*Organometallics* 1987, *6*, 2228–2235

# Cluster Synthesis. 16. Synthesis and Structural Characterizations of a Series of Sulfido Ruthenium Carbonyl Cluster Compounds Containing a Bridging PhC≡CH Ligand

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

*Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208*

*Received March 30, 1987*

The reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) with $HC_2Ph$ yields the new cluster $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2) in 52% yield. Compound 2 was characterized structurally: space group $P\bar{1}$, $a = 14.429$ (2) Å, $b = 16.053$ (4) Å, $c = 10.222$ (2) Å, $\alpha = 107.00$ (2)°, $\beta = 101.13$ (2)°, $\gamma = 97.16$ (2)°, $Z = 4$, $\rho_{calcd} = 2.02$ g/cm³. The structure was solved by the heavy-atom method and was refined (2641 reflections) to the final values of the residuals $R = 0.0327$ and $R_w = 0.0310$. The molecule consists of an open triangular cluster of three metal atoms with triply bridging alkyne and sulfido ligands on opposite sides of the cluster. Compound 2 reacts with $Ru(CO)_5$ at 80 °C to yield $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3; 50%) and $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4; 8%). Both compounds were characterized structurally. For 3: space group $P\bar{1}$, $a = 9.384$ (2) Å, $b = 14.542$ (4) Å, $c = 8.972$ (3) Å, $\alpha = 92.61$ (2)°, $\beta = 98.80$ (2)°, $\gamma = 98.00$ (2)°, $Z = 2$, $\rho_{calcd} = 2.35$ g/cm³. The structure was solved by the heavy-atom method and was refined (3060 reflections) to the final values of the residuals $R = 0.0224$ and $R_w = 0.0240$. The structure of 3 consists of planar cluster of four metal atoms with quadruply bridging alkyne and sulfido ligands on opposite sides of the cluster. For 4: space group $P2_1/n$,$a = 8.842$ (2) Å, $b = 20.214$ (5) Å, $c = 15.943$ (3) Å, $\beta = 92.37$ (2)°, $Z = 4$, $\rho_{calcd} = 2.41$ g/cm³. The structure was solved by direct methods and was refined (3772 reflections) to the final values of the residuals $R = 0.0206$ and $R_w = 0.0225$. The structure of 4 consists of a planar cluster analogous to that of 3 with quadruply bridging alkyne and sulfido ligands but differs from 3 due to the presence of an $Ru(CO)_4$ group on one edge of the tetraruthenium cluster. Compound 4 was also obtained by the reaction of 3 with $Ru(CO)_5$ (26% yield).

## Introduction

Recent developments[1] in the understanding of the structure and bonding of transition-metal cluster compounds may provide a basis for the development of rational syntheses.[2-5] We have recently prepared a range of new osmium carbonyl cluster compounds that contain sulfido ligands.[4] It is believed that the sulfido ligands play an important role both in stabilizing the clusters[6] and in facilitating their assembly.[4]

We have recently extended these studies to include the element ruthenium and have discovered a variety of new structural types.[7-10] These studies were made possible by use of the precursor $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) which we have recently prepared in good yield. In the continuation of our studies of cluster synthesis we have now prepared the alkyne complex $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2) by the reaction of 1 with HC≡CPh and have found that this cluster can be readily enlarged by the sequential addition of mononuclear ruthenium carbonyl fragments. The results of these studies are reported here.

## Experimental Section

**General Data.** All reactions were performed under an atmosphere of carbon monoxide. Reagent grade solvents were stored over 4-Å molecular sieves. *n*-Heptane was purified by distillation from sodium diphenyl ketyl and was stored over sodium under an atmosphere of nitrogen. $Ru_3(CO)_{12}$ was purchased from Strem Chemical Co. and was used as received. Phenylacetylene was purchased from Aldrich Chemical Co. and was vacuum distilled before use. CP grade carbon monoxide was purchased from Linde Co. and was used without further purification. $Ru(CO)_5$ was prepared by the published procedures.[11] $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) was prepared as previously reported.[7]

All chromatographic separations were performed in air. TLC separations were performed on plates (0.25 mm Kieselgel 60 $F_{254}$, E. Merck, West Germany) purchased from Bodman Chemicals, USA. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. ¹H NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

**Reaction of $Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}S)$ (1) with Phenylacetylene.** Compound 1 (20 mg, 0.032 mmol) dissolved in 20 mL of *n*-heptane was combined with 18 μL (0.164 mmol) of phenylacetylene. This solution was refluxed for 30 min under a continuous purge with carbon monoxide. The *n*-heptane was removed in vacuo; the residue was dissolved in a minimal amount of $CH_2Cl_2$ and was chromatographed by TLC on silica gel. Elution with hexane solvent yielded 11.6 mg of yellow $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2, 52%): IR (ν(CO), cm⁻¹, in hexane) 2100 (vw), 2078 (vs), 2056 (s), 2030 (s), 2014 (m), 2007 (w, sh), ¹H NMR (δ in $CDCl_3$) 8.83 (s, 1 H), 7.24–7.00 (m, 5 H).

**Reaction of $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2) with $Ru(CO)_5$.** Compound 2 (20 mg, 0.029 mmol) was dissolved in 40 mL of cyclohexane and was heated to reflux under a continuous carbon monoxide purge. An 80-mL cyclohexane solution of $Ru(CO)_5$ (0.235 mmol) was added from a dropping funnel over a period of approximately 30 min. The reaction solution was then refluxed

---

(1) (a) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (b) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251; *Inorg. Chem.* **1984**, *23*, 1257. (c) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (d) Johnson, B. F. G.; Benfield, R. E. In *Topics in Stereochemistry*; Geoffroy, G. L., Ed.; Wiley: 1981; Vol. 12.

(2) Geoffroy, G. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Chapter 40.

(3) Geoffroy, G. L. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: New York, 1986.

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

(5) Vahrenkamp, V. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *308*, 17.

(6) Vahrenkamp, V. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

(7) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514.

(8) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics*, submitted for publication.

(9) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4460.

(10) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.*, in press.

(11) Huq, R.; Poë, A. J.; Charola, S. *Inorg. Chim. Acta* **1980**, *38*, 121.

0276-7333/87/2306-2228$01.50/0

**Table I. Crystallographic Data for the Structural Analyses for Compounds 2–4**

| | 2 | 3 | 4 |
|---|---|---|---|
| | (A) Crystal Data | | |
| formula | $Ru_3SO_8C_{16}H_6$ | $Ru_4SO_{11}C_{19}H_6$ | $Ru_5SO_{14}C_{22}H_6$ |
| temp, ± 3 °C | 23 | 23 | 23 |
| space group | No. 2, $P\bar{1}$ | No. 2, $P\bar{1}$ | No. 14, $P2_1/n$ |
| $a$, Å | 14.429 (2) | 9.384 (2) | 8.842 (2) |
| $b$, Å | 16.053 (4) | 14.542 (4) | 20.214 (5) |
| $c$, Å | 10.222 (2) | 8.972 (3) | 15.943 (3) |
| $\alpha$, deg | 107.00 (2) | 92.61 (2) | 90.0 |
| $\beta$, deg | 101.13 (2) | 98.80 (2) | 92.37 (2) |
| $\gamma$, deg | 97.16 (2) | 98.00 (2) | 90.0 |
| $V$, Å$^3$ | 2179.9 (9) | 1195.4 (5) | 2847 (1) |
| $M_r$ | 663.5 | 846.5 | 1031.7 |
| $Z$ | 4 | 2 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 2.02 | 2.35 | 2.41 |
| | (B) Measurement of Intensity Data | | |
| radiatn | Mo K$\alpha$ (0.71069 Å) | Mo K$\alpha$ (0.71069 Å) | Mo K$\alpha$ (0.71069 Å) |
| monochromator | graphite | graphite | graphite |
| detector aperture, mm | | | |
| horizontal | 2.0 | 2.0 | 2.0 |
| vertical | 2.0 | 2.0 | 2.0 |
| cryst faces | $01\bar{1}$, $0\bar{1}1$, 010, $0\bar{1}0$, $\bar{1}10$, $1\bar{1}0$ | $0\bar{1}0$, 010, $\bar{2}10$, $2\bar{1}0$, 011, $0\bar{1}\bar{1}$ | $0\bar{1}\bar{1}$, 011, $0\bar{1}1$, $01\bar{1}$, $20\bar{1}$, $\bar{2}01$ |
| cryst size, mm | 0.036 × 0.260 × 0.201 | 0.028 × 0.322 × 0.233 | 0.165 × 0.138 × 0.348 |
| cryst orientatn directn, deg from $\phi$ axis | [211]; 0.61 | [210]; 0.79 | [011]; 1.24 |
| reflctns measd | $h,\pm k,\pm l$ | $+h,\pm k,\pm l$ | $+h,+k,\pm l$ |
| max 2$\theta$, deg | 40 | 48 | 48 |
| scan type | moving crystal–stationary counter | moving crystal–stationary counter | moving crystal–stationary counter |
| $\omega$-scan width:[a] (A + 0.347 tan $\theta$)°, $A$ = | 1.10 | 1.10 | 1.10 |
| background: time at each end of scan | $^1/_4$ scan time | $^1/_4$ scan time | $^1/_4$ scan time |
| $\omega$-scan rate, deg/min | 4.0 | 4.0 | 4.0 |
| no. of reflctns measd | 4406 | 4016 | 4992 |
| data used ($F^2 \geq 3.0\sigma(F^2)$) | 2641 | 3060 | 3772 |
| | (C) Treatment of Data | | |
| abs correctn | none | numerical | analytical |
| coeff, cm$^{-1}$ | 21.31 | 25.59 | 26.66 |
| grid | | 16 × 4 × 14 | |
| transmissn coeff | | | |
| max | | 0.931 | 0.728 |
| min | | 0.514 | 0.637 |
| $P$ factor | 0.02 | 0.02 | 0.02 |
| final residuals | | | |
| $R_F$ | 0.0327 | 0.0224 | 0.0206 |
| $R_{wF}$ | 0.0310 | 0.0240 | 0.0225 |
| esd of unit weight observn | 1.228 | 1.277 | 1.244 |
| largest shift/error value of final cycle | 0.006 | 0.043 | 0.097 |
| largest peak in final diff Fourier, e/Å$^3$ | 0.43 | 0.49 | 0.43 |
| no. of variables | 541 | 340 | 403 |

[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 first scan etc. A maximum of three scans was permitted per reflection.

**Table II. Positional Parameters and $B$(eq) for $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2)**

| atom | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ |
|---|---|---|---|---|
| Ru1A | −0.257991 (94) | 0.264207 (84) | −0.19885 (12) | 4.94 (5) |
| Ru1B | 0.232083 (82) | 0.230927 (78) | 0.70963 (12) | 4.22 (5) |
| Ru2A | −0.119595 (77) | 0.240258 (70) | 0.01155 (11) | 3.48 (4) |
| Ru2B | 0.165325 (78) | 0.336193 (72) | 0.55556 (12) | 3.64 (5) |
| Ru3A | −0.183080 (77) | 0.056862 (70) | −0.11841 (11) | 3.49 (4) |
| Ru3B | 0.329121 (76) | 0.332872 (68) | 0.44734 (11) | 3.31 (4) |
| S1A | −0.15789 (27) | 0.15932 (24) | −0.23722 (37) | 4.5 (2) |
| S1B | 0.24098 (24) | 0.21073 (22) | 0.47729 (36) | 3.9 (1) |
| O11A | −0.4462 (10) | 0.1494 (10) | −0.3814 (15) | 10.0 (8) |
| O11B | 0.40987 (82) | 0.17392 (81) | 0.8303 (12) | 7.9 (6) |
| O12A | −0.3370 (10) | 0.43088 (84) | −0.0772 (14) | 9.4 (7) |
| O12B | 0.17206 (94) | 0.30119 (89) | 0.9834 (13) | 9.2 (7) |
| O13A | −0.1836 (12) | 0.34656 (96) | −0.4061 (16) | 11.9 (9) |
| O13B | 0.10174 (96) | 0.04222 (87) | 0.6008 (14) | 10.7 (7) |
| O21A | −0.11691 (75) | 0.34107 (66) | 0.3137 (11) | 6.1 (5) |
| O21B | 0.11177 (76) | 0.39667 (81) | 0.3004 (12) | 7.6 (6) |
| O22A | −0.00687 (90) | 0.39919 (75) | −0.0331 (13) | 8.7 (6) |
| O22B | −0.02551 (77) | 0.20723 (75) | 0.4848 (12) | 7.4 (5) |
| O23A | 0.06156 (78) | 0.17346 (66) | 0.1042 (12) | 6.8 (5) |
| O23B | 0.09483 (98) | 0.48311 (84) | 0.7488 (15) | 9.2 (7) |
| O31A | −0.03391 (72) | −0.03646 (67) | −0.2577 (11) | 6.3 (5) |
| O31B | 0.30744 (75) | 0.21479 (72) | 0.1402 (10) | 6.6 (5) |
| O32A | −0.17844 (78) | −0.05366 (65) | 0.0762 (11) | 6.2 (5) |
| O32B | 0.38542 (84) | 0.49859 (66) | 0.3704 (12) | 7.4 (5) |
| O33A | −0.36367 (80) | −0.05589 (77) | −0.3257 (12) | 7.9 (6) |
| O33B | 0.52913 (80) | 0.30725 (73) | 0.5308 (13) | 7.3 (5) |
| C1A | −0.28251 (91) | 0.21975 (92) | −0.0403 (13) | 4.2 (6) |
| C1B | 0.29198 (87) | 0.36072 (76) | 0.7455 (13) | 3.6 (5) |
| C2A | −0.25712 (88) | 0.14359 (88) | −0.0071 (13) | 3.8 (5) |
| C2B | 0.32619 (83) | 0.39976 (83) | 0.6514 (13) | 3.2 (5) |
| C11A | −0.3757 (14) | 0.1928 (13) | −0.3226 (18) | 7 (1) |
| C11B | 0.3420 (12) | 0.19428 (94) | 0.7862 (18) | 5.6 (7) |
| C12A | −0.3089 (13) | 0.3670 (12) | −0.1217 (17) | 6.6 (8) |
| C12B | 0.1955 (11) | 0.2702 (11) | 0.8799 (18) | 5.9 (8) |
| C13A | −0.2112 (15) | 0.3154 (12) | −0.3309 (18) | 7 (1) |
| C13B | 0.1472 (12) | 0.1100 (11) | 0.6417 (16) | 5.9 (7) |
| C21A | −0.11858 (97) | 0.30400 (93) | 0.1991 (17) | 4.1 (6) |
| C21B | 0.1372 (11) | 0.3741 (10) | 0.3944 (17) | 5.4 (7) |
| C22A | −0.0531 (11) | 0.3414 (11) | −0.0189 (15) | 5.0 (7) |
| C22B | 0.0460 (12) | 0.2568 (11) | 0.5164 (17) | 6.1 (8) |
| C23A | −0.0097 (11) | 0.19478 (88) | 0.0649 (16) | 4.7 (6) |
| C23B | 0.1197 (11) | 0.4295 (11) | 0.6728 (18) | 5.5 (7) |
| C31A | −0.0890 (10) | −0.00273 (84) | −0.2039 (14) | 4.0 (6) |
| C31B | 0.31177 (99) | 0.2599 (10) | 0.2497 (16) | 5.0 (6) |
| C32A | −0.1802 (11) | −0.01339 (96) | 0.0033 (14) | 4.8 (7) |
| C32B | 0.3671 (10) | 0.43796 (96) | 0.4047 (15) | 4.8 (6) |
| C33A | −0.2952 (11) | −0.01517 (95) | −0.2520 (16) | 5.2 (7) |
| C33B | 0.4530 (12) | 0.31692 (92) | 0.4974 (17) | 5.1 (7) |
| C41A | −0.2954 (10) | 0.12351 (80) | 0.1075 (15) | 3.8 (6) |
| C41B | 0.36966 (98) | 0.49609 (86) | 0.7156 (14) | 3.4 (6) |
| C42A | −0.2407 (11) | 0.12421 (82) | 0.2330 (16) | 4.8 (6) |
| C42B | 0.33209 (88) | 0.56225 (92) | 0.6740 (12) | 3.5 (5) |
| C43A | −0.2785 (17) | 0.1031 (12) | 0.3342 (17) | 8 (1) |
| C43B | 0.3761 (12) | 0.6507 (10) | 0.7349 (16) | 4.8 (7) |
| C44A | −0.3780 (23) | 0.0828 (14) | 0.3062 (26) | 10 (1) |
| C44B | 0.4624 (11) | 0.67280 (94) | 0.8367 (17) | 4.8 (7) |
| C45A | −0.4348 (15) | 0.0831 (13) | 0.1881 (25) | 9 (1) |
| C45B | 0.49940 (96) | 0.6084 (12) | 0.8763 (15) | 5.1 (6) |
| C46A | −0.3938 (11) | 0.10338 (92) | 0.0891 (15) | 5.1 (7) |
| C46B | 0.4546 (11) | 0.52187 (92) | 0.8180 (16) | 4.3 (6) |

for an additional 30 min. while the CO purge was continued. During this time, the solution turned to dark green. The reaction solution was concentrated and chromatographed over a Florisil column by using hexane solvent. The first yellow band was $Ru_3(CO)_{12}$ (11.3 mg). A second dark green band was eluted with $CH_2Cl_2$ and was subsequently purified further by TLC. Elution with hexane/$CH_2Cl_2$ (v/v, 95/5) solvent mixture yielded 13.8 mg of $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3, 50%) as an orange band and 2.7 mg of $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4, 8%) as a green band. For 3: IR ($\nu$(CO), cm$^{-1}$; in hexane) 2095 (w), 2062 (s), 2042 (vs), 2008 (m), 1993 (w), 1858 (w); $^1H$ NMR ($\delta$ in $CDCl_3$) 7.04–7.02 (m, 3 H), 6.41–6.38 (m, 2 H), 4.33 (s, 1 H). Anal. Calcd for $Ru_4SO_{11}C_{19}H_6$: C, 26.96; H, 0.71; Found: C, 27.17; H, 0.71%. For 4: IR ($\nu$(CO), cm$^{-1}$, in hexane) 2110 (w), 2080 (vs), 2048 (s, sh), 2042 (vs), 2031 (s), 2020 (m), 2008 (w), 1992 (m), 1980 (vw), 1962 (w), 1901 (vw); $^1H$ NMR ($\delta$ in $CDCl_3$) 7.19–7.14 (m,

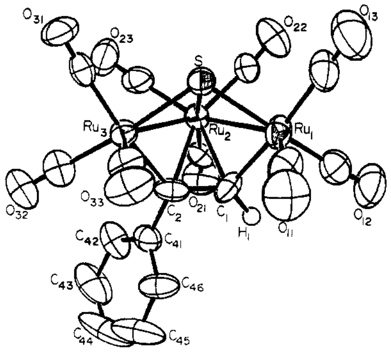


**Figure 1.** An ORTEP diagram of $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (**2**) showing 50% probability thermal ellipsoids. The hydrogen atom H(1) is shown with an artificially reduced thermal parameter, $B = 1.0$ Å$^2$.

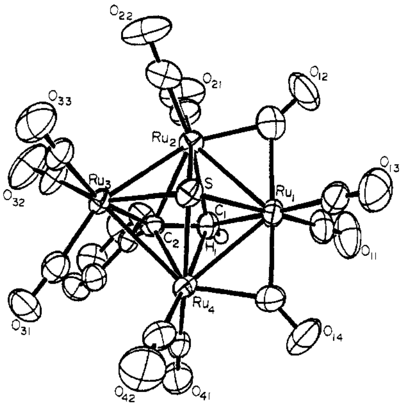


**Figure 2.** An ORTEP diagram of $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (**3**) showing 50% probability thermal ellipsoids. The hydrogen atom H(1) is shown with an artificially reduced thermal parameter, $B = 1.0$ Å$^2$.

3 H), 6.83–6.80 (m, 2 H), 5.10 (s, 1 H). Anal. Calcd for $Ru_5SO_{14}C_{22}H_6$: C, 25.61; H, 0.59; Found: C, 25.45; H, 0.64.

**Reaction of $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3) with $Ru(CO)_5$.** The reaction of 12.3 mg (0.014 mmol) of compound **3** with an 80-mL solution of $Ru(CO)_5$ (0.188 mmol) was performed as described in the previous section. The solution turned dark green. Workup as described above yielded 1.1 mg of compound **3**, 3.6 mg of compound **4** (26%), and 2.0 mg of $Ru_6(CO)_{17}(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (**5**,[12,13] 12%). IR for **5**: ($\nu$(CO) in hexane) 2115 (vw), 2091 (s), 2074 (vs), 2050 (m), 2043 (s), 2030 (vs), 2023 (s), 2009 (m), 1999 (vw), 1987, (vw), 1962 (w), 1956 (w); $^1$H NMR ($\delta$ in $CDCl_3$) 7.20–7.00 (m). The yields of compounds **4** and **5** were calculated from amount of **3** consumed.

**Crystallographic Analyses.** Crystals of **2** were grown from hexane solutions at −20 °C under a CO atmosphere. Crystals of **3** and **4** were grown by slow evaporation of solvent from $CH_2Cl_2$/hexane solutions at 5 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo K$\alpha$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the AFC6 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 II computer by using the Molecular Structure Corp. TEXSAN structure solving program library. Neutral atom scattering factors were obtained from the standard sources.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o)^2/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o)^2]^{1/2}/Lp$.

**Table III. Intramolecular Distances (Å) for $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2)**

| atom | atom | dist | atom | atom | dist |
|---|---|---|---|---|---|
| Ru1A | C11A | 1.91 (2) | Ru3A | C2A | 2.07 (1) |
| Ru1A | C12A | 1.91 (2) | Ru3A | S1A | 2.345 (4) |
| Ru1A | C13A | 1.95 (2) | Ru3B | C33B | 1.83 (2) |
| Ru1A | C1A | 2.02 (1) | Ru3B | C32B | 1.90 (2) |
| Ru1A | S1A | 2.348 (4) | Ru3B | C31B | 1.97 (2) |
| Ru1A | Ru2A | 2.789 (2) | Ru3B | C2B | 2.06 (1) |
| Ru1B | C11B | 1.87 (2) | Ru3B | S1B | 2.331 (3) |
| Ru1B | C12B | 1.87 (2) | O11A | C11A | 1.11 (2) |
| Ru1B | C13B | 2.01 (2) | O11B | C11B | 1.12 (2) |
| Ru1B | C1B | 2.05 (1) | O12A | C12A | 1.15 (2) |
| Ru1B | S1B | 2.332 (4) | O12B | C12B | 1.16 (2) |
| Ru1B | Ru2B | 2.764 (2) | O13A | C13A | 1.14 (2) |
| Ru2A | C23A | 1.88 (2) | O13B | C13B | 1.11 (2) |
| Ru2A | C21A | 1.89 (2) | O21A | C21A | 1.14 (1) |
| Ru2A | C22A | 1.92 (2) | O21B | C21B | 1.14 (2) |
| Ru2A | C1A | 2.27 (1) | O22A | C22A | 1.13 (1) |
| Ru2A | C2A | 2.30 (1) | O22B | C22B | 1.15 (2) |
| Ru2A | S1A | 2.410 (4) | O23A | C23A | 1.16 (1) |
| Ru2A | Ru3A | 2.800 (2) | O23B | C23B | 1.13 (2) |
| Ru2B | C23B | 1.90 (2) | O31A | C31A | 1.15 (1) |
| Ru2B | C22B | 1.91 (2) | O31B | C31B | 1.13 (1) |
| Ru2B | C21B | 1.91 (2) | O32A | C32A | 1.12 (1) |
| Ru2B | C1B | 2.30 (1) | O32B | C32B | 1.15 (1) |
| Ru2B | C2B | 2.31 (1) | O33A | C33A | 1.11 (1) |
| Ru2B | S1B | 2.415 (4) | O33B | C33B | 1.13 (2) |
| Ru2B | Ru3B | 2.796 (2) | C1A | C2A | 1.43 (2) |
| Ru3A | C33A | 1.89 (2) | C1B | C2B | 1.42 (2) |
| Ru3A | C32A | 1.91 (2) | C2A | C41A | 1.49 (2) |
| Ru3A | C31A | 1.95 (2) | C2B | C41B | 1.49 (2) |

Compounds **2** and **3** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed for each by the successful solution and refinement of the structures. Compound **4** crystallizes in the monoclinic crystal system. The space group $P2_1/n$ was determined from systematic absences observed in the data. The structures of **2** and **3** were solved by a combination of Patterson and difference Fourier techniques. Compound **2** crystallizes with two independent molecules in the asymmetric unit. The structure of **4** was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. Absorption corrections of a Gaussian integration type were performed for compounds **3** and **4**. All non-hydrogen atoms were refined with anisotropic thermal parameters in all structures. For **2**, the alkyne hydrogen atom position was located from a difference Fourier synthesis. Phenyl hydrogen atom positions were calculated by assuming idealized planar geometry. The contribution of hydrogen atoms were added to the structure factor calculations, but their positions were not refined. For **3** and **4**, all hydrogen atom positions were located by difference Fourier syntheses and refined with isotropic thermal parameters. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters.

## Results

The reaction of **1** with $HC_2Ph$ at 97 °C led to the formation of $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (**2**) in 52% yield by the decarbonylation of **1** and the addition of 1 equiv of $HC_2Ph$. Compound **2** was characterized by IR and $^1$H

---

(12) Compound **5** has recently been characterized by X-ray crystallographic methods. It has a structure analogous to **3** in which both bridging CO ligands were replaced with $Ru(CO)_4$ groups.

(13) Adams, R. D.; Babin, J. E.; Tasi, M.; Wolfe, T. A., report in preparation.

(14) *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.

**Table IV. Intramolecular Bond Angles (deg) for $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ (2)**

| atom | atom | atom | angle | atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C11A | Ru1A | C12A | 97.0 (8) | C2A | Ru2A | Ru1A | 75.3 (3) | C32B | Ru3B | C31B | 90.9 (6) |
| C11A | Ru1A | C13A | 98.3 (8) | C2A | Ru2A | Ru3A | 46.6 (3) | C32B | Ru3B | C2B | 94.4 (5) |
| C11A | Ru1A | C1A | 91.6 (7) | S1A | Ru2A | Ru1A | 53.1 (1) | C32B | Ru3B | S1B | 164.4 (4) |
| C11A | Ru1A | S1A | 99.1 (6) | S1A | Ru2A | Ru3A | 52.9 (1) | C32B | Ru3B | Ru2B | 112.6 (4) |
| C11A | Ru1A | Ru2A | 134.0 (6) | Ru1A | Ru2A | Ru3A | 88.01 (5) | C31B | Ru3B | C2B | 171.2 (5) |
| C12A | Ru1A | C13A | 91.5 (7) | C23B | Ru2B | C22B | 91.1 (7) | C31B | Ru3B | S1B | 87.3 (4) |
| C12A | Ru1A | C1A | 89.5 (6) | C23B | Ru2B | C21B | 94.4 (7) | C31B | Ru3B | Ru2B | 117.1 (4) |
| C12A | Ru1A | S1A | 163.4 (5) | C23B | Ru2B | C1B | 86.8 (6) | C2B | Ru3B | S1B | 85.7 (4) |
| C12A | Ru1A | Ru2A | 109.7 (5) | C23B | Ru2B | C2B | 94.9 (5) | C2B | Ru3B | Ru2B | 54.3 (3) |
| C13A | Ru1A | C1A | 169.8 (7) | C23B | Ru2B | S1B | 161.8 (5) | S1B | Ru3B | Ru2B | 55.3 (1) |
| C13A | Ru1A | S1A | 90.4 (5) | C23B | Ru2B | Ru1B | 109.1 (5) | Ru3A | S1A | Ru1A | 111.6 (1) |
| C13A | Ru1A | Ru2A | 117.0 (6) | C23B | Ru2B | Ru3B | 132.5 (4) | Ru3A | S1A | Ru2A | 72.1 (1) |
| C1A | Ru1A | S1A | 85.8 (4) | C22B | Ru2B | C21B | 97.5 (6) | Ru1A | S1A | Ru2A | 71.8 (1) |
| C1A | Ru1A | Ru2A | 53.4 (4) | C22B | Ru2B | C1B | 124.7 (5) | Ru3B | S1B | Ru1B | 113.8 (1) |
| S1A | Ru1A | Ru2A | 55.1 (1) | C22B | Ru2B | C2B | 159.0 (5) | Ru3B | S1B | Ru2B | 72.2 (1) |
| C11B | Ru1B | C12B | 95.1 (7) | C22B | Ru2B | S1B | 89.6 (5) | Ru1B | S1B | Ru2B | 71.2 (1) |
| C11B | Ru1B | C13B | 95.0 (6) | C22B | Ru2B | Ru1B | 83.0 (4) | C2A | C1A | Ru1A | 129 (1) |
| C11B | Ru1B | C1B | 98.6 (5) | C22B | Ru2B | Ru3B | 135.4 (5) | C2A | C1A | Ru2A | 73.0 (7) |
| C11B | Ru1B | S1B | 103.5 (5) | C21B | Ru2B | C1B | 137.8 (6) | Ru1A | C1A | Ru2A | 80.9 (5) |
| C11B | Ru1B | Ru2B | 144.1 (5) | C21B | Ru2B | C2B | 102.2 (5) | C2B | C1B | Ru1B | 129 (1) |
| C12B | Ru1B | C13B | 95.5 (7) | C21B | Ru2B | S1B | 103.5 (5) | C2B | C1B | Ru2B | 72.6 (7) |
| C12B | Ru1B | C1B | 87.2 (6) | C21B | Ru2B | Ru1B | 156.5 (5) | Ru1B | C1B | Ru2B | 78.8 (4) |
| C12B | Ru1B | S1B | 160.7 (5) | C21B | Ru2B | Ru3B | 73.8 (4) | C1A | C2A | C41A | 116 (1) |
| C12B | Ru1B | Ru2B | 105.5 (5) | C1B | Ru2B | C2B | 35.9 (4) | C1A | C2A | Ru3A | 124 (1) |
| C13B | Ru1B | C1B | 165.9 (5) | C1B | Ru2B | S1B | 77.9 (3) | C1A | C2A | Ru2A | 70.4 (7) |
| C13B | Ru1B | S1B | 88.2 (4) | C1B | Ru2B | Ru1B | 46.7 (3) | C41A | C2A | Ru3A | 120 (1) |
| C13B | Ru1B | Ru2B | 111.5 (4) | C1B | Ru2B | Ru3B | 74.6 (3) | C41A | C2A | Ru2A | 128.5 (9) |
| C1B | Ru1B | S1B | 84.8 (4) | C2B | Ru2B | S1B | 78.6 (3) | Ru3A | C2A | Ru2A | 79.5 (4) |
| C1B | Ru1B | Ru2B | 54.5 (3) | C2B | Ru2B | Ru1B | 76.0 (3) | C1B | C2B | C41B | 114 (1) |
| S1B | Ru1B | Ru2B | 55.8 (1) | C2B | Ru2B | Ru3B | 46.4 (3) | C1B | C2B | Ru3B | 126 (1) |
| C23A | Ru2A | C21A | 93.6 (6) | S1B | Ru2B | Ru1B | 53.01 (9) | C1B | C2B | Ru2B | 71.5 (7) |
| C23A | Ru2A | C22A | 96.3 (6) | S1B | Ru2B | Ru3B | 52.53 (9) | C41B | C2B | Ru3B | 119.9 (8) |
| C23A | Ru2A | C1A | 147.1 (5) | Ru1B | Ru2B | Ru3B | 89.30 (5) | C41B | C2B | Ru2B | 127.5 (8) |
| C23A | Ru2A | C2A | 110.5 (5) | C33A | Ru3A | C32A | 95.0 (6) | Ru3B | C2B | Ru2B | 79.3 (4) |
| C23A | Ru2A | S1A | 97.7 (4) | C33A | Ru3A | C31A | 97.6 (6) | O11A | C11A | Ru1A | 172 (2) |
| C23A | Ru2A | Ru1A | 149.8 (4) | C33A | Ru3A | C2A | 94.3 (5) | O11B | C11B | Ru1B | 178 (2) |
| C23A | Ru2A | Ru3A | 77.3 (4) | C33A | Ru3A | S1A | 96.3 (5) | O12A | C12A | Ru1A | 177 (2) |
| C21A | Ru2A | C22A | 93.5 (6) | C33A | Ru3A | Ru2A | 134.2 (5) | O12B | C12B | Ru1B | 174 (1) |
| C21A | Ru2A | C1A | 88.3 (5) | C32A | Ru3A | C31A | 90.2 (6) | O13A | C13A | Ru1A | 179 (2) |
| C21A | Ru2A | C2A | 90.8 (5) | C32A | Ru3A | C2A | 93.5 (6) | O13B | C13B | Ru1B | 178 (2) |
| C21A | Ru2A | S1A | 167.5 (4) | C32A | Ru3A | S1A | 168.7 (4) | O21A | C21A | Ru2A | 178 (1) |
| C21A | Ru2A | Ru1A | 116.3 (4) | C32A | Ru3A | Ru2A | 116.5 (4) | O21B | C21B | Ru2B | 173 (1) |
| C21A | Ru2A | Ru3A | 125.4 (4) | C31A | Ru3A | C2A | 167.2 (5) | O22A | C22A | Ru2A | 174 (1) |
| C22A | Ru2A | C1A | 116.4 (5) | C31A | Ru3A | S1A | 87.4 (4) | O22B | C22B | Ru2B | 176 (2) |
| C22A | Ru2A | C2A | 152.5 (5) | C31A | Ru3A | Ru2A | 113.6 (4) | O23A | C23A | Ru2A | 175 (1) |
| C22A | Ru2A | S1A | 90.7 (5) | C2A | Ru3A | S1A | 86.6 (4) | O23B | C23B | Ru2B | 176 (2) |
| C22A | Ru2A | Ru1A | 78.5 (4) | C2A | Ru3A | Ru2A | 53.9 (3) | O31A | C31A | Ru3A | 178 (1) |
| C22A | Ru2A | Ru3A | 140.7 (5) | S1A | Ru3A | Ru2A | 55.0 (1) | O31B | C31B | Ru3B | 174 (1) |
| C1A | Ru2A | C2A | 36.5 (4) | C33B | Ru3B | C32B | 93.7 (6) | O32A | C32A | Ru3A | 179 (1) |
| C1A | Ru2A | S1A | 79.3 (3) | C33B | Ru3B | C31B | 92.9 (7) | O32B | C32B | Ru3B | 175 (1) |
| C1A | Ru2A | Ru1A | 45.7 (3) | C33B | Ru3B | C2B | 93.7 (6) | O33A | C33A | Ru3A | 177 (1) |
| C1A | Ru2A | Ru3A | 75.0 (3) | C33B | Ru3B | S1B | 101.9 (4) | O33B | C33B | Ru3B | 179 (2) |
| C2A | Ru2A | S1A | 80.2 (3) | C33B | Ru3B | Ru2B | 138.4 (5) | | | | |

NMR spectroscopy and by a single-crystal X-ray diffraction analysis. The compound crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar. An ORTEP diagram of one of these is shown in Figure 1. Final positional parameters are listed in Table II. Intramolecular bond distances and angles are listed in Tables III and IV. The molecule consists of an open triangular cluster of three ruthenium atoms with two Ru–Ru bonds. The metal atoms are bridged by a triply bridging sulfido ligand and a triply bridging $HC_2Ph$ ligand. The $HC_2Ph$ has adopted the familiar $\mu_3$-‖ bonding mode with the unsubstituted carbon C(1) bonded to Ru(1) and Ru(2) and the phenyl-substituted carbon C(2) bonded to Ru(2) and Ru(3). In both molecules the Ru(1)–Ru(2) bond was found to be slightly shorter than the Ru(2)–Ru(3) bond, 2.789 (2) Å [2.764 (2) Å] vs. 2.800 (2) Å [2.796 (2) Å]. The value in brackets is for the second independent molecule. The Ru–S distances to the central metal atom Ru(2), 2.410 [2.415 (4)] Å, are significantly longer than those to external metal atoms, Ru(1)–S, 2.348 (4) [2.332 (4)] Å, and Ru(3)–S, 2.345 (4) [2.331 (3)] Å. A similar effect was observed in the compounds $Fe_3(CO)_9(\mu_3\text{-}S)_2$[15] and $Os_3(CO)_9(\mu_3\text{-}S)_2$.[16] This could be attributed to steric crowding as a result of the higher coordination number of the central metal atom. The C(1)–C(2) distance in the alkyne ligand at 1.43 (2) [1.42 (2)] Å is typical of that observed for triply bridging alkyne ligands.[17] The hydrogen atom on C(1) was located

---

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

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

[17] Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Radiochem.* **1985**, *29*, 169.

**Table V. Positional Parameters and $B$(eq) for $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3)**

| atom | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ |
|---|---|---|---|---|
| Ru1 | −0.077490 (41) | 0.137606 (27) | −0.227357 (45) | 3.3 |
| Ru2 | −0.352103 (40) | 0.162854 (26) | −0.190933 (40) | 2.9 |
| Ru3 | −0.412669 (37) | 0.259123 (26) | −0.448222 (38) | 2.5 |
| Ru4 | −0.103993 (39) | 0.272873 (27) | −0.426646 (43) | 3.3 |
| S | −0.27968 (12) | 0.127803 (82) | −0.43771 (13) | 2.9 |
| O11 | 0.15315 (50) | 0.17603 (31) | 0.04848 (54) | 5.8 |
| O12 | −0.23952 (53) | 0.00931 (32) | −0.01156 (51) | 10.3 |
| O13 | 0.00708 (44) | −0.04990 (29) | −0.31449 (52) | 6.5 |
| O14 | 0.17868 (42) | 0.19464 (31) | −0.39236 (58) | 9.4 |
| O21 | −0.46133 (52) | 0.21717 (33) | 0.09244 (49) | 7.4 |
| O22 | −0.63809 (46) | 0.03444 (33) | −0.27139 (48) | 5.2 |
| O31 | −0.36098 (44) | 0.38975 (30) | −0.69116 (44) | 6.0 |
| O32 | −0.62120 (45) | 0.37627 (36) | −0.33909 (60) | 7.1 |
| O33 | −0.65088 (42) | 0.12564 (31) | −0.65633 (46) | 4.4 |
| O41 | 0.09220 (43) | 0.45720 (30) | −0.38403 (52) | 5.9 |
| O42 | −0.08019 (53) | 0.26151 (37) | −0.75725 (50) | 9.7 |
| C1 | −0.15004 (50) | 0.26937 (31) | −0.18484 (51) | 2.8 |
| C2 | −0.25729 (46) | 0.31644 (30) | −0.25822 (46) | 2.7 |
| C11 | 0.06720 (60) | 0.15844 (37) | −0.05611 (66) | 4.4 |
| C12 | −0.24107 (63) | 0.06790 (39) | −0.09201 (60) | 5.0 |
| C13 | −0.02422 (54) | 0.01815 (38) | −0.27917 (62) | 4.2 |
| C14 | 0.06357 (55) | 0.20067 (37) | −0.36461 (65) | 4.8 |
| C21 | −0.41726 (58) | 0.19905 (38) | −0.01479 (61) | 4.6 |
| C22 | −0.53077 (61) | 0.08346 (40) | −0.24073 (58) | 4.5 |
| C31 | −0.37472 (53) | 0.33921 (37) | −0.60076 (57) | 3.6 |
| C32 | −0.54529 (55) | 0.33185 (41) | −0.38071 (62) | 3.9 |
| C33 | −0.56590 (54) | 0.17682 (38) | −0.58280 (55) | 3.6 |
| C41 | 0.01707 (53) | 0.38832 (41) | −0.40281 (59) | 4.7 |
| C42 | −0.08856 (57) | 0.26576 (41) | −0.63364 (66) | 5.8 |
| C51 | −0.26377 (47) | 0.41295 (32) | −0.19534 (49) | 2.7 |
| C52 | −0.25739 (56) | 0.48889 (36) | −0.28351 (61) | 4.3 |
| C53 | −0.26498 (68) | 0.57653 (40) | −0.22271 (79) | 5.4 |
| C54 | −0.28047 (82) | 0.58878 (47) | −0.07430 (86) | 5.8 |
| C55 | −0.28689 (82) | 0.51573 (46) | 0.01307 (74) | 6.6 |
| C56 | −0.27541 (74) | 0.42939 (44) | −0.04444 (66) | 5.5 |
| H1 | −0.0927 (38) | 0.3054 (26) | −0.1022 (41) | 1.1 |
| H52 | −0.2469 (50) | 0.4784 (33) | −0.4048 (55) | 4.1 |
| H53 | −0.2453 (63) | 0.6290 (44) | −0.2837 (67) | 6.5 |
| H54 | −0.2823 (66) | 0.6416 (45) | −0.0451 (70) | 6.2 |
| H55 | −0.3021 (66) | 0.5265 (45) | 0.1137 (72) | 7.2 |
| H56 | −0.2811 (55) | 0.3853 (36) | −0.0017 (58) | 3.5 |

in the structural analysis. This hydrogen shows a characteristically low-field shift, δ 8.83, in the $^1H$ NMR spectrum.[18] Compound 2 is structurally similar to the related iron compound $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}PC_6H_4OMe)$.[19]

When solutions of 2 and $Ru(CO)_5$ were heated to reflux in cyclohexane solvent, two new higher nuclearity cluster complexes $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3) and $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4) were obtained in 50% and 8% yields, respectively. Compound 4 was obtained independently from the reaction of 3 with $Ru(CO)_5$ in refluxing cyclohexane in 26% yield. Both 3 and 4 were characterized by IR and $^1H$ NMR spectroscopy and by single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of 3 is shown in Figure 2. Final positonal parameters are listed in Table V. Intramolecular bond distances and angles are listed in Tables VI and VII. The molecule consists of a cluster of four ruthenium atoms arranged approximately in the shape of a parallelogram. There are four Ru–Ru bonds. Two of these, Ru(1)–Ru(2) = 2.7188 (8) Å and Ru (1)–Ru(4) = 2.7293 (9) Å, are relatively short. One is of intermediate length, Ru(2)–Ru(3) = 2.780 (1) Å, and fourth, Ru(3)–Ru(4) = 2.8514 (8) Å, is comparatively long. On one side of the cluster is a quadruply bridging sulfido ligand. On the other side is a quadruply bridging $HC_2Ph$ ligand. This molecule is structurally very similar to the compound $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}PPh)$ (6) that was recently reported by Carty.[20] Compound 6, however, contained two long and two short Ru–Ru bonds. In both 3 and 6, the two short Ru–Ru bonds contain bridging carbonyl ligands. The cluster is distorted from the shape of a square due to the coordination of the two carbon atoms of the alkyne ligand. This distortion is shown by the bond angles Ru(2)–Ru(1)–Ru(4) = 83.78 (2)°, Ru(1)–Ru(2)–Ru(3) = 96.77 (3)°, Ru(2)–Ru(3)–Ru(4) = 80.47 (2)°, and Ru(1)–Ru(4)–Ru(3) = 94.86 (3)°. Both carbon atoms of the alkyne are each bonded to three metal atoms. The ligand could be viewed as σ-bonded to the metal atoms Ru(1) and Ru(3) and π-bonded to Ru(2) and Ru(4).[17] The C(1)–C(2) bond distance, 1.395 (6) Å, is not significantly different from that in 2. The Ru–S bond distances in 3 are significantly longer than those in 2. It appears to be a general property that metal–sulfur distances to quadruply bridging sulfido ligands are longer than the metal–sulfur distances to triply bridging sulfido ligands.[21] The osmium compound $Os_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ (7) has a structure similar to 3 but has only one bridging carbonyl ligand instead of two.[22] There is a well-known tendency of metal carbonyl complexes of the second- and third-row elements to favor structures with terminal CO ligands over those with bridging CO ligands.[23] The difference between 3 and 7 may be an example of this effect operating to a lesser degree between elements of the second and third rows.

**Table VI. Intramolecular Distances (Å) for $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3)**

| atom | atom | dist | atom | atom | dist |
|---|---|---|---|---|---|
| Ru1 | C11 | 1.871 (6) | Ru3 | Ru4 | 2.8514 (8) |
| Ru1 | C13 | 1.930 (6) | Ru4 | C41 | 1.875 (6) |
| Ru1 | C14 | 2.091 (5) | Ru4 | C42 | 1.884 (6) |
| Ru1 | C1 | 2.158 (5) | Ru4 | C14 | 2.032 (5) |
| Ru1 | C12 | 2.260 (6) | Ru4 | C1 | 2.278 (5) |
| Ru1 | S | 2.447 (1) | Ru4 | C2 | 2.363 (4) |
| Ru1 | Ru2 | 2.7188 (8) | Ru4 | S | 2.478 (1) |
| Ru1 | Ru4 | 2.7293 (9) | O11 | C11 | 1.134 (6) |
| Ru2 | C21 | 1.860 (5) | O12 | C12 | 1.142 (6) |
| Ru2 | C22 | 1.879 (6) | O13 | C13 | 1.117 (6) |
| Ru2 | C12 | 2.002 (6) | O14 | C14 | 1.159 (6) |
| Ru2 | C1 | 2.267 (5) | O21 | C21 | 1.138 (6) |
| Ru2 | C2 | 2.425 (4) | O22 | C22 | 1.138 (6) |
| Ru2 | S | 2.465 (1) | O31 | C31 | 1.129 (6) |
| Ru2 | Ru3 | 2.780 (1) | O32 | C32 | 1.119 (6) |
| Ru3 | C31 | 1.880 (6) | O33 | C33 | 1.120 (6) |
| Ru3 | C32 | 1.890 (6) | O41 | C41 | 1.132 (6) |
| Ru3 | C33 | 1.954 (5) | O42 | C42 | 1.123 (6) |
| Ru3 | C2 | 2.121 (4) | C1 | C2 | 1.395 (6) |
| Ru3 | S | 2.420 (1) | C2 | C51 | 1.501 (6) |

An ORTEP drawing of 4 is shown in Figure 3. Final positional parameters are listed in Table VIII. Intramolecular bond distances and angles are listed in Tables IX and X. Compound 4 is very similar to 3 with the excep-

---

(18) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(19) Knoll, K.; Orama, O.; Huttner, G. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 976.

(20) Lunniss, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1985**, *4*, 2066.

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

(22) Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1272.

(23) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

**Table VII. Intramolecular Bond Angles (deg) for $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (3)**

| atom | atom | atom | angle | atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C11 | Ru1 | C13 | 92.4 (2) | C1 | Ru2 | Ru1 | 50.3 (1) | C1 | Ru4 | C2 | 34.9 (1) |
| C11 | Ru1 | C14 | 92.2 (2) | C1 | Ru2 | Ru3 | 75.7 (1) | C1 | Ru4 | S | 77.6 (1) |
| C11 | Ru1 | C1 | 92.1 (2) | S | Ru2 | Ru1 | 56.07 (3) | C1 | Ru4 | Ru1 | 50.1 (1) |
| C11 | Ru1 | C12 | 91.4 (2) | S | Ru2 | Ru3 | 54.56 (3) | C1 | Ru4 | Ru3 | 74.1 (1) |
| C11 | Ru1 | S | 172.4 (2) | Ru1 | Ru2 | Ru3 | 96.77 (3) | C2 | Ru4 | S | 79.0 (1) |
| C11 | Ru1 | Ru2 | 117.4 (2) | C31 | Ru3 | C32 | 92.4 (2) | C2 | Ru4 | Ru1 | 80.2 (1) |
| C11 | Ru1 | Ru4 | 119.7 (2) | C31 | Ru3 | C33 | 93.2 (2) | C2 | Ru4 | Ru3 | 46.8 (1) |
| C13 | Ru1 | C14 | 89.9 (2) | C31 | Ru3 | C2 | 103.7 (2) | S | Ru4 | Ru1 | 55.80 (4) |
| C13 | Ru1 | C1 | 175.5 (2) | C31 | Ru3 | S | 114.5 (2) | S | Ru4 | Ru3 | 53.45 (3) |
| C13 | Ru1 | C12 | 90.0 (2) | C31 | Ru3 | Ru2 | 157.5 (1) | Ru1 | Ru4 | Ru3 | 94.86 (3) |
| C13 | Ru1 | S | 95.0 (2) | C31 | Ru3 | Ru4 | 78.0 (2) | Ru3 | S | Ru1 | 115.28 (5) |
| C13 | Ru1 | Ru2 | 123.6 (2) | C32 | Ru3 | C33 | 93.2 (2) | Ru3 | S | Ru2 | 69.35 (4) |
| C13 | Ru1 | Ru4 | 123.3 (2) | C32 | Ru3 | C2 | 88.4 (2) | Ru3 | S | Ru4 | 71.19 (4) |
| C14 | Ru1 | C1 | 89.9 (2) | C32 | Ru3 | S | 153.1 (2) | Ru1 | S | Ru2 | 67.21 (4) |
| C14 | Ru1 | C12 | 176.4 (2) | C32 | Ru3 | Ru2 | 98.8 (2) | Ru1 | S | Ru4 | 67.30 (4) |
| C14 | Ru1 | S | 89.5 (2) | C32 | Ru3 | Ru4 | 136.6 (2) | Ru2 | S | Ru4 | 94.75 (5) |
| C14 | Ru1 | Ru2 | 131.4 (1) | C33 | Ru3 | C2 | 162.9 (2) | C2 | C1 | Ru1 | 134.6 (3) |
| C14 | Ru1 | Ru4 | 47.6 (1) | C33 | Ru3 | S | 85.7 (2) | C2 | C1 | Ru2 | 79.0 (3) |
| C1 | Ru1 | C12 | 89.9 (2) | C33 | Ru3 | Ru2 | 105.5 (2) | C2 | C1 | Ru4 | 75.9 (3) |
| C1 | Ru1 | S | 80.5 (1) | C33 | Ru3 | Ru4 | 129.1 (1) | Ru1 | C1 | Ru2 | 75.8 (1) |
| C1 | Ru1 | Ru2 | 53.9 (1) | C2 | Ru3 | S | 85.2 (1) | Ru1 | C1 | Ru4 | 75.9 (1) |
| C1 | Ru1 | Ru4 | 54.0 (1) | C2 | Ru3 | Ru2 | 57.4 (1) | Ru2 | C1 | Ru4 | 106.3 (2) |
| C12 | Ru1 | S | 86.9 (1) | C2 | Ru3 | Ru4 | 54.4 (1) | C1 | C2 | C51 | 117.2 (4) |
| C12 | Ru1 | Ru2 | 46.3 (1) | S | Ru3 | Ru2 | 56.10 (3) | C1 | C2 | Ru3 | 124.1 (3) |
| C12 | Ru1 | Ru4 | 130.0 (1) | S | Ru3 | Ru4 | 55.36 (3) | C1 | C2 | Ru4 | 69.2 (2) |
| S | Ru1 | Ru2 | 56.72 (3) | Ru2 | Ru3 | Ru4 | 80.47 (2) | C51 | C2 | Ru3 | 118.6 (3) |
| S | Ru1 | Ru4 | 56.90 (4) | C41 | Ru4 | C42 | 89.4 (2) | C51 | C2 | Ru4 | 127.1 (3) |
| Ru2 | Ru1 | Ru4 | 83.78 (2) | C41 | Ru4 | C14 | 93.6 (2) | Ru3 | C2 | Ru4 | 78.8 (1) |
| C21 | Ru2 | C22 | 86.8 (2) | C41 | Ru4 | C1 | 97.2 (2) | O11 | C11 | Ru1 | 176.1 (5) |
| C21 | Ru2 | C12 | 93.8 (2) | C41 | Ru4 | C2 | 94.5 (2) | O12 | C12 | Ru2 | 147.2 (5) |
| C21 | Ru2 | C1 | 101.4 (2) | C41 | Ru4 | S | 173.5 (2) | O12 | C12 | Ru1 | 133.8 (5) |
| C21 | Ru2 | S | 173.8 (2) | C41 | Ru4 | Ru1 | 123.5 (1) | Ru2 | C12 | Ru1 | 79.0 (2) |
| C21 | Ru2 | Ru1 | 128.2 (2) | C41 | Ru4 | Ru3 | 121.8 (2) | O13 | C13 | Ru1 | 177.3 (5) |
| C21 | Ru2 | Ru3 | 119.3 (2) | C42 | Ru4 | C14 | 94.6 (2) | O14 | C14 | Ru4 | 139.4 (5) |
| C22 | Ru2 | C12 | 95.9 (2) | C42 | Ru4 | C1 | 172.7 (2) | O14 | C14 | Ru1 | 137.7 (5) |
| C22 | Ru2 | C1 | 166.9 (2) | C42 | Ru4 | C2 | 141.7 (2) | Ru4 | C14 | Ru1 | 82.9 (2) |
| C22 | Ru2 | S | 92.7 (2) | C42 | Ru4 | S | 95.7 (2) | O21 | C21 | Ru2 | 176.7 (5) |
| C22 | Ru2 | Ru1 | 131.1 (2) | C42 | Ru4 | Ru1 | 128.0 (2) | O22 | C22 | Ru2 | 179.1 (6) |
| C22 | Ru2 | Ru3 | 91.3 (2) | C42 | Ru4 | Ru3 | 99.8 (2) | O31 | C31 | Ru3 | 175.0 (5) |
| C12 | Ru2 | C1 | 93.8 (2) | C14 | Ru4 | C1 | 88.1 (2) | O32 | C32 | Ru3 | 178.4 (5) |
| C12 | Ru2 | S | 92.4 (2) | C14 | Ru4 | C2 | 123.1 (2) | O33 | C33 | Ru3 | 176.2 (5) |
| C12 | Ru2 | Ru1 | 54.7 (2) | C14 | Ru4 | S | 90.0 (2) | O41 | C41 | Ru4 | 177.8 (5) |
| C12 | Ru2 | Ru3 | 146.5 (2) | C14 | Ru4 | Ru1 | 49.5 (2) | O42 | C42 | Ru4 | 179.6 (5) |
| C1 | Ru2 | S | 78.0 (1) | C14 | Ru4 | Ru3 | 141.6 (2) | C52 | C51 | C56 | 117.3 (5) |

tion that the Ru(1)–Ru(4) bond in 4 is bridged by a Ru$(CO)_4$ group instead of a carbonyl ligand. This change produces a significant lengthening of the Ru(1)–Ru(4) bond, 2.8340 (7) Å in 4 vs. 2.7293 (9) Å in 3. The Ru(1)–Ru(2) and Ru(2)–Ru(3) bonds have both become shorter by approximately 0.03 Å. The Ru(3)–Ru(4) bond has not changed in length significantly. The Ru–Ru bonds to the bridging $Ru(CO)_4$ group, 2.7535 (8) and 2.7449 (7) Å, are not unusual.[24] There are no significant differences in the metal–ligand bonding between 3 and 4.

## Discussion

The results of this study are summarized in Scheme I. The formation and structure of compound 2 are fully explicable in terms of the conventional bonding theories.[1] An alkyne ligand serving as a four-electron donor was substituted for a CO ligand in 1, and the electron-precise open cluster 2 was formed. The polyhedral electron count (PEC) for 2 is 56 and leads to the prediction of a nido-pentagonal-bipyramidal shape for the cluster according to the polyhedral skeletal electron pair theory.[1a] Examination of the structure of 2 shows that it does, indeed, possess this shape. The sulfur atom, the two external ruthenium atoms, and the two alkyne carbon atoms define the pentagonal plane. The central ruthenium atom is one apical vertex. The other apical vertex is missing.

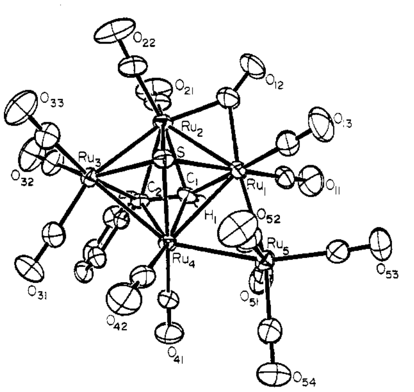
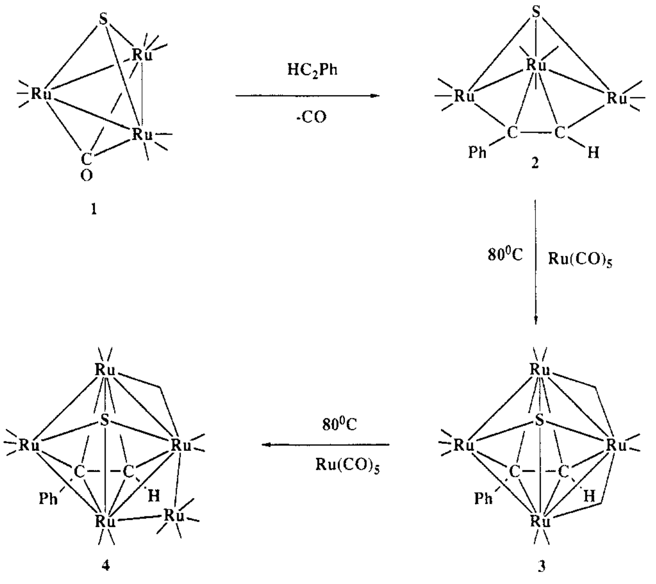


**Figure 3.** An ORTEP diagram of $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4) showing 50% probability thermal ellipsoids. The hydrogen atom H(1) is shown with an artificially reduced thermal parameter, $B = 1.0$ Å$^2$.

---

[24] Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, F., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 32.6.

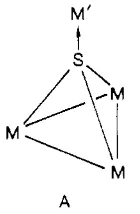
**Scheme I**



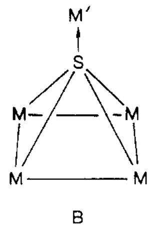
Compound 2 readily adds one metal carbonyl containing group to form 3. The cluster of 3 can be viewed as a pentagonal bipyramid formed by filling the missing vertex in 2 with a ruthenium atom. The PEC of 70 for 3 leads to the prediction of a closo-pentagonal-bipyramidal cluster.[1a] Curiously, compound 3 violates the EAN rule by being electron deficient by the amount of two electrons. This electron deficiency could, in part, be responsible for the short lengths of two of the Ru–Ru bonds, but the presence of the bridging carbonyl ligands across these bonds also appears to have an important influence.[25]

Compound 3 also adds a mononuclear ruthenium carbonyl group to form 4. This occurs by the substitution of one of the bridging carbonyl groups in 3 with a $Ru(CO)_4$ group. The electron count in the cluster is not changed by this substitution. The PEC of 84 is consistent with the observed structure but would also be consistent with that of a closo polyhedron containing eight vertices.[1a] Simple electron counting does not allow one to distinguish between the two possibilities; however, the bonding advantages of bridging $M(CO)_4$ groups have been discussed recently by Mingos.[26] As in 3 the cluster in 4 is also electron deficient by the amount of two electrons according to the EAN rule.

We have demonstrated previously the ability of transition-metal clusters to undergo enlargements by condensation and agglomerization reactions.[4] It is believed that the lone pair of electrons on the bridging sulfido ligands plays a key role in the initial attachment of the unsaturated metal fragment by the formation of an S→M coordinate bond. A number of examples of such adducts A and B



A



B

**Table VIII. Positional Parameters and *B*(eq) for $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4)**

| atom | *x* | *y* | *z* | *B*(eq), Å$^2$ |
|---|---|---|---|---|
| Ru1 | 0.410776 (37) | 0.176747 (16) | 0.328878 (21) | 2.15 (1) |
| Ru2 | 0.460959 (36) | 0.115840 (17) | 0.182226 (21) | 2.12 (1) |
| Ru3 | 0.202841 (36) | 0.039792 (16) | 0.168739 (20) | 1.95 (1) |
| Ru4 | 0.190974 (35) | 0.075520 (16) | 0.340923 (20) | 1.86 (1) |
| Ru5 | 0.224493 (40) | 0.170859 (17) | 0.462873 (21) | 2.45 (2) |
| S | 0.20774 (11) | 0.153171 (50) | 0.222343 (65) | 2.23 (4) |
| O11 | 0.67990 (41) | 0.19014 (21) | 0.45000 (24) | 5.4 (2) |
| O12 | 0.63772 (49) | 0.24292 (20) | 0.21190 (25) | 6.2 (2) |
| O13 | 0.36916 (47) | 0.32580 (17) | 0.34292 (25) | 5.3 (2) |
| O21 | 0.75367 (41) | 0.05737 (21) | 0.12844 (25) | 5.8 (2) |
| O22 | 0.40788 (50) | 0.16551 (24) | 0.00592 (24) | 6.7 (2) |
| O31 | −0.05179 (38) | −0.04946 (18) | 0.21826 (24) | 4.4 (2) |
| O32 | 0.34682 (46) | −0.06813 (21) | 0.06891 (24) | 5.8 (2) |
| O33 | 0.03273 (45) | 0.08830 (21) | 0.00918 (23) | 5.6 (2) |
| O41 | 0.18026 (44) | −0.02485 (17) | 0.47899 (22) | 4.7 (2) |
| O42 | −0.14798 (38) | 0.08443 (20) | 0.33959 (24) | 5.1 (2) |
| O51 | 0.46638 (42) | 0.07173 (18) | 0.52928 (21) | 4.4 (2) |
| O52 | −0.02585 (45) | 0.24367 (20) | 0.35993 (23) | 5.2 (2) |
| O53 | 0.33198 (52) | 0.29398 (19) | 0.55684 (24) | 5.7 (2) |
| O54 | 0.00389 (48) | 0.13468 (23) | 0.59619 (26) | 6.5 (2) |
| C1 | 0.44422 (45) | 0.07254 (20) | 0.31498 (26) | 2.1 (2) |
| C2 | 0.37243 (41) | 0.02281 (19) | 0.26559 (23) | 1.8 (2) |
| C11 | 0.57724 (52) | 0.18510 (23) | 0.40501 (30) | 3.2 (2) |
| C12 | 0.55540 (57) | 0.20016 (25) | 0.22605 (31) | 3.8 (2) |
| C13 | 0.37949 (53) | 0.26991 (24) | 0.33731 (29) | 3.2 (2) |
| C21 | 0.64386 (52) | 0.07876 (25) | 0.15061 (29) | 3.4 (2) |
| C22 | 0.42900 (53) | 0.14539 (25) | 0.07159 (31) | 3.6 (2) |
| C31 | 0.04140 (51) | −0.01382 (23) | 0.20177 (29) | 3.0 (2) |
| C32 | 0.29240 (53) | −0.02757 (25) | 0.10627 (29) | 3.4 (2) |
| C33 | 0.09228 (53) | 0.07032 (23) | 0.06866 (30) | 3.3 (2) |
| C41 | 0.18487 (48) | 0.01283 (22) | 0.42592 (28) | 2.7 (2) |
| C42 | −0.01899 (53) | 0.08164 (24) | 0.34173 (27) | 3.1 (2) |
| C51 | 0.37937 (53) | 0.10906 (23) | 0.50556 (27) | 2.9 (2) |
| C52 | 0.06979 (58) | 0.21761 (24) | 0.39508 (29) | 3.4 (2) |
| C53 | 0.29337 (59) | 0.24791 (24) | 0.52472 (29) | 3.5 (2) |
| C54 | 0.08488 (56) | 0.14760 (26) | 0.54636 (32) | 3.8 (2) |
| C61 | 0.42726 (44) | −0.04677 (19) | 0.27704 (24) | 2.0 (2) |
| C62 | 0.33215 (53) | −0.09693 (21) | 0.30125 (28) | 2.7 (2) |
| C63 | 0.38466 (61) | −0.16042 (23) | 0.31294 (31) | 3.4 (2) |
| C64 | 0.53284 (60) | −0.17555 (24) | 0.30074 (30) | 3.3 (2) |
| C65 | 0.62741 (60) | −0.12688 (26) | 0.27674 (32) | 3.6 (2) |
| C66 | 0.57800 (53) | −0.06243 (24) | 0.26606 (30) | 3.1 (2) |
| H1 | 0.5278 (41) | 0.0579 (18) | 0.3460 (22) | 1.3 (8) |
| H62 | 0.2292 (43) | −0.0886 (18) | 0.3073 (23) | 1.6 (8) |
| H63 | 0.3227 (59) | −0.1918 (27) | 0.3318 (32) | 5 (1) |
| H64 | 0.5681 (52) | −0.2184 (24) | 0.3056 (28) | 4 (1) |
| H65 | 0.7137 (41) | −0.1346 (18) | 0.2696 (22) | 1.1 (8) |
| H66 | 0.6390 (49) | −0.0290 (21) | 0.2532 (27) | 3 (1) |

**Table IX. Intramolecular Distances (Å) for $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4)**

| atom | atom | dist | atom | atom | dist |
|---|---|---|---|---|---|
| Ru1 | C11 | 1.876 (5) | Ru4 | C1 | 2.295 (4) |
| Ru1 | C13 | 1.909 (5) | Ru4 | C2 | 2.305 (4) |
| Ru1 | C1 | 2.140 (4) | Ru4 | S | 2.466 (1) |
| Ru1 | C12 | 2.173 (5) | Ru4 | Ru5 | 2.7449 (7) |
| Ru1 | S | 2.466 (1) | Ru5 | C54 | 1.911 (5) |
| Ru1 | Ru2 | 2.6954 (6) | Ru5 | C53 | 1.929 (5) |
| Ru1 | Ru5 | 2.7535 (8) | Ru5 | C52 | 1.952 (5) |
| Ru1 | Ru4 | 2.8340 (7) | Ru5 | C51 | 1.955 (5) |
| Ru2 | C21 | 1.870 (5) | O11 | C11 | 1.138 (5) |
| Ru2 | C22 | 1.873 (5) | O12 | C12 | 1.158 (5) |
| Ru2 | C12 | 2.011 (5) | O13 | C13 | 1.137 (5) |
| Ru2 | C1 | 2.301 (4) | O21 | C21 | 1.133 (5) |
| Ru2 | C2 | 2.450 (4) | O22 | C22 | 1.132 (6) |
| Ru2 | S | 2.472 (1) | O31 | C31 | 1.134 (5) |
| Ru2 | Ru3 | 2.7526 (8) | O32 | C32 | 1.132 (5) |
| Ru3 | C32 | 1.881 (5) | O33 | C33 | 1.126 (5) |
| Ru3 | C31 | 1.884 (5) | O41 | C41 | 1.141 (5) |
| Ru3 | C33 | 1.937 (5) | O42 | C42 | 1.141 (5) |
| Ru3 | C2 | 2.135 (4) | O51 | C51 | 1.132 (5) |
| Ru3 | S | 2.446 (1) | O52 | C52 | 1.126 (6) |
| Ru3 | Ru4 | 2.8447 (7) | O53 | C53 | 1.110 (5) |
| Ru4 | C41 | 1.858 (5) | O54 | C54 | 1.122 (6) |
| Ru4 | C42 | 1.861 (5) | C1 | C2 | 1.411 (6) |

---

(25) (a) Vahrenkamp, H.; Wolters, D. *J. Organomet. Chem.* **1982**, *224*, C17. (b) Jaeger, T.; Aime, S.; Vahrenkamp, H. *Organometallics* **1986**, *5*, 245.

(26) Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435.

**Table X. Intramolecular Bond Angles (deg) for $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ (4)**

| atom | atom | atom | angle | atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C11 | Ru1 | C13 | 88.7 (2) | C32 | Ru3 | C31 | 94.1 (2) | C54 | Ru5 | C53 | 92.4 (2) |
| C11 | Ru1 | C1 | 92.7 (2) | C32 | Ru3 | C33 | 90.2 (2) | C54 | Ru5 | C52 | 92.7 (2) |
| C11 | Ru1 | C12 | 89.9 (2) | C32 | Ru3 | C2 | 88.2 (2) | C54 | Ru5 | C51 | 93.6 (2) |
| C11 | Ru1 | S | 172.8 (1) | C32 | Ru3 | S | 149.5 (2) | C54 | Ru5 | Ru4 | 105.5 (1) |
| C11 | Ru1 | Ru2 | 116.7 (1) | C32 | Ru3 | Ru2 | 94.6 (2) | C54 | Ru5 | Ru1 | 167.2 (1) |
| C11 | Ru1 | Ru5 | 88.9 (1) | C32 | Ru3 | Ru4 | 136.7 (1) | C53 | Ru5 | C52 | 95.2 (2) |
| C11 | Ru1 | Ru4 | 122.9 (1) | C31 | Ru3 | C33 | 92.9 (2) | C53 | Ru5 | C51 | 97.8 (2) |
| C13 | Ru1 | C1 | 178.1 (2) | C31 | Ru3 | C2 | 102.9 (2) | C53 | Ru5 | Ru4 | 162.1 (1) |
| C13 | Ru1 | C12 | 86.0 (2) | C31 | Ru3 | S | 116.4 (1) | C53 | Ru5 | Ru1 | 100.1 (1) |
| C13 | Ru1 | S | 97.8 (1) | C31 | Ru3 | Ru2 | 159.1 (1) | C52 | Ru5 | C51 | 165.2 (2) |
| C13 | Ru1 | Ru2 | 122.8 (1) | C31 | Ru3 | Ru4 | 79.5 (1) | C52 | Ru5 | Ru4 | 84.0 (1) |
| C13 | Ru1 | Ru5 | 84.0 (1) | C33 | Ru3 | C2 | 164.2 (2) | C52 | Ru5 | Ru1 | 88.7 (1) |
| C13 | Ru1 | Ru4 | 127.3 (1) | C33 | Ru3 | S | 89.4 (1) | C51 | Ru5 | Ru4 | 81.5 (1) |
| C1 | Ru1 | C12 | 92.8 (2) | C33 | Ru3 | Ru2 | 106.0 (1) | C51 | Ru5 | Ru1 | 82.2 (1) |
| C1 | Ru1 | S | 80.7 (1) | C33 | Ru3 | Ru4 | 132.6 (1) | Ru4 | Ru5 | Ru1 | 62.05 (2) |
| C1 | Ru1 | Ru2 | 55.4 (1) | C2 | Ru3 | S | 84.0 (1) | Ru3 | S | Ru1 | 115.06 (4) |
| C1 | Ru1 | Ru5 | 97.3 (1) | C2 | Ru3 | Ru2 | 58.5 (1) | Ru3 | S | Ru4 | 70.78 (3) |
| C1 | Ru1 | Ru4 | 52.7 (1) | C2 | Ru3 | Ru4 | 52.8 (1) | Ru3 | S | Ru2 | 68.08 (3) |
| C12 | Ru1 | S | 87.5 (1) | S | Ru3 | Ru2 | 56.41 (3) | Ru1 | S | Ru4 | 70.13 (3) |
| C12 | Ru1 | Ru2 | 47.3 (1) | S | Ru3 | Ru4 | 54.95 (3) | Ru1 | S | Ru2 | 66.17 (3) |
| C12 | Ru1 | Ru5 | 169.9 (1) | Ru2 | Ru3 | Ru4 | 81.16 (2) | Ru4 | S | Ru2 | 95.04 (4) |
| C12 | Ru1 | Ru4 | 129.4 (1) | C41 | Ru4 | C42 | 88.9 (2) | C2 | C1 | Ru1 | 134.3 (3) |
| S | Ru1 | Ru2 | 57.01 (3) | C41 | Ru4 | C1 | 99.9 (2) | C2 | C1 | Ru4 | 72.5 (2) |
| S | Ru1 | Ru5 | 94.83 (3) | C41 | Ru4 | C2 | 96.1 (2) | C2 | C1 | Ru2 | 78.6 (2) |
| S | Ru1 | Ru4 | 54.94 (3) | C41 | Ru4 | S | 176.1 (1) | Ru1 | C1 | Ru4 | 79.4 (1) |
| Ru2 | Ru1 | Ru5 | 141.12 (2) | C41 | Ru4 | Ru5 | 88.2 (1) | Ru1 | C1 | Ru2 | 74.6 (1) |
| Ru2 | Ru1 | Ru4 | 82.35 (2) | C41 | Ru4 | Ru1 | 125.6 (1) | Ru4 | C1 | Ru2 | 104.8 (2) |
| Ru5 | Ru1 | Ru4 | 58.83 (2) | C41 | Ru4 | Ru3 | 122.3 (1) | C1 | C2 | C61 | 117.7 (3) |
| C21 | Ru2 | C22 | 88.4 (2) | C42 | Ru4 | C1 | 169.8 (2) | C1 | C2 | Ru3 | 125.1 (3) |
| C21 | Ru2 | C12 | 94.7 (2) | C42 | Ru4 | C2 | 138.6 (2) | C1 | C2 | Ru4 | 71.7 (2) |
| C21 | Ru2 | C1 | 100.6 (2) | C42 | Ru4 | S | 93.1 (1) | C61 | C2 | Ru3 | 117.0 (3) |
| C21 | Ru2 | S | 174.0 (2) | C42 | Ru4 | Ru5 | 91.5 (1) | C61 | C2 | Ru4 | 126.9 (3) |
| C21 | Ru2 | Ru1 | 126.3 (2) | C42 | Ru4 | Ru1 | 129.8 (1) | Ru3 | C2 | Ru4 | 79.6 (1) |
| C21 | Ru2 | Ru3 | 118.6 (2) | C42 | Ru4 | Ru3 | 95.7 (1) | O11 | C11 | Ru1 | 178.8 (4) |
| C22 | Ru2 | C12 | 95.8 (2) | C1 | Ru4 | C2 | 35.7 (1) | O12 | C12 | Ru2 | 145.1 (4) |
| C22 | Ru2 | C1 | 167.1 (2) | C1 | Ru4 | S | 77.8 (1) | O12 | C12 | Ru1 | 134.7 (4) |
| C22 | Ru2 | S | 92.5 (1) | C1 | Ru4 | Ru5 | 93.9 (1) | Ru2 | C12 | Ru1 | 80.1 (2) |
| C22 | Ru2 | Ru1 | 130.4 (2) | C1 | Ru4 | Ru1 | 47.9 (1) | O13 | C13 | Ru1 | 176.3 (5) |
| C22 | Ru2 | Ru3 | 90.7 (2) | C1 | Ru4 | Ru3 | 75.2 (1) | O21 | C21 | Ru2 | 177.3 (4) |
| C12 | Ru2 | C1 | 92.5 (2) | C2 | Ru4 | S | 80.2 (1) | O22 | C22 | Ru2 | 177.4 (5) |
| C12 | Ru2 | S | 91.1 (1) | C2 | Ru4 | Ru5 | 129.5 (1) | O31 | C31 | Ru3 | 175.2 (4) |
| C12 | Ru2 | Ru1 | 52.6 (1) | C2 | Ru4 | Ru1 | 78.7 (1) | O32 | C32 | Ru3 | 179.7 (4) |
| C12 | Ru2 | Ru3 | 146.3 (1) | C2 | Ru4 | Ru3 | 47.6 (1) | O33 | C33 | Ru3 | 177.6 (5) |
| C1 | Ru2 | S | 77.6 (1) | S | Ru4 | Ru5 | 95.05 (3) | O41 | C41 | Ru4 | 178.8 (4) |
| C1 | Ru2 | Ru1 | 50.0 (1) | S | Ru4 | Ru1 | 54.93 (3) | O42 | C42 | Ru4 | 177.7 (4) |
| C1 | Ru2 | Ru3 | 77.0 (1) | S | Ru4 | Ru3 | 54.27 (3) | O51 | C51 | Ru5 | 177.9 (4) |
| S | Ru2 | Ru1 | 56.82 (3) | Ru5 | Ru4 | Ru1 | 59.12 (2) | O52 | C52 | Ru5 | 175.5 (4) |
| S | Ru2 | Ru3 | 55.51 (3) | Ru5 | Ru4 | Ru3 | 148.71 (2) | O53 | C53 | Ru5 | 176.6 (4) |
| Ru1 | Ru2 | Ru3 | 99.04 (2) | Ru1 | Ru4 | Ru3 | 93.73 (2) | O54 | C54 | Ru5 | 178.9 (5) |

have been isolated and structurally characterized.[27] Ligand eliminations from such adducts could pave the way for metal–metal bond formation and enlargement of the clusters. If ligand loss is facile, the adducts will not be observed. It is believed that a mechanism such as this is operative in the formation of the compounds **3** and **4**. By combining such synthetic methodologies with an understanding of bonding that allows the prediction of structure, it is expected that the synthesis of cluster compounds will eventually change from that of an art to that of a true science.

**Acknowledgment.** The research was supported by the National Science Foundation under Grant No. CHE-8612862. The AM-300 NMR spectrometer was purchased with funds from the National Science Foundation, Grant No. CHE-8411172.

**Registry No.** **1**, 105121-22-0; **2**, 110078-05-2; **3**, 110078-06-3; **4**, 110078-07-4; **5**, 110078-08-5; $Ru(CO)_5$, 16406-48-7; $Ru_3(CO)_{12}$, 15243-33-1; phenylacetylene, 536-74-3.

**Supplementary Material Available:** Tables of hydrogen atom parameters for **2** and intramolecular distances and angles for the phenyl rings in **2–4**, and anisotropic thermal parameters (*U* values) for **2–4** (10 pages); listings of structure factor amplitudes for **2–4** (64 pages). Ordering information is given on any current masthead page.

---

[27] (a) Adams, R. D.; Horvath, I. T.; Wang, S. *Inorg. Chem.* **1985**, *24*, 1728. (b) Winter, A.; Jibril, I.; Huttner, G. *J. Organomet. Chem.* **1983**, *242*, 259. (c) Adams, R. D.; Babin, J. E.; Natarajan K. *J. Am. Chem. Soc.* **1986**, *108*, 3518.