13)-C(13)-Ru(3)	137.9 (4)
C(13)-Ru(1)-Ru(2)	136.8 (2)	Ru(1)-Ru(2)-Ru(4)	92.38 (2)	P(2)-Ru(4)-Ru(3)	120.33 (4)	O(13)-C(13)-Ru(1)	139.0 (4)
C(12)-Ru(1)-P(1)	90.7 (2)	C(31)-Ru(3)-C(32)	89.7 (3)	S(1)-Ru(4)-S(2)	76.74 (5)	Ru(3)-C(13)-Ru(1)	83.0 (2)
C(12)-Ru(1)-S(2)	93.0 (2)	C(31)-Ru(3)-C(13)	93.4 (2)	S(1)-Ru(4)-Ru(2)	55.17 (3)	O(21)-C(21)-Ru(2)	178.8 (5)
C(12)-Ru(1)-S(1)	90.4 (2)	C(31)-Ru(3)-S(1)	94.0 (2)	S(1)-Ru(4)-Ru(3)	54.64 (3)	O(22)-C(22)-Ru(2)	177.1 (5)
C(12)-Ru(1)-Ru(3)	136.7 (2)	C(31)-Ru(3)-S(2)	169.0 (2)	S(2)-Ru(4)-Ru(2)	55.64 (3)	O(31)-C(31)-Ru(3)	175.7 (6)
C(12)-Ru(1)-Ru(2)	47.7 (2)	C(31)-Ru(3)-Ru(1)	122.7 (2)	S(2)-Ru(4)-Ru(3)	55.49 (3)	O(32)-C(32)-Ru(3)	178.9 (6)
P(1)-Ru(1)-S(2)	93.87 (5)	C(31)-Ru(3)-Ru(4)	114.6 (2)	Ru(2)-Ru(4)-Ru(3)	86.67 (2)	O(41)-C(41)-Ru(4)	176.5 (7)
P(1)-Ru(1)-S(1)	167.32 (5)	C(32)-Ru(3)-C(13)	96.0 (3)	Ru(3)-S(1)-Ru(2)	103.67 (5)	O(42)-C(42)-Ru(4)	176.3 (7)
P(1)-Ru(1)-Ru(3)	117.99 (4)	C(32)-Ru(3)-S(1)	165.1 (2)	Ru(3)-S(1)-Ru(4)	70.12 (4)	C(52)-C(51)-C(56)	118.5 (5)
P(1)-Ru(1)-Ru(2)	118.71 (4)	C(32)-Ru(3)-S(2)	97.6 (2)	Ru(3)-S(1)-Ru(1)	65.83 (4)	C(52)-C(51)-P(1)	118.6 (4)
S(2)-Ru(1)-S(1)	73.47 (4)	C(32)-Ru(3)-Ru(1)	129.2 (2)	Ru(2)-S(1)-Ru(4)	69.12 (4)	C(56)-C(51)-P(1)	122.8 (4)
S(2)-Ru(1)-Ru(3)	56.03 (3)	C(32)-Ru(3)-Ru(4)	110.2 (2)	Ru(2)-S(1)-Ru(1)	65.92 (4)	C(53)-C(52)-C(51)	121.9 (6)
S(2)-Ru(1)-Ru(2)	55.64 (3)	C(13)-Ru(3)-S(1)	98.2 (2)	Ru(4)-S(1)-Ru(1)	104.29 (5)	C(54)-C(53)-C(52)	118.6 (6)
S(1)-Ru(1)-Ru(3)	54.57 (3)	C(13)-Ru(3)-S(2)	94.0 (2)	Ru(2)-S(2)-Ru(4)	68.57 (4)	C(55)-C(54)-C(53)	120.6 (6)
S(1)-Ru(1)-Ru(2)	54.57 (3)	C(13)-Ru(3)-Ru(1)	49.3 (2)	Ru(2)-S(2)-Ru(3)	101.88 (5)	C(54)-C(55)-C(56)	121.4 (6)
Ru(3)-Ru(1)-Ru(2)	89.16 (2)	C(13)-Ru(3)-Ru(4)	140.9 (2)	Ru(2)-S(2)-Ru(1)	66.41 (4)	C(55)-C(56)-C(51)	118.9 (6)
C(21)-Ru(2)-C(22)	89.9 (2)	S(1)-Ru(3)-S(2)	76.91 (5)	Ru(4)-S(2)-Ru(3)	69.31 (4)	C(62)-C(61)-C(66)	119.1 (5)
C(21)-Ru(2)-C(12)	95.9 (2)	S(1)-Ru(3)-Ru(1)	59.60 (3)	Ru(4)-S(2)-Ru(1)	105.50 (5)	C(62)-C(61)-P(2)	122.2 (4)
C(21)-Ru(2)-S(1)	95.7 (2)	S(1)-Ru(3)-Ru(4)	55.24 (3)	Ru(3)-S(2)-Ru(1)	66.09 (4)	C(66)-C(61)-P(2)	118.8 (4)
C(21)-Ru(2)-S(2)	165.7 (2)	S(2)-Ru(3)-Ru(1)	57.88 (3)	C(1)-P(1)-C(2)	103.6 (3)	C(61)-C(62)-C(63)	119.5 (6)
C(21)-Ru(2)-Ru(1)	129.0 (2)	S(2)-Ru(3)-Ru(4)	55.19 (4)	C(1)-P(1)-C(51)	105.5 (3)	C(64)-C(63)-C(62)	121.0 (6)
C(21)-Ru(2)-Ru(4)	109.9 (2)	Ru(1)-Ru(3)-Ru(4)	91.74 (2)	C(1)-P(1)-Ru(1)	115.0 (2)	C(65)-C(64)-C(63)	119.0 (6)
C(22)-Ru(2)-C(12)	96.3 (2)	C(42)-Ru(4)-C(41)	94.9 (3)	C(2)-P(1)-C(51)	102.5 (3)	C(64)-C(65)-C(66)	121.0 (6)
C(22)-Ru(2)-S(1)	165.2 (2)	C(42)-Ru(4)-P(2)	87.6 (2)	C(2)-P(1)-Ru(1)	112.9 (2)	C(65)-C(66)-C(61)	120.4 (6)

all the others, 2.441–2.479 (1) Å. This latter observation could be due to the fact that Ru(1), which is bonded to both bridging carbonyl ligands, is formally eight coordinate while the other three ruthenium atoms are only seven coordinate. Each ruthenium atom in 7 contains two terminally coordinated carbonyl ligands, except Ru(1), which has only one. Atoms Ru(1) and Ru(3) each contain a PMe_2Ph ligand. These ligands are directed to opposite sides of the Ru_4 plane. Compounds 5 and 6 are believed to be structurally similar to 7 but contain zero and one phosphine ligand, respectively.

Discussion

Pyrolysis or photolysis of $Ru(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ under a CO atmosphere leads to the formation of the new sulfidoruthenium carbonyl cluster 1. This reaction is similar to the photoinduced elimination of benzene from $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$, which yields the osmium homologue of 1.[13] Compounds 1 and 3 can also be prepared in good yield by the reaction of $Ru_3(CO)_{12}$ with ethylene sulfide. Similarly, the osmium homologues of 1 and 3 can be prepared in good yield by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with ethylene sulfide.[20] Both 1 and 3 lose CO and add hydrogen to yield the hydrides 2 and 4, respectively. Interestingly, some 2 is also formed in the reaction of 3 with hydrogen. This indicates that sulfur can be removed from the cluster, presumably as H_2S. Curiously, compound 4 could be converted back to 3 by reaction with CO. These reactions are summarized in Scheme I.

Scheme I



It was found that the metal nuclearity of compound 3 could be increased by one unit by the reaction of 3 with $Ru(CO)_5$ in the presence of UV irradiation. The tetranuclear product 5 was found to undergo facile ligand substitution by reaction with PMe_2Ph, and both the mono- and disubstituted derivatives were obtained. As indicated by IR, mass spectral, and X-ray crystallographic analyses of the disubstituted derivative 7, all three compounds are believed to contain square clusters of four metal atoms with quadruply bridging sulfido ligands on opposite sides of the cluster and two bridging carbonyl ligands on two adjacent edges. Interestingly, these clusters contain only 62 valence electrons, thus they are formally electron deficient by two electrons. These compounds are isoelectronic to the known bis(phosphinidene) clusters $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu\text{-}PPh)_2$ (8)[21] and $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)_2$ (9).[22] Both 8 and 9 contain square

---

[20] Adams, R. D.; Babin, J. E., unpublished results.

[21] Vahrenkamp, H.; Wolters, D. *J. Organomet. Chem.* **1982**, *224*, C17.

[22] Field, J. S.; Haines, R. J.; Smit, D. N. *J. Organomet. Chem.* **1982**, *224*, C49.

arrangements of the four metal atoms with quadruply bridging phosphinidene ligands on the opposite sides of the cluster, but with only one bridging carbonyl ligand. In both of these compounds the carbonyl-bridged metal–metal bond is significantly shorter than the other three metal–metal bonds. Vahrenkamp has proposed that this shortening could be due to the existence of a localized multiple bond, but more recently has acknowledged that this could also be due to the influence of the bridging carbonyl ligand. The structure of **7** seems to support the latter explanation, since compound **7** contains two carbonyl-bridged metal–metal bonds and both of these metal–metal bonds are significantly shorter than the others. It should be mentioned that even though the clusters **7**–**9** are unsaturated according to the EAN rule, they do obey the polyhedral skeletal electron pair theory and the latter does not predict localized unsaturation.[23] Nevertheless, the high reactivity of **7** may be due to its unsaturation. Vahrenkamp has shown that the iron clusters undergo facile ligand substitution via a ligand addition/elimination sequence.[24] A simple mechanism could be operative for compounds **7** and **8**, but we have not been able to isolate any ligand adducts of these.

The formation and structure of compound **7** contrasts significantly with that of known osmium chemistry.[5] For example, the reaction of $Os_3(CO)_9(\mu_3\text{-}S)_2$ with $Os(CO)_5$ yields the cluster $Os_4(CO)_{13}(\mu_3\text{-}S)_2$.[6a] This loses CO to form $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, which contains a butterfly tetrahedral cluster of osmium atoms. We have recently described a remarkable transformation of a butterfly cluster into a square,[25] but to date, the compound $Os_4(CO)_{11}(\mu_4\text{-}S)_2$ has not been prepared.

Acknowledgment. The research was supported by the National Science Foundation under Grant No. CHE-8416460. The AM-300 NMR spectrometer was purchased with funds from the National Science Foundation, Grant No. CHE-8411172.

Supplementary Material Available: Tables of anisotropic thermal parameters (U values) and hydrogen atom parameters (2 pages); tables of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

---

(23) (a) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (b) Johnson, B. F. G.; Benfield, R. E. *Top. Stereochem.* **1981**, *12*.

(24) Jaeger, T.; Aime, S.; Vahrenkamp, H. *Organometallics* **1986**, *5*, 245.

(25) Adams, R. D.; Wang, S., submitted for publication in *J. Am. Chem. Soc.*

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843, and Departamento de Quimica Inorganica,
Instituto de Ciencias de Materiales de Aragon, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Synthesis, Structure, and Reactivity of $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$, a Novel Chain Polymeric Pt–Ag Compound. Structure of $(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ and $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag_2(PPh_2Me)_2]$

Rafael Usôn,* Juan Forniês, Milagros Tomâs, Josê M. Casas, F. Albert Cotton,* and Larry R. Falvello

Received June 4, 1986

Reaction of $(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2]$ with $AgNO_3$ or $AgClO_4$ yields the novel polymeric $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I), which reacts with neutral ligands L to give either anionic binuclear complexes of the type $(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]$, L = PPh_3 (II), PEt_3 (III), $AsPh_3$ (IV), $SbPh_3$ (V), or neutral trinuclear ones of the type $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$, L = $PMePh_2$ (VI), $PEtPh_2$ (VII), PMe_2Ph (VIII). The structures of the parent compound I and one example of each of the last two types, II and VI, have been solved by single-crystal X-ray diffraction. A direct Pt–Ag bond is present in complex II but not in I or VI. Ag···Cl contacts with *o*-chlorine atoms of the C_6Cl_5 group present in complexes I and II appear to contribute to the stability of these compounds. Compound I gives monoclinic crystals, space group $C2/c$, with a = 19.300 (3) Å, b = 26.523 (4) Å, c = 8.450 (2) Å, β = 103.53 (2)°, V = 4205 (2) Å^3, and Z = 4. The crystal structure was refined to final residuals of R = 0.0610 and R_w= 0.0651. Compound II crystallizes in the monoclinic system, space group $P2_1/n$, with a = 20.076 (6) Å, b = 28.507 (5) Å, c = 9.479 (3) Å, β = 97.17 (3)°, V = 5382 (5) Å^3, and Z = 4. The structure was refined to residuals of R = 0.0433 and R_w = 0.0547. Crystals of compound VI are triclinic, space group $P\bar{1}$, with a = 10.821 (3) Å, b = 12.462 (3) Å, c = 9.268 (2) Å, α = 109.23 (2)°, β = 99.87 (2)°, γ = 70.85 (2)°, V = 1111.9 (4) Å^3, and Z = 1. The structure was refined to residuals of R = 0.0279 and R_w = 0.0423.

Introduction

Several mixed heteronuclear complexes containing silver atoms and other transition metals are known.[1-12] A few complexes containing Pt and Ag had been structurally characterized prior to 1980, and some of them showed short Pt–Ag distances. However, the existence of metal–metal bonding is not certain because the presence of bridging ligands might be responsible for the close approach of the metal atoms.[8,13-17]

Recently we have described the syntheses and structures of some clusters containing Pt–Ag bonds,[18-20] all of which were prepared by using pentafluorophenyl anionic platinum complexes, which can act as Lewis bases. One of them, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$,[18,19] was obtained by reacting $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ with $AgClO_4$ and displays the following features: quite strong Pt–Ag bonds, perhaps weak Ag–Ag bonds, and Ag···F interactions that help in the stabilization of this unusual anion. The reaction of that compound with PPh_3 gave rise to

---

* To whom correspondence should be addressed: R.U., Universidad de Zaragoza-CSIC; F.A.C., Texas A&M University.

(1) van Koten, G; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551.

(2) van Koten, G; Jastrzebski, J. T. B. H.; Noltes, J. G. *Inorg. Chem.* **1977**, *16*, 1782.

(3) Usôn, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 285.

(4) Nesmeyanov, A. N.; Perevalova, E. G.; Grandberg, K. I.; Lemonovskii, D. A.; Bankov, T. V.; Afanassova, O. B. *J. Organomet. Chem.* **1974**, *131*, 65.

(5) Hackett, P.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1606.

(6) Legzdins, P.; Nurse, C. R. *Inorg. Chem.* **1982**, *21*, 3110.

(7) Salter, I. D.; Stone, F. G. A. *J. Organomet. Chem.* **1984**, *260*, C71.

(8) Lippert, B.; Neugebauer, D. *Inorg. Chim. Acta* **1980**, *46*, 171.

(9) Heaton, B. T.; Strona, L.; Martinengo, S.; Strumolo, D.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2175.

(10) Hackett, P.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1606.

(11) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.

(12) Connelly, N. G.; Howard, J. A. K.; Spencer, J. L.; Woodly, P. *J. Chem. Soc. Dalton Trans.* **1984**, 2003.

0020-1669/86/1325-4519$01.50/0