of information[13,30] that shows that molybdenum is a borderline case in group VIb between chromium, which follows a D mechanism, and tungsten, which reacts associatively.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the Volkswagen-Stiftung.

Registry No. $Cr(phen)(CO)_4$, 14168-63-9; $Mo(phen)(CO)_4$, 15740-78-0; $P(OMe)_3$, 121-45-9.

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Cluster Synthesis. 26. Condensation of $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ to $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)_2(\mu_4\text{-}S)_2$ and $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$

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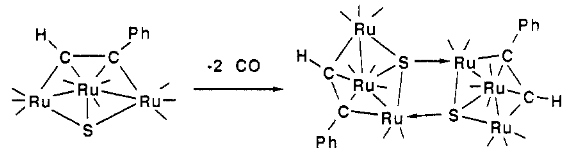
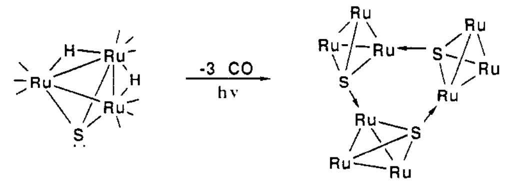
$Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **1**, undergoes a sequence of decarbonylations that leads to the coupling and fusing of two triruthenium groups. The hexaruthenium compounds $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$, **2**, and $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$, **3**, were obtained by decarbonylation at 97 °C. Compound **2** was converted to **3** independently by decarbonylation at 97 °C. **2** and **3** were both characterized crystallographically. Compound **2** consists of a doubly spiked electron-rich butterfly tetrahedral cluster of metal atoms held together by sulfido ligands with inverted tetrahedral geometries, two bridging ynamine ligands, and one normal and two weak ruthenium–ruthenium bonds. Compound **3** consists of a monocapped pentagonal bipyramidal cluster for six ruthenium atoms and two sulfido ligands. It contains one-edge bridging and one triply bridging ynamine ligand. Crystal data for **2**: space group $P2_1/c$, $a = 14.912$ (5) Å, $b = 11.207$ (3) Å, $c = 24.046$ (4) Å, $\beta = 103.75$ (2)°, $V = 3903$ (2) Å^3, $Z = 4$, $R = 0.040$, and $R_w = 0.046$ for 3060 reflections. For **3**: space group $P2_1/n$, $a = 9.564$ (2) Å, $b = 31.383$ (5) Å, $c = 11.527$ (2) Å, $\beta = 103.80$ (1)°, $V = 3360$ (2) Å^3, $Z = 4$, $R = 0.027$, and $R_w = 0.028$ for 2280 reflections.

Introduction

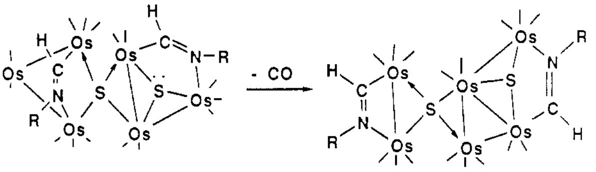
The ability of sulfido ligands to promote the synthesis of metal carbonyl cluster complexes by facilitating the agglomerization of metal-containing groups has been amply demonstrated.[1-6] In recent studies, we have shown that sulfido ligands can assist in the agglomerization of clusters through formation of donor/acceptor bonds, S → M, from the sulfido ligand on one cluster to a metal atom of another cluster, eqs 1[3] and 2[4]. Vacant sites on the metal are usually formed by thermal decarbonylation processes. In this first step, the agglomerization may occur without the formation of metal–metal bonds between the clusters. In certain cases, we have observed cluster growth by the transfer of a metal atom from one cluster to the other, e.g., eq 3.[5,6]

2


(1)

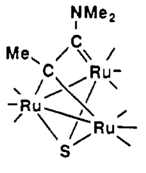
3


(2)



(3)

In our recent studies of the chemistry of ynamine ligands in metal carbonyl cluster complexes, we have prepared the complex $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **1**.[7]



1

We have now observed that **1** undergoes a facile thermal elimination of CO accompanied by the condensation of two triruthenium cluster groupings. A sequence of two hexaruthenium cluster complexes, $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)_2(\mu_4\text{-}S)_2$, **2**, and $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$, **3**, are formed in which the fusing of the clusters by metal–metal bond formation is a central

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[6] Adams, R. D.; Wang, J. G. *Polyhedron* **1989**, *11*, 1437.

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Table I. Crystal Data for the Structural Analyses

	2	3
emp formula	$Ru_6S_2O_{14}C_{24}N_2H_{18}\cdot 0.5CH_2Cl_2$	$Ru_6S_2O_{13}C_{23}N_2H_{18}$
formula wt	1271.40	1200.94
cryst syst	monoclinic	monoclinic
lattice ps		
a, Å	14.912 (5)	9.564 (2)
b, Å	11.207 (3)	31.384 (5)
c, Å	24.046 (4)	11.527 (2)
β, deg	103.75 (2)	103.80 (1)
V, Å^3	3903 (2)	3360 (2)
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	4
D_{calc}, g/cm^3	2.18	2.37
F_{000}	2420	2280
μ(Mo Kα), cm^{-1}	24.75	27.61
abs corr	empirical	empirical
temp, °C	23	23
$2\theta_{max}$, deg	44.0	45.0
no obsns ($I > 3\sigma(I)$)	3060	3198
no. variables	445	415
residuals: R, R_w	0.040, 0.046	0.027, 0.028
goodness of fit indicator	1.73	1.22
max shift in final cycle	0.42	0.02
largest peak in final diff map, e$^-$/A^3	1.46	1.46

feature. These results are described herein.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored over 4-Å molecular sieves. All chromatographic separations were performed in air on TLC plates (0.25-mm Kiesegel 60 F_{254}, E. Merck, West Germany). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were taken at 300 MHz on a Brüker AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, 1, was prepared by the previously reported precedure.[7]

Thermal Decarbonylation of 1. 1 (10.0 mg, 0.015 mmol) was dissolved in 30 mL of heptane. The solution was heated to reflux for 15 min under a continuous purge with nitrogen. The color of the reaction solution changed from orange to green. The solvent was evaporated to dryness in vacuo, and the residue was chromatographed by TLC with a hexane/CH_2Cl_2, 3/2, solvent mixture. This yielded two bands in order of elution: brown **3**, 2.0 mg (22%) and green **2**, 6.8 mg (74%). The yields of **2** and **3** are related to reaction period since **2** will undergo further decarbonylation to yield **3** (see below).

IR (in hexane solution) for **2** 2069 (vs), 2017 (s), 2005 (m), 1997 (vs), 1987 (sh); for **3** 2066 (m), 2037 (vs), 2026 (s), 2016 (vs), 2006 (m), 1992 (w), 1986 (m), 1963 (m), 1849 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) for **2** δ 3.20 (s, 6 H NMe), 3.11 (s, 6 H NMe), 2.04 (s, 6 H CMe); for **3** δ 4.19 (s, 3 H NMe), 4.08 (s, 3 H NMe), 2.64 (s, 3 H CMe), 2.45 (s, 6 H NMe_2), 2.26 (s, 3 H, CMe). Elemental analyses: calcd (found) for **2**·$0.5CH_2Cl_2$: C, 23.14 (22.67); H, 1.51 (1.28); N, 2.05 (2.20); for **3**: C, 23.00 (23.10); H, 1.51 (1.38); N, 2.33 (2.33).

Transformation of 2 into 3. **2** (15.5 mg) was dissolved in 40 mL of heptane. The solution was heated to reflux for 40 min under a continuous purge of nitrogen. The color of solution changed from green to brown. The reaction mixture was separated as described above to give 2.7 mg of **3** (18%) and 3.8 mg of starting material **2**.

Crystallographic Analyses. Crystals of **2** and **3** suitable for X-ray diffraction analyses were obtained from solutions in CH_2Cl_2/heptane, 1/1, solvent mixtures by cooling to −20 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cells were determined from 15 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 intensity measurements were made by using the standard ω-scan (moving crystal–stationary counter) technique. Background measurements were made by one-quarter additional scan at each end of the scan. All data processing was performed on a Digital Equipment Corp. Microvax II computer by using the TEXSAN structure-solving program library (version 2.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

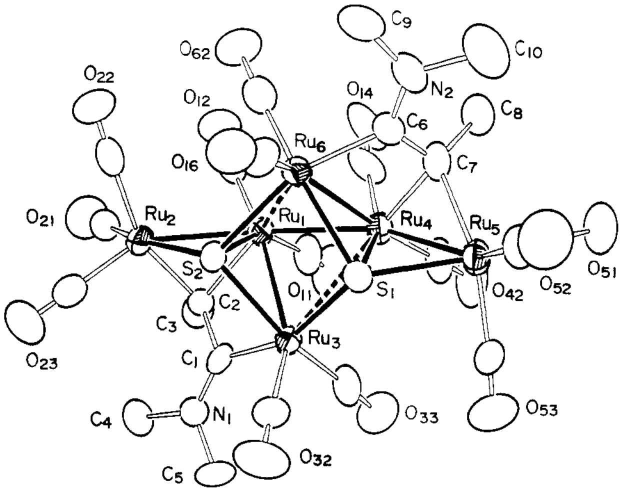

Figure 1. ORTEP drawing of $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)_2(\mu_4\text{-}S)_2$, **2**, showing 50% probability thermal ellipsoids.

The space groups $P2_1/c$ and $P2_1/n$ were identified uniquely for **2** and **3**, respectively, on the basis of the systematic absences observed during the collection of data. Both of the structures were solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined by using anisotropic thermal parameters. The hydrogen atom positions were calculated by assuming idealized geometries and employing observed positions whenever possible. The contribution of these hydrogen atoms was added to the structure factor calculations, but their positions were not refined. In the final stages of refinement of **2**, a molecule of CH_2Cl_2 solvent of crystallization was found in the lattice. This was included in the final refinements and was satisfactorily refined with an occupancy of 0.5. Error analyses for the structures were calculated from the inverse matrix obtained on the final cycle of refinement.

Results and Discussion

Compounds **2** and **3** were both formed when compound **1** was decarbonylated in refluxing heptane solutions. If the reaction period was short (~15 min), **2** was the major product (74% yield). With longer reaction periods, **3** became the major product. This is due to the thermal decarbonylation of **2** and transformation to **3**. This was proven by an independent experiment. Compounds **2** and **3** were characterized by IR and ^{1}H NMR spectroscopy and by single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The molecule contains six ruthenium atoms. The central group of four metal atoms, Ru(1), Ru(3), Ru(4), and Ru(6), could be viewed as a butterfly tetrahedron. Two of the oppositely positioned hinge-to-wingtip metal–metal bonds, Ru(1)–Ru(6) and Ru(3)–Ru(4), are significantly longer than the others, 3.106 (2) and 3.093 (2) Å vs 2.745 (2)–2.786 (2) Å.

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

Table II. Positional Parameters and *B*(eq) for 2

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru(1)	0.76847 (9)	0.21002 (12)	0.59768 (5)	2.90 (6)
Ru(2)	0.71016 (10)	0.01634 (12)	0.53383 (5)	3.38 (6)
Ru(3)	0.76102 (9)	0.09599 (11)	0.69888 (5)	2.67 (5)
Ru(4)	0.74551 (9)	0.36892 (11)	0.68007 (5)	2.96 (6)
Ru(5)	0.67533 (10)	0.42114 (12)	0.76958 (5)	3.40 (6)
Ru(6)	0.57691 (9)	0.28353 (11)	0.61618 (5)	2.81 (6)
Cl(1)	0.0444 (16)	0.188 (2)	0.0043 (10)	18.3 (8)
Cl(2)	0.1271 (14)	0.0374 (20)	0.0937 (9)	16.0 (7)
S(1)	0.6427 (3)	0.2407 (3)	0.71449 (16)	3.0 (2)
S(2)	0.6460 (3)	0.0846 (4)	0.61063 (15)	2.9 (2)
O(11)	0.9620 (10)	0.3018 (14)	0.6450 (6)	7.6 (8)
O(12)	0.7632 (11)	0.3083 (13)	0.4793 (5)	7.4 (8)
O(21)	0.8207 (11)	−0.0177 (14)	0.4436 (6)	7.5 (9)
O(22)	0.5390 (10)	0.1042 (13)	0.4421 (6)	6.9 (8)
O(23)	0.6588 (10)	−0.2471 (12)	0.5335 (6)	6.8 (8)
O(32)	0.6910 (9)	−0.0897 (12)	0.7692 (6)	6.3 (7)
O(33)	0.9316 (10)	0.1543 (12)	0.7903 (6)	7.1 (8)
O(41)	0.7754 (11)	0.5232 (11)	0.5861 (7)	7.9 (9)
O(42)	0.9116 (10)	0.4793 (13)	0.7597 (6)	7.3 (8)
O(51)	0.7583 (11)	0.6545 (12)	0.8195 (6)	6.8 (8)
O(52)	0.4988 (10)	0.4415 (14)	0.8125 (6)	6.9 (8)
O(53)	0.7959 (12)	0.2756 (14)	0.8685 (6)	8 (1)
O(61)	0.3907 (9)	0.1729 (11)	0.6080 (5)	5.2 (6)
O(62)	0.5403 (9)	0.3699 (12)	0.4932 (5)	5.7 (7)
N(1)	0.8709 (9)	−0.1159 (11)	0.6727 (5)	3.3 (6)
N(2)	0.4758 (10)	0.5044 (11)	0.6385 (6)	3.8 (7)
C(1)	0.8324 (10)	−0.0126 (14)	0.6567 (6)	3.0 (7)
C(2)	0.8324 (11)	0.0359 (13)	0.5990 (6)	3.3 (7)
C(3)	0.9294 (11)	0.0318 (16)	0.5852 (7)	4.2 (8)
C(4)	0.8964 (12)	−0.2056 (15)	0.6347 (7)	5.0 (9)
C(5)	0.8888 (11)	−0.1624 (15)	0.7305 (7)	4.3 (8)
C(6)	0.5554 (11)	0.4443 (14)	0.6474 (6)	3.1 (7)
C(7)	0.6392 (12)	0.4948 (14)	0.6851 (6)	3.6 (8)
C(8)	0.6606 (12)	0.6268 (14)	0.6745 (7)	4.2 (8)
C(9)	0.3920 (12)	0.4719 (16)	0.5974 (8)	4.6 (9)
C(10)	0.4601 (12)	0.6074 (17)	0.6727 (8)	6 (1)
C(11)	0.8851 (15)	0.2735 (17)	0.6279 (8)	5 (1)
C(12)	0.7635 (12)	0.2646 (15)	0.5230 (8)	4.4 (9)
C(21)	0.7787 (15)	−0.0049 (16)	0.4768 (8)	5 (1)
C(22)	0.5990 (14)	0.0701 (15)	0.4753 (8)	4 (1)
C(23)	0.6791 (13)	−0.1483 (18)	0.5339 (7)	4 (1)
C(32)	0.7210 (11)	−0.0207 (15)	0.7418 (7)	3.5 (8)
C(33)	0.8659 (13)	0.1356 (15)	0.7564 (8)	4.3 (9)
C(41)	0.7645 (15)	0.4543 (16)	0.6200 (8)	6 (1)
C(42)	0.8469 (14)	0.4384 (17)	0.7307 (8)	5 (1)
C(51)	0.7267 (13)	0.5678 (16)	0.8003 (7)	4.0 (8)
C(52)	0.5648 (14)	0.4365 (16)	0.7976 (7)	5 (1)
C(53)	0.7517 (14)	0.3302 (16)	0.8342 (7)	5 (1)
C(61)	0.4623 (13)	0.2213 (16)	0.6109 (7)	4.1 (8)
C(62)	0.5542 (11)	0.3357 (15)	0.5401 (7)	3.7 (8)
C(100)	0.155 (2)	0.165 (3)	0.0334 (14)	4.7 (8)

Table III. Intramolecular Distances for 2[a]

Ru(1)–C(11)	1.86 (2)	Ru(5)–C(51)	1.89 (2)
Ru(1)–C(12)	1.88 (2)	Ru(5)–C(52)	1.93 (2)
Ru(1)–C(2)	2.17 (1)	Ru(5)–C(53)	1.98 (2)
Ru(1)–S(2)	2.384 (4)	Ru(5)–C(7)	2.14 (2)
Ru(1)–Ru(2)	2.682 (2)	Ru(5)–S(1)	2.403 (4)
Ru(1)–Ru(4)	2.745 (2)	Ru(6)–C(61)	1.82 (2)
Ru(1)–Ru(3)	2.774 (2)	Ru(6)–C(62)	1.87 (2)
Ru(2)–C(23)	1.90 (2)	Ru(6)–C(6)	2.01 (2)
Ru(2)–C(21)	1.91 (2)	Ru(6)–S(1)	2.383 (4)
Ru(2)–C(22)	2.00 (2)	Ru(6)–S(2)	2.473 (4)
Ru(2)–C(2)	2.11 (2)	N(1)–C(1)	1.31 (2)
Ru(2)–S(2)	2.398 (4)	N(1)–C(5)	1.45 (2)
Ru(3)–C(32)	1.85 (2)	N(1)–C(4)	1.47 (2)
Ru(3)–C(33)	1.88 (2)	N(2)–C(6)	1.34 (2)
Ru(3)–C(1)	2.04 (2)	N(2)–C(9)	1.44 (2)
Ru(3)–S(2)	2.394 (4)	N(2)–C(10)	1.47 (2)
Ru(3)–S(1)	2.490 (4)	C(1)–C(2)	1.49 (2)
Ru(4)–C(41)	1.81 (2)	C(2)–C(3)	1.56 (2)
Ru(4)–C(42)	1.87 (2)	C(6)–C(7)	1.47 (2)
Ru(4)–C(7)	2.15 (2)	C(7)–C(8)	1.55 (2)
Ru(4)–S(1)	2.387 (4)	O–C(av)	1.14 (2)
Ru(4)–Ru(5)	2.672 (2)	Ru(1)–Ru(6)	3.105 (2)
Ru(4)–Ru(6)	2.786 (2)	Ru(3)–Ru(4)	3.093 (2)

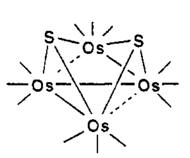
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Intramolecular Bond Angles for 2[a]

C(2)–Ru(1)–S(2)	79.4 (4)	Ru(6)–S(1)–Ru(4)	71.5 (1)
C(2)–Ru(1)–Ru(2)	50.3 (4)	Ru(6)–S(1)–Ru(5)	111.1 (2)
C(2)–Ru(1)–Ru(4)	134.7 (4)	Ru(6)–S(1)–Ru(3)	96.9 (1)
C(2)–Ru(1)–Ru(3)	71.4 (4)	Ru(4)–S(1)–Ru(5)	67.8 (1)
S(2)–Ru(1)–Ru(2)	56.2 (1)	Ru(4)–S(1)–Ru(3)	78.7 (1)
S(2)–Ru(1)–Ru(4)	93.3 (1)	Ru(5)–S(1)–Ru(3)	125.0 (2)
S(2)–Ru(1)–Ru(3)	54.7 (1)	Ru(1)–S(2)–Ru(3)	71.0 (1)
Ru(2)–Ru(1)–Ru(4)	149.24 (7)	Ru(1)–S(2)–Ru(2)	68.2 (1)
Ru(2)–Ru(1)–Ru(3)	93.11 (6)	Ru(1)–S(2)–Ru(6)	79.5 (1)
Ru(4)–Ru(1)–Ru(3)	68.16 (5)	Ru(3)–S(2)–Ru(2)	111.5 (2)
C(2)–Ru(2)–S(2)	80.1 (4)	Ru(3)–S(2)–Ru(6)	97.1 (1)
C(2)–Ru(2)–Ru(1)	52.1 (4)	Ru(2)–S(2)–Ru(6)	125.2 (2)
S(2)–Ru(2)–Ru(1)	55.6 (1)	C(1)–N(1)–C(5)	125 (1)
C(1)–Ru(3)–S(2)	82.9 (4)	C(1)–N(1)–C(4)	126 (1)
C(1)–Ru(3)–S(1)	159.4 (4)	C(5)–N(1)–C(4)	110 (1)
C(1)–Ru(3)–Ru(1)	72.8 (4)	C(6)–N(2)–C(9)	125 (1)
S(2)–Ru(3)–S(1)	77.5 (1)	C(6)–N(2)–C(10)	124 (1)
S(2)–Ru(3)–Ru(1)	54.3 (1)	C(9)–N(2)–C(10)	111 (1)
S(1)–Ru(3)–Ru(1)	90.5 (1)	N(1)–C(1)–C(2)	120 (1)
C(7)–Ru(4)–S(1)	80.4 (4)	N(1)–C(1)–Ru(3)	129 (1)
C(7)–Ru(4)–Ru(5)	51.3 (4)	C(2)–C(1)–Ru(3)	111 (1)
C(7)–Ru(4)–Ru(1)	133.4 (4)	C(1)–C(2)–C(3)	113 (1)
C(7)–Ru(4)–Ru(6)	71.1 (4)	C(1)–C(2)–Ru(2)	117 (1)
S(1)–Ru(4)–Ru(5)	56.4 (1)	C(1)–C(2)–Ru(1)	104 (1)
S(1)–Ru(4)–Ru(1)	93.5 (1)	C(3)–C(2)–Ru(2)	121 (1)
S(1)–Ru(4)–Ru(6)	54.2 (1)	C(3)–C(2)–Ru(1)	117 (1)
Ru(5)–Ru(4)–Ru(1)	149.68 (7)	Ru(2)–C(2)–Ru(1)	77.5 (5)
Ru(5)–Ru(4)–Ru(6)	92.56 (6)	N(2)–C(6)–C(7)	120 (1)
Ru(1)–Ru(4)–Ru(6)	68.29 (5)	N(2)–C(6)–Ru(6)	127 (1)
C(7)–Ru(5)–S(1)	80.2 (4)	C(7)–C(6)–Ru(6)	113 (1)
C(7)–Ru(5)–Ru(4)	51.5 (4)	C(6)–C(7)–C(8)	116 (1)
S(1)–Ru(5)–Ru(4)	55.8 (1)	C(6)–C(7)–Ru(5)	115 (1)
C(6)–Ru(6)–S(1)	82.8 (4)	C(6)–C(7)–Ru(4)	104 (1)
C(6)–Ru(6)–S(2)	159.3 (5)	C(8)–C(7)–Ru(5)	121 (1)
C(6)–Ru(6)–Ru(4)	71.9 (5)	C(8)–C(7)–Ru(4)	116 (1)
S(1)–Ru(6)–S(2)	78.1 (1)	Ru(5)–C(7)–Ru(4)	77.2 (6)
S(1)–Ru(6)–Ru(4)	54.3 (1)	O–C(av)–Ru	176 (2)
S(2)–Ru(6)–Ru(4)	90.4 (1)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

These longer and weaker bonds are indicated by dashed lines between the atoms in Figure 1. Similar distortions were also observed in the electron-rich 64-electron cluster complexes $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, **4**[9] and $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$[10] and to a lesser degree in the central cluster of the related complex $Os_6(CO)_{15}(\mu\text{-}HCNPh)_2(\mu_4\text{-}S)_2$, **5**.[5] One additional ruthenium atom is bonded to each of the hinge atoms of the butterfly, Ru(1)–Ru(2) = 2.682 (2) Å and Ru(4)–Ru(5) = 2.672 (2) Å. Compound **2** contains two quadruply bridging sulfido ligands. The four metal atoms are arranged about each sulfido ligand in an umbrella-like shape. Tetravalent carbon atoms that exhibit similar geometries in which all four substituents lie on the same side of a plane have been described as



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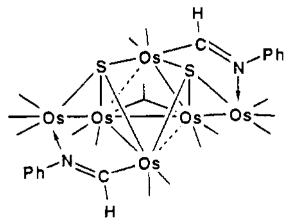

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[10] Adams, R. D.; Horvâth, I. T.; Mathur, P. *J. Am. Chem. Soc.* **1984**, *106*, 6292.

[11] Deleted in proof.

Table V. Positional Parameters and B(eq) for 3

atom	x	y	z	B(eq), Å^2
Ru(1)	0.07321 (7)	0.181452 (20)	0.70773 (5)	2.83 (3)
Ru(2)	0.30632 (7)	0.12324 (2)	0.46054 (6)	3.43 (3)
Ru(3)	0.03015 (7)	0.15342 (2)	0.45908 (6)	3.15 (3)
Ru(4)	−0.02363 (7)	0.09586 (2)	0.66061 (6)	3.07 (3)
Ru(5)	0.14002 (7)	0.11255 (2)	0.89281 (6)	3.17 (3)
Ru(6)	0.28525 (7)	0.10826 (2)	0.70835 (6)	2.95 (3)
S(1)	0.2621 (2)	0.17673 (6)	0.59599 (18)	3.17 (9)
S(2)	0.1244 (2)	0.08045 (6)	0.52556 (18)	3.4 (1)
O(11)	0.1116 (8)	0.27566 (20)	0.6717 (6)	6.2 (4)
O(13)	−0.2358 (6)	0.1849 (2)	0.5644 (5)	5.1 (3)
O(21)	0.5125 (7)	0.1807 (3)	0.3747 (6)	7.1 (4)
O(22)	0.4047 (8)	0.0476 (2)	0.3381 (7)	7.6 (4)
O(23)	0.1269 (7)	0.1509 (2)	0.2244 (5)	5.9 (3)
O(31)	−0.0548 (7)	0.2383 (2)	0.3411 (6)	6.3 (4)
O(32)	−0.2400 (7)	0.1158 (2)	0.3006 (7)	7.6 (4)
O(41)	−0.2605 (6)	0.12002 (20)	0.7803 (6)	5.4 (3)
O(42)	−0.2286 (7)	0.0303 (2)	0.5169 (6)	6.7 (4)
O(51)	−0.0736 (8)	0.0989 (2)	1.0408 (6)	6.9 (4)
O(52)	0.3767 (8)	0.1072 (3)	1.1147 (6)	7.8 (4)
O(61)	0.5056 (6)	0.1537 (2)	0.8996 (5)	5.4 (3)
O(62)	0.5230 (7)	0.0490 (2)	0.6770 (6)	6.2 (4)
N(1)	−0.1107 (8)	0.2094 (2)	0.8883 (6)	4.2 (3)
N(2)	0.0278 (9)	0.0130 (2)	0.8180 (6)	4.7 (4)
C(1)	−0.0042 (9)	0.1922 (2)	0.5803 (7)	3.3 (4)
C(2)	0.1316 (9)	0.1796 (2)	0.9019 (6)	3.2 (4)
C(3)	0.2352 (10)	0.2080 (3)	0.9861 (7)	4.5 (4)
C(4)	−0.1073 (11)	0.2114 (3)	1.0155 (9)	6.1 (5)
C(5)	−0.2382 (10)	0.2283 (3)	0.8112 (9)	6.0 (5)
C(6)	0.0847 (10)	0.0516 (2)	0.7879 (7)	3.5 (4)
C(7)	0.2299 (10)	0.0583 (2)	0.8096 (7)	3.7 (4)
C(8)	0.3398 (11)	0.0284 (3)	0.8841 (8)	5.9 (5)
C(9)	−0.1121 (11)	0.0132 (3)	0.8421 (9)	6.5 (6)
C(10)	0.0556 (13)	−0.0231 (3)	0.7501 (10)	7.6 (6)
C(11)	0.0978 (9)	0.2410 (3)	0.6872 (7)	3.7 (4)
C(13)	−0.1133 (10)	0.1775 (3)	0.5932 (7)	3.9 (4)
C(21)	0.4417 (10)	0.1577 (3)	0.4128 (7)	4.4 (4)
C(22)	0.3683 (10)	0.0768 (3)	0.3835 (8)	4.7 (5)
C(23)	0.1496 (9)	0.1432 (3)	0.3269 (8)	3.9 (4)
C(31)	−0.0221 (9)	0.2072 (3)	0.3885 (8)	4.1 (4)
C(32)	−0.1388 (10)	0.1305 (3)	0.3589 (8)	4.5 (4)
C(41)	−0.1662 (9)	0.1105 (3)	0.7376 (8)	4.2 (4)
C(42)	−0.1500 (10)	0.0540 (3)	0.5733 (8)	4.6 (5)
C(51)	0.0114 (11)	0.1039 (3)	0.9855 (8)	4.7 (5)
C(52)	0.2844 (10)	0.1092 (3)	1.0314 (8)	4.7 (5)
C(61)	0.4182 (10)	0.1363 (3)	0.8329 (8)	3.9 (4)
C(62)	0.4342 (10)	0.0726 (3)	0.6829 (7)	4.2 (4)

Table VI. Intramolecular Distances for 3[a]

Ru(1)–C(11)	1.91 (1)	Ru(4)–Ru(6)	2.899 (1)
Ru(1)–C(13)	1.95 (1)	Ru(5)–C(51)	1.83 (1)
Ru(1)–C(1)	1.985 (7)	Ru(5)–C(52)	1.85 (1)
Ru(1)–C(2)	2.175 (7)	Ru(5)–C(2)	2.111 (8)
Ru(1)–S(1)	2.460 (2)	Ru(5)–C(7)	2.225 (7)
Ru(1)–Ru(4)	2.851 (1)	Ru(5)–C(6)	2.259 (8)
Ru(1)–Ru(3)	2.932 (1)	Ru(5)–Ru(6)	2.8067 (9)
Ru(1)–Ru(5)	2.9976 (9)	Ru(6)–C(62)	1.89 (1)
Ru(2)–C(21)	1.87 (1)	Ru(6)–C(61)	1.89 (1)
Ru(2)–C(22)	1.88 (1)	Ru(6)–C(7)	2.096 (8)
Ru(2)–C(23)	1.978 (9)	Ru(6)–S(2)	2.454 (2)
Ru(2)–S(1)	2.398 (2)	Ru(6)–S(1)	2.492 (2)
Ru(2)–S(2)	2.453 (2)	N(1)–C(1)	1.32 (1)
Ru(2)–Ru(3)	2.802 (1)	N(1)–C(5)	1.45 (1)
Ru(2)–Ru(6)	2.949 (1)	N(1)–C(4)	1.46 (1)
Ru(3)–C(31)	1.89 (1)	N(2)–C(6)	1.40 (1)
Ru(3)–C(32)	1.89 (1)	N(2)–C(9)	1.43 (1)
Ru(3)–C(23)	2.135 (8)	N(2)–C(10)	1.44 (1)
Ru(3)–C(13)	2.420 (8)	C(1)–C(2)	1.35 (1)
Ru(3)–S(1)	2.505 (2)	C(2)–C(3)	1.50 (1)
Ru(3)–S(2)	2.513 (2)	C(6)–C(7)	1.37 (1)
Ru(4)–C(41)	1.85 (1)	C(7)–C(8)	1.51 (1)
Ru(4)–C(42)	1.90 (1)	Ru(1)–Ru(6)	3.0631 (9)
Ru(4)–C(6)	2.106 (8)	Ru(3)–Ru(4)	3.0813 (9)
Ru(4)–S(2)	2.390 (2)	O–C(av)	1.15 (1)
Ru(4)–Ru(5)	2.809 (1)		

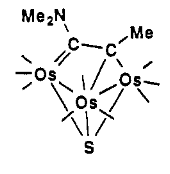
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Intramolecular Bond Angles for 3[a]

C(1)–Ru(1)–C(2)	37.6 (3)	C(7)–Ru(5)–Ru(4)	68.4 (2)
C(1)–Ru(1)–S(1)	155.3 (3)	C(7)–Ru(5)–Ru(1)	106.5 (2)
C(1)–Ru(1)–Ru(4)	98.6 (2)	C(6)–Ru(5)–Ru(6)	69.4 (2)
C(1)–Ru(1)–Ru(3)	150.1 (2)	C(6)–Ru(5)–Ru(4)	47.6 (2)
C(1)–Ru(1)–Ru(5)	65.9 (2)	C(6)–Ru(5)–Ru(1)	104.3 (2)
C(2)–Ru(1)–S(1)	119.8 (2)	Ru(6)–Ru(5)–Ru(4)	62.17 (2)
C(2)–Ru(1)–Ru(4)	99.4 (2)	Ru(6)–Ru(5)–Ru(1)	63.60 (2)
C(2)–Ru(1)–Ru(3)	160.1 (2)	Ru(4)–Ru(5)–Ru(1)	58.71 (2)
C(2)–Ru(1)–Ru(5)	44.7 (2)	C(7)–Ru(6)–S(2)	91.3 (2)
S(1)–Ru(1)–Ru(4)	95.12 (5)	C(7)–Ru(6)–S(1)	158.7 (2)
S(1)–Ru(1)–Ru(3)	54.52 (5)	C(7)–Ru(6)–Ru(5)	51.5 (2)
S(1)–Ru(1)–Ru(5)	105.70 (5)	C(7)–Ru(6)–Ru(4)	67.9 (2)
Ru(4)–Ru(1)–Ru(3)	64.37 (2)	C(7)–Ru(6)–Ru(2)	138.0 (2)
Ru(4)–Ru(1)–Ru(5)	57.34 (2)	S(2)–Ru(6)–S(1)	84.29 (7)
Ru(3)–Ru(1)–Ru(5)	115.83 (3)	S(2)–Ru(6)–Ru(5)	110.20 (5)
S(1)–Ru(2)–S(2)	86.34 (7)	S(2)–Ru(6)–Ru(4)	52.22 (5)
S(1)–Ru(2)–Ru(3)	56.97 (5)	S(2)–Ru(6)–Ru(2)	53.03 (5)
S(1)–Ru(2)–Ru(6)	54.37 (5)	S(1)–Ru(6)–Ru(5)	110.71 (5)
S(2)–Ru(2)–Ru(3)	56.67 (5)	S(1)–Ru(6)–Ru(4)	93.25 (5)
S(2)–Ru(2)–Ru(6)	53.08 (5)	S(1)–Ru(6)–Ru(2)	51.47 (5)
Ru(3)–Ru(2)–Ru(6)	77.16 (3)	Ru(5)–Ru(6)–Ru(4)	58.96 (2)
S(1)–Ru(3)–S(2)	82.80 (7)	Ru(5)–Ru(6)–Ru(2)	152.46 (3)
S(1)–Ru(3)–Ru(2)	53.36 (5)	Ru(4)–Ru(6)–Ru(2)	98.01 (3)
S(1)–Ru(3)–Ru(1)	53.11 (5)	C(1)–N(1)–C(5)	124.5 (7)
S(2)–Ru(3)–Ru(2)	54.63 (5)	C(1)–N(1)–C(4)	121.2 (8)
S(2)–Ru(3)–Ru(1)	91.07 (5)	C(5)–N(1)–C(4)	114.3 (7)
Ru(2)–Ru(3)–Ru(1)	100.55 (3)	C(6)–N(2)–C(9)	118.7 (8)
C(6)–Ru(4)–S(2)	92.9 (2)	C(6)–N(2)–C(10)	114.3 (7)
C(6)–Ru(4)–Ru(5)	52.4 (2)	C(9)–N(2)–C(10)	114.3 (8)
C(6)–Ru(4)–Ru(1)	113.9 (2)	N(1)–C(1)–C(2)	135.3 (8)
C(6)–Ru(4)–Ru(6)	69.3 (2)	N(1)–C(1)–Ru(1)	144.7 (7)
S(2)–Ru(4)–Ru(5)	112.11 (6)	Ru(5)–C(2)–Ru(1)	88.8 (3)
S(2)–Ru(4)–Ru(1)	95.67 (5)	C(7)–C(6)–N(2)	121.7 (8)
S(2)–Ru(4)–Ru(6)	54.26 (5)	N(2)–C(6)–Ru(4)	125.9 (6)
Ru(5)–Ru(4)–Ru(1)	63.95 (2)	N(2)–C(6)–Ru(5)	130.8 (5)
Ru(5)–Ru(4)–Ru(6)	58.88 (2)	Ru(4)–C(6)–Ru(5)	80.0 (3)
Ru(1)–Ru(4)–Ru(6)	64.37 (2)	Ru(6)–C(7)–Ru(5)	81.0 (3)
C(2)–Ru(5)–C(7)	143.9 (3)	O(13)–C(13)–Ru(1)	151.2 (7)
C(2)–Ru(5)–C(6)	149.9 (3)	O(13)–C(13)–Ru(3)	124.5 (6)
C(2)–Ru(5)–Ru(6)	96.7 (2)	Ru(1)–C(13)–Ru(3)	83.5 (3)
C(2)–Ru(5)–Ru(4)	102.4 (2)	O(23)–C(23)–Ru(2)	140.6 (7)
C(2)–Ru(5)–Ru(1)	46.5 (2)	O(23)–C(23)–Ru(3)	133.3 (7)
C(7)–Ru(5)–C(6)	35.5 (3)	Ru(2)–C(23)–Ru(3)	85.8 (3)
C(7)–Ru(5)–Ru(6)	47.5 (2)	O–C(av)–Ru	176 (1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

"inverted" tetrahedra.[12] Electron-counting procedures suggest that the sulfido ligands in **2** are similar to those in **5** and two of the μ_4-sulfido ligands in $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **6**.[13] They are believed to employ all six of their valence electrons for bonding and, accordingly, may also be described as "inverted" tetrahedra.[13] Compound **2** contains two triply bridging ynamine, MeC_2NMe_2, ligands. Both are coordinated in a fashion similar to that found in the triosmium complex $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$, **7**,[7] and the μ_3-MeC_2NMe_2 ligand in the complex $Os_3(CO)_7(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **8**.[14] The C–N distances, C(1)–N(1) = 1.31 (2) Å and C(6)–N(2) = 1.34 (2) Å, are relatively short and indicative of partial multiple bonding which occurs



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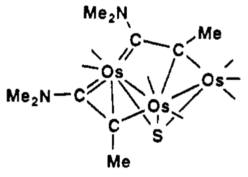

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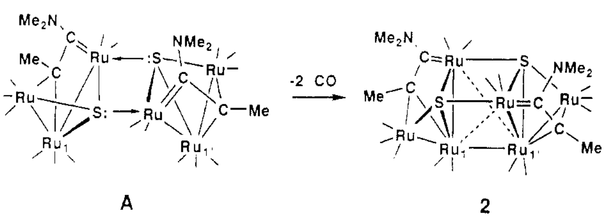
Scheme I



by donation of the lone pair of electrons on the nitrogen atom to the carbon atom. Accordingly, the nitrogen atoms exhibit planar geometries. The ^{1}H NMR spectrum of 2 shows that the *N*-methyl groups are inequivalent due to hindered rotations about the C–N bonds. These features were also observed for the μ_3-MeC$_2$NMe$_2$ ligands in 7 and 8 and this has led to the proposal that the NMe$_2$-substituted carbon atom contains carbene-like character. Overall, compound 2 contains an approximate 2-fold rotational symmetry. The C_2 axis lies perpendicular to the Ru(1)–Ru(4) and S(1)–S(2) vectors. As a result, the two ynamine ligands are spectroscopically equivalent.

The compound contains 14 carbonyl ligands. If one assumes that the ynamine ligands serve as four-electron donors and the sulfido ligands serve as six-electron donors, then the molecule contains a total of 96 valence electrons. The structure can be rationalized by use of the polyhedral skeletal electron pair (PSEP) theory and the principle of condensed polyhedra in the following way.[15] The central butterfly tetrahedron contains 64 electrons as found in 4, and the metal atoms Ru(2) and Ru(5) bonded by a single metal–metal bond contribute 16 electrons each. It is not possible to associate 18 electrons with each metal atom in this cluster. The formation of 2 from two clusters of 1 can be envisaged in the following way. Two enantiomerically similar units of 1 decarbonylate and form the intermediate dimer A (see Scheme I) by the formation of donor/acceptor bonds from the sulfido ligand of one cluster to a metal atom of the other. No metal–metal bonds are formed in the formation of A. This process is similar to that shown in eq 1.[4] In fact, the *R*,*R* dimer obtained from the decarbonylation of Ru$_3$(CO)$_8$(PMe$_2$Ph)(μ_3-HC$_2$Ph)(μ_3-S) has a structure similar to that of A.[4] The transformation of A to 2 involves the loss of two carbonyl ligands, one from Ru(1) and one from Ru(1′), and the formation of a strong metal–metal bond between Ru(1) and Ru(1′) and the two weak metal–metal bonds as indicated by the dashed bonds. Since only two CO ligands were eliminated, three full metal–metal bonds were not formed, and the molecule adopted the electron-rich butterfly tetrahedral cluster grouping.[9,10]

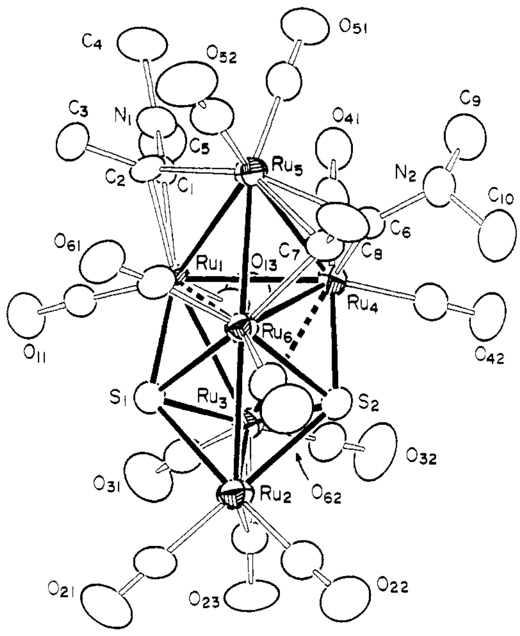


Figure 2. ORTEP drawing of Ru$_6$(CO)$_{13}$(μ-MeC$_2$NMe$_2$)(μ_3-MeC$_2$NMe$_2$)(μ_4-S)$_2$, 3, showing 50% probability thermal ellipsoids.

An ORTEP drawing of the molecular structure of 3 is shown in Figure 2. The cluster of six ruthenium atoms and two sulfido ligands could be viewed as a monocapped pentagonal bipyramid. The capping atom is Ru(5). Atoms Ru(1), Ru(2), Ru(4), S(1), and S(2) define the equatorial plane of the pentagonal bipyramid with Ru(3) and Ru(6) as the apexes. Two of the metal–metal bonds in the cluster are unusually long, Ru(1)–Ru(6) = 3.0631 (9) Å and Ru(3)–Ru(4) = 3.0813 (9) Å. These are indicated by dashed lines connecting the atoms. A similar but less pronounced distortion in the metal–metal bonding was also observed in the complex Os$_7$(CO)$_{20}$(μ_4-S)$_2$, which contains an Os$_5$S$_2$ cluster with a pentagonal bipyramidal geometry.[16] Compound 3 contains two ynamine ligands. One of these bridges the Ru(1)–Ru(5) bond. This ligand exhibits the twisted bridging coordination with C(2) bonded to both metal atoms and C(1) bonded only to one, Ru(1). This geometry has been observed for other edge-bridging ynamine ligands and has been attributed to carbene-like character at the NMe$_2$-substituted carbon atom.[17] The C(1)–N(1) distance is short, 1.32 (1) Å. The nitrogen atom N(1) is planar, and the ^{1}H NMR spectrum shows two *N*-methyl resonances (4.08 and 4.29 ppm) that arise due to hindered rotation about the C(1)–N(1) bond. The other ynamine ligand is a triple bridge, and unlike most triply bridging ynamine ligands,[7,18] this one exhibits an undistorted μ-parallel coordination.[19] In this ligand the nitrogen atom N(2) has a definite pyramidal geometry. The C–N–C angles are only slightly larger than the tetrahedral value, 114.3°, 114.3°, and 118.7°, and the nitrogen atom lies 0.30 Å out of the plane defined by the carbon atoms C(6), C(9), and C(10). The C(6)–N(2) distance of 1.40 (1) Å is much longer than the corresponding C–N distances of ynamine ligands containing planar nitrogen atoms.[7,18] The *N*-methyl groups are spectroscopically equivalent, δ = 2.45 ppm (6 H), due to rapid rotation about the C(6)–N(2) bond. It can be concluded that lone-pair donation from N(2) to C(6) is considerably less than that in other ynamine ligand complexes.[7,18] Calculations have indicated that the more common slipped-μ-perpendicular bridging mode that has been observed for triply bridging ynamine ligands is due to strong donation of the electron pair of the nitrogen atom to the neighboring carbon atom.[20] This is further supported by the structure of 3, which shows that the alkyne adopts the normal μ_3-parallel bonding mode when the lone-pair donation to the adjacent carbon atom is not strong. Compound 3 contains 13 carbonyl ligands. One

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of these is a semibridge across the Ru(1)–Ru(3) bond, Ru(3)···C(13) = 2.420 (8) Å. Compound **3** contains 94 valence electrons. According to the PSEP theory, a capped pentagonal bipyramidal cluster containing two main-group elements should contain 92 electrons; thus **3**, like **2**, is electron-rich by two electrons, and this may account for the weakening and lengthening of the two metal–metal bonds Ru(1)–Ru(6) and Ru(3)–Ru(4). The transformation of **2** to **3** involves the loss of only one carbonyl ligand, but there has been a considerable rearrangement of the metal–metal and metal–sulfur bonding and a repositioning of the ynamine ligands. At this time, we cannot predict the course of this transformation.

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Supplementary Material Available: Tables of bond angles, anisotropic thermal parameters, and positional parameters of the hydrogen atoms for all three crystal analyses (17 pages); listings of structure factor amplitudes for 2 and 3 (43 pages). Ordering information is given on any current masthead page.

Biphasic and Phase Transfer Catalyzed N-Monoacylation and N,N′-Diacylation of Azobenzenes by Cobalt Carbonyl

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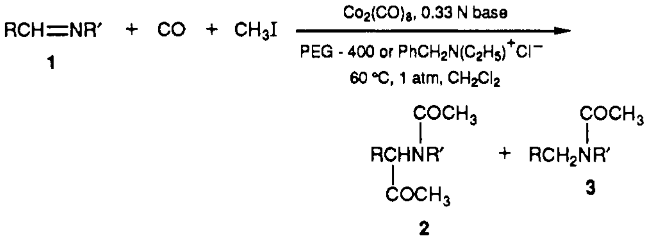
Azobenzenes react with a stoichiometric amount of cobalt carbonyl and excess methyl iodide under phase-transfer conditions (benzene, water, and benzyltriethylammonium chloride as the phase-transfer agent) to give acetic acid 1,2-diaryl-2-acetylhydrazides in reasonable yields. Byproducts arising from nitrogen–nitrogen bond cleavage were formed in several of the reactions. Reductive monoacylation of azobenzenes occurs on reaction with $Co_2(CO)_8$, methyl iodide, and a catalytic amount of *p*-toluenesulfonic acid under biphasic conditions.

One of the most useful organometallic phase-transfer-catalyzed processes is that which involves the in situ generation of acylcobalt tetracarbonyl[1] by treatment of cobalt carbonyl with carbon monoxide and methyl iodide in an organic–aqueous biphasic system containing a phase-transfer agent.[2,3] Examples include the conversion of alkynes to lactones[4] and the acylation of conjugated dienes[5] as well as azadienes.[6] Recently, the diacylation of Schiff bases (i.e., **1** → **2**) was observed with reductive monoacylation (**3**) occurring, to some extent, in most cases.[7]



Most of the chemistry of azobenzenes with metal carbonyls has involved the formation of either ortho-metalated complexes[8] or π-complexes.[9] Heterocyclic compounds such as 2-phenylindazolones have been synthesized by carbonylation of several of the ortho-metalated complexes. We now report that azobenzenes undergo diacylation or monoacylation with cobalt carbonyl and methyl iodide, under phase-transfer or biphasic conditions.

Table I. Phase-Transfer-Catalyzed N,N′-Diacylation of Azobenzenes[a]

Ar_1, Ar_2 for **4**	amt of **5**, %	amt of **6**/**7**, %	amt of recovered **4**, %
Ph	54[b]	0	16
p-$CH_3C_6H_4$	52	0	23
m-$CH_3C_6H_4$	52	0	28
p-ClC_6H_4	36	0	38
Ph, *p*-$CH_3OC(O)C_6H_4$	53	0	28
Ph, *p*-HOC_6H_4	28[d]	17	14[c]
Ph, *p*-$CH_3OC_6H_4$	18	13	38
p-$CH_3OC_6H_4$	14	21	20
$C_5H_{10}NC(O)$	0[e]	0	0

[a] Reaction conditions: **4** (2.0 mmol), $Co_2(CO)_8$ (4.0 mmol), CH_3I (62 mmol), $PhCH_2N(C_2H_5)_3^+Cl^-$ (0.5 mmol), C_6H_6 (24 mL), H_2O (24 mL), 60 °C, overnight, N_2 atmosphere. Yields of all products, and recovered **4**, are for pure materials. Crude yields were higher. [b] 1% of PhNHN(Ph)$COCH_3$ was also formed in the reaction. [c] 23% of PhN=$NC_6H_4OCOCH_3$-*p* was also isolated. [d] Consisted of 19% **5** (Ar_1 = Ph, Ar_2 = *p*-$CH_3COOC_6H_4$) and 9% **5** (Ar_1 = Ph, Ar_2 = *p*-HOC_6H_4). [e] 93% of $C_5H_{10}NCONHN(CONC_5H_{10})COCH_3$.

Results and Discussion

Treatment of azobenzene (**4**, $Ar_1 = Ar_2$ = Ph) with cobalt carbonyl and methyl iodide in benzene and water containing benzyltriethylammonium chloride as the phase-transfer agent, overnight at 60 °C (nitrogen atmosphere), afforded acetic acid 1,2-diphenyl-2-acetylhydrazide (**5**, $Ar_1 = Ar_2$ = Ph) in 54% isolated yield. A 2/1 ratio of $Co_2(CO)_8$/azobenzene was used in these reactions (use of a 1/1 and 1/2 ratios of $Co_2(CO)_8$/azobenzene gave **5** in 18% and 5% yields, respectively). The best ratio of **4**/benzyltriethylammonium chloride was 4/1. The reaction is applicable to other azo compounds, and the results are presented in Table I. Reasonable yields of pure acetic acid

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