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Cluster Synthesis. 19. The Synthesis of Ruthenium Carbonyl Cluster Complexes Containing Quadruply Bridging Aminocarbyne Ligands

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Pyrolysis of $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (1) at 185 °C resulted in the formation of three new higher nuclearity cluster complexes in low yield. These have been identified as $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (2), $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3), and $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4). Compound 2 was also obtained in 60% yield from the reaction of 1 with $Ru(CO)_5$ in refluxing hexane. The three products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. For 2: space group $P2_1/n$, $a = 9.911$ (2) Å, $b = 15.469$ (6) Å, $c = 14.765$ (3) Å, $\beta = 90.80$ (2)°, $V = 2263$ (1) Å^3, $Z = 4$. Solution by direct methods: final residuals $R = 0.0269$, $R_w = 0.0291$ based on 3274 reflections. For 3: space group $P\bar{1}$, $a = 11.329$ (1) Å, $b = 14.456$ (3) Å, $c = 10.583$ (3) Å, $\alpha = 91.31$ (2)°, $\beta = 92.71$ (2)°, $\gamma = 109.51(1)$°, $V = 1630$ (1) Å^3, $Z = 2$. Solution by heavy-atom method: final residuals $R = 0.0305$, $R_w = 0.0298$ based on 3604 reflections. For 4: space group $C2/c$, $a = 11.735$ (5) Å, $b = 17.673$ (5) Å, $c = 14.683$ (3) Å, $\beta = 99.30$ (2)°, $V = 3005$ (2) Å^3, $Z = 4$. Solution by direct methods: final residuals $R = 0.0243$, $R_w = 0.0252$ based on 2453 reflections. The molecular structure of 2 consists of a butterfly of four ruthenium atoms with a quadruply bridging (dimethylamino)carbyne ligand, C–N = 1.434 (6) Å. Compound 3 contains a cluster of five ruthenium atoms in the form of a capped butterfly tetrahedron. A quadruply bridging (dimethylamino)carbyne ligand lies in the fold of the butterfly, C–N = 1.435 (7) Å, and an edge-bridging (dimethylamino)carbyne ligand bridges a bond between one of the hinge metal atoms and the capping atom, C–N = 1.307 (8) Å. Compound 4 consists of an octahedral cluster of six ruthenium atoms with an interstitial carbido ligand. Two (dimethylamino)carbyne ligands bridge opposite edges of the octahedron, C–N = 1.287 (6) Å. Compounds 2 and 3 are believed to have been formed by the combination of $Ru(CO)_4$ and $Ru_2(CO)_6(CNMe_2)(H)$ units from a fragmented cluster of 1 with an unfragmented molecule of 1, respectively. Compound 4 is believed to have been formed by the fusion of two formula equivalents of 1.

Introduction

One of the distinguishing features of the chemistry of polynuclear metal complexes is their ability to engage ligands in multiply bonded bridging coordination modes. Bridging coordination can significantly alter the intraligand bonding and thus modify the reactivity of the ligand.[1-4]

In our recent studies, we have been investigating the chemistry of (dialkylamino)carbene and -carbyne ligands in osmium cluster complexes.[5-9] We have now found that the ruthenium complex $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (1) can be transformed pyrolytically into higher nuclearity ruthenium carbonyl clusters and two of these products have been found to contain the first examples of quadruply bridging (dialkylamino)carbyne ligands. The preparation and structural characterization of these compounds are described in this report.

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. Chromatographic separations were performed by TLC in air on Kieselgel, 0.25 mm, 60 F_{254}, E. Merck, West Germany. IR spectra were recorded on a Nicolet 5 DXB FTIR spectrophotometer. NMR spectra were run on a Brüker AM-300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$[10] and $Ru(CO)_5$[11] were prepared by the published procedures. Percent yields were calculated on the basis of the amount of $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ consumed in the reaction.

Pyrolysis of $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (1) in the Absence of Solvent. 1 (50 mg) was heated in a sealed tube in vacuo at 185 °C for 30 min, and a black residue formed. This was extracted with a minimum of CH_2Cl_2 and was then chromatographed by TLC with a hexane/CH_2Cl_2 (6/4) solvent mixture. This yielded the following bands in order of elution: 30 mg of 1, 1.5 mg of pale yellow $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$, (2(6%)), 1.5 mg of red $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3 (5%)), and 1.5 mg of pale yellow $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4 (6%)). Traces of other higher nuclearity products were observed. These are currently under study. Pyrolysis of 1 for 1.5 h produced compound 4 in 20% yield, only a small amount of 2, and no 3. For 2: IR (hexane) ν(CO) 2091 (w), 2058 (vs), 2049 (vs), 2037 (w), 2011 (s), 1968 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 3.03 (s, 6 H), −22.56 (s, 1 H). Anal. Calcd: C, 22.60; H, 0.89; N, 1.76. Found: C, 22.72; H, 0.84; N, 1.70. For 3: IR (hexane) ν(CO) 2079 (m), 2041 (vs), 2029 (vs), 2013 (vs), 2002 (w), 1991 (m), 1967 (w), 1946 (w), 1935 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 3.34 (s, 3 H) 3.36 (s, 3 H), 3.69 (s, 3 H), 3.75 (s, 3 H). Anal. Calcd: C, 23.22; H, 1.23; N, 2.85. Found: C, 23.22; H, 1.33; N, 3.34. For 4: IR (hexane) ν(CO) 2021 (vs), 2010 (m), 1995 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 3.80 (s, 6 H), 3.89 (s, 6 H).

Pyrolysis of 1 in Nonane Solvent. 1 (25 mg) was refluxed in 30 mL of nonane for 1 h. The solvent was removed in vacuo. Workup of the residue as described above gave the following bands in order of elution: 10 mg of compound 1, a trace amount of compound 2, 1.0 mg of compound 3 (7%), and 1.0 mg of compound 4 (6%).

Reaction of 1 with $Ru(CO)_5$. A hexane solution (150 mL) of $Ru(CO)_5$ (0.470 mmol) was added dropwise to a refluxing hexane

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Table I. Crystallographic Data for the Structural Analyses for Compounds 2, 3, and 4

	2	3	4
formula	$Ru_4O_{12}NC_{15}H_7$	$Ru_5O_{13}N_2C_{19}H_{12}\cdot C_6H_6$	$Ru_6O_{14}N_2C_{21}H_{12}$
temp (±3 °C)	23 °C	23 °C	23 °C
space group	$P2_1/n$, No. 14	$P\bar{1}$, No. 2	$C2/c$, No. 15
a (Å)	9.911 (2)	11.329 (1)	11.735 (5)
b (Å)	15.469 (6)	14.456 (3)	17.673 (5)
c (Å)	14.765 (3)	10.583 (3)	14.683 (3)
α (deg)	90.0	91.31 (2)	90.0
β (deg)	90.80 (2)	92.71 (2)	99.30 (2)
γ (deg)	90.0	109.51 (1)	90.0
V (Å^3)	2263 (1)	1630 (1)	3005 (2)
M_r	797.5	1059.8	1122.8
Z	4.0	2.0	4.0
ρ_{calcd} (g/cm^3)	2.34	2.16	2.50
(A) Measurement of Intensity Data			
radiation		Mo Kα	
monochromator		graphite	
detector aperture (mm)			
horizontal		2.0	
vertical		2.0	
cryst faces	001, $00\bar{1}$, $1\bar{1}1$ $\bar{1}1\bar{1}$, $\bar{1}\bar{1}\bar{1}$, 111	010, $0\bar{1}0$, 100 $\bar{1}00$, $\bar{1}22$, $\bar{1}1\bar{2}$	110, $\bar{1}\bar{1}0$, $\bar{1}10$ $1\bar{1}0$, 001, $00\bar{1}$
cryst size (mm)	0.11 × 0.25 × 0.23	0.14 × 0.29 × 0.24	0.09 × 0.12 × 0.41
cryst orientatn			
lattice direction	[$\bar{1}\bar{2}\bar{1}$]; 0.68	[001]; 3.1	[$00\bar{1}$]; 3.8
deg from ϕ axis	4.4°	10.4	7.7
reflctns measd	$h,k,\pm l$	$h,\pm k,\pm l$	$h,k,\pm l$
max 2θ	46°	45°	54°
scan type		moving crystal–stationary counter	
ω-scan width (A + 0.347 tan θ)°, A =		1.10	
background		$^1/_4$ scan time at each end of scan	
ω-scan rate (deg/min)[a]		4.0	
data used ($F^2 \geq 3.0\sigma(F^2)$)	3274	3604	2453
(C) Treatment of Data			
absorptn correctn	empirical	empirical	empirical
coeff (cm^{-1})	26.14	22.72	29.34
transmissn coeff			
max	1.000	1.000	1.000
min	0.734	0.722	0.850
P factor	0.02	0.01	0.02
final residuals			
R_F	0.0269	0.0305	0.0243
R_{wF}	0.0291	0.0298	0.0252
esd of unit weight observn	1.54	2.45	1.12
largest shift/error value of final cycle	0.20	0.45	0.03
largest peak in final diff Fourier (e/Å^3)	0.60	1.32	0.420
no. of variables	294	376	195

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

solution (50 mL) of 1 (50 mg, 0.080 mmol) over a period of 1 h. This produced a brown solution that was stirred for an additional 30 min at this temperature. The solvent was removed in vacuo, and the brown residue was dissolved in a minimum of CH_2Cl_2. Chromatography by TLC with a hexane/CH_2Cl_2 (7/3) solvent mixture gave the following bands in order of elution: 10 mg of $Ru_3(CO)_{12}$, 28 mg of 1, 16 mg of 2 (60%), 0.3 mg of a light green compound (IR (hexane) ν(CO) 2105 (w), 2077 (m), 2054 (vs), 2052 (w), 2032 (m), 2012 (w) cm^{-1}), 0.3 mg of a brown compound (IR (hexane) ν(CO) 2112 (m), 2088 (m), 2073 (s), 2055 (vs), 2045 (sh), 2038 (vs), 2007 (w), 1994 (w), 1845 (w) cm^{-1}), 2 mg of a dark brown compound (IR (hexane) ν(CO) 2095 (w), 2064 (s), 2059 (vs), 2048 (s), 2039 (s), 2023 (s), 2011 (s), 2000 (m), 1996 (m), 1964 (w) cm^{-1}), and 2.5 mg of a dark green compound (IR (hexane) ν(CO) 2095 (m), 2059 (s), 2040 (s), 2029 (s), 2011 (vs), 1998 (m), 1985 (m), 1973 (s), 1957 (m), 1821 (s) cm^{-1}. These compounds were observed in trace amounts in the pyrolysis reactions described above and are currently under further study.

Crystallographic Analyses. Orange-red crystals of 2 were obtained by slow evaporation of solvent from a benzene solution at 5 °C. Deep red crystals of 3 were obtained by slow evaporation of solvent from a benzene solution at 25 °C. Orange crystals of 4 were obtained by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 (7/3) solvent mixture at 5 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer using graphite-monochromatized 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 TEXSAN structure-solving program library obtained from the Molecular Structure Corp., College Staion, TX. Neutral atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified on the basis of the systematic absences observed during the collection of data. The coordinates

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

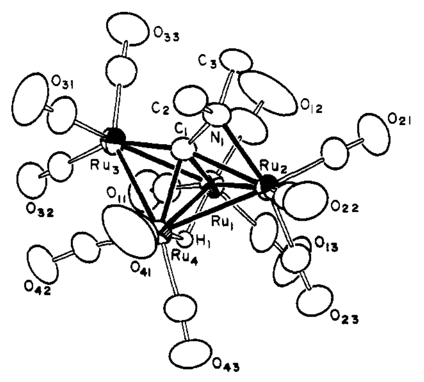

Figure 1. An ORTEP diagram of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-CNMe}_2)(\mu\text{-H})$ (2) showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and B(eq) for $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-CNMe}_2)(\mu\text{-H})$ (2)

atom	x	y	z	B(eq), Å^2
Ru1	0.562 263 (39)	0.080 063 (26)	0.298 128 (27)	2.96 (2)
Ru2	0.710 140 (37)	0.198 929 (26)	0.194 173 (26)	2.74 (2)
Ru3	0.304 145 (39)	0.140 725 (28)	0.248 315 (28)	3.18 (2)
Ru4	0.503 702 (38)	0.258 843 (25)	0.308 413 (26)	2.74 (2)
O11	0.388 44 (44)	−0.026 63 (32)	0.424 79 (33)	6.4 (3)
O12	0.602 29 (85)	−0.078 93 (34)	0.184 51 (39)	11.3 (4)
O13	0.817 98 (46)	0.044 07 (37)	0.409 67 (40)	8.2 (3)
O21	0.898 32 (49)	0.071 38 (35)	0.103 30 (38)	7.7 (3)
O22	0.815 91 (46)	0.357 07 (29)	0.095 49 (31)	5.9 (2)
O23	0.913 65 (40)	0.230 02 (28)	0.344 47 (28)	5.2 (2)
O31	0.112 50 (47)	0.263 86 (39)	0.154 50 (39)	8.0 (3)
O32	0.122 92 (40)	0.091 28 (30)	0.411 46 (29)	5.5 (2)
O33	0.222 50 (53)	−0.005 83 (34)	0.124 08 (36)	7.4 (3)
O41	0.466 13 (69)	0.430 49 (32)	0.214 22 (37)	9.2 (4)
O42	0.263 16 (43)	0.289 99 (30)	0.428 66 (32)	6.1 (2)
O43	0.683 99 (52)	0.347 54 (36)	0.448 16 (38)	7.9 (3)
N1	0.534 64 (39)	0.180 11 (26)	0.109 36 (25)	3.0 (2)
C1	0.481 39 (45)	0.169 03 (31)	0.198 44 (31)	2.8 (2)
C2	0.476 83 (54)	0.255 07 (38)	0.058 22 (34)	4.0 (3)
C3	0.524 69 (54)	0.102 99 (37)	0.049 54 (33)	3.9 (2)
C11	0.446 21 (55)	0.016 31 (38)	0.377 56 (40)	4.1 (3)
C12	0.586 64 (82)	−0.017 93 (42)	0.224 37 (46)	6.2 (4)
C13	0.725 59 (58)	0.057 29 (40)	0.367 23 (46)	4.9 (3)
C21	0.827 29 (55)	0.118 55 (41)	0.135 49 (41)	4.5 (3)
C22	0.773 79 (52)	0.299 35 (36)	0.133 35 (37)	3.7 (2)
C23	0.834 09 (52)	0.217 95 (36)	0.289 27 (36)	3.7 (2)
C31	0.184 19 (56)	0.217 55 (42)	0.189 71 (44)	4.7 (3)
C32	0.187 94 (51)	0.109 31 (36)	0.353 14 (39)	3.8 (3)
C33	0.250 91 (59)	0.049 69 (42)	0.171 99 (42)	4.7 (3)
C41	0.477 66 (67)	0.363 77 (39)	0.247 26 (42)	4.9 (3)
C42	0.346 39 (55)	0.271 03 (36)	0.380 28 (37)	4.0 (3)
C43	0.621 08 (59)	0.314 41 (40)	0.394 37 (42)	4.6 (3)
H1	0.5537 (44)	0.1668 (30)	0.3650 (32)	3 (1)
H21	0.4723	0.3042	0.0951	5.0
H22	0.5296	0.2673	0.0058	5.0
H23	0.3672	0.2325	0.0348	5.0
H31	0.5801	0.1160	−0.0012	5.0
H32	0.5688	0.0569	0.0785	5.0
H33	0.4245	0.1048	0.0196	5.0

of the heavy atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The bridging hydride ligand was located crystallographically and was successfully refined. The positions of the methyl hydrogen atoms were calculated by assuming idealized tetrahedral geometry about the carbon atoms. The contributions of the methyl hydrogen atoms were added to the structure factor (SF) calculations, but their positions were not refined.

Compound 3 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. The structure was solved by a combination of Patterson and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Compound 3 crystallized with one molecule of benzene in the asymmetric crystal unit. Its carbon atoms were refined without difficulty. All hydrogen atom positions were calculated by assuming idealized tetrahedral and sixfold planar geometries. The contributions of the hydrogen atoms were added to the SF calculations, but their positions were not refined.

Compound 4 crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with either of the space groups $C2/c$ or Cc. The former was selected initially and confirmed by the successful solution and refinement of the

Table III. Intramolecular Distances (Å) for $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-CNMe}_2)(\mu\text{-H})$ (2)[a]

atom	atom	dist	atom	atom	dist
Ru1	C12	1.884 (7)	Ru4	C43	1.914 (6)
Ru1	C11	1.926 (6)	Ru4	C1	2.146 (5)
Ru1	C13	1.934 (6)	O11	C11	1.125 (6)
Ru1	C1	2.161 (5)	O12	C12	1.124 (8)
Ru1	Ru3	2.8131 (7)	O13	C13	1.121 (7)
Ru1	Ru2	2.8191 (8)	O21	C21	1.124 (7)
Ru1	Ru4	2.830 (1)	O22	C22	1.136 (6)
Ru2	C23	1.876 (5)	O23	C23	1.141 (6)
Ru2	C22	1.906 (6)	O31	C31	1.131 (7)
Ru2	C21	1.916 (6)	O32	C32	1.118 (6)
Ru2	N1	2.149 (4)	O33	C33	1.145 (7)
Ru2	C1	2.316 (5)	O41	C41	1.147 (7)
Ru2	Ru4	2.8260 (7)	O42	C42	1.137 (6)
Ru3	C33	1.875 (6)	O43	C43	1.126 (7)
Ru3	C31	1.883 (6)	N1	C1	1.434 (6)
Ru3	C1	1.964 (5)	N1	C2	1.486 (7)
Ru3	C32	2.002 (6)	N1	C3	1.487 (6)
Ru3	Ru4	2.8264 (8)	Ru1	H1	1.67 (5)
Ru4	C41	1.874 (6)	Ru4	H1	1.72 (5)
Ru4	C42	1.908 (5)			

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

Table IV. Intramolecular Bond Angles (deg) for $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-CNMe}_2)(\mu\text{-H})$ (2)[a]

atom	atom	atom	angle	atom	atom	atom	angle
C12	Ru1	Ru3	103.9 (2)	C32	Ru3	Ru4	108.8 (2)
C12	Ru1	Ru2	97.9 (2)	Ru1	Ru3	Ru4	60.25 (2)
C12	Ru1	Ru4	147.7 (2)	C41	Ru4	Ru2	95.3 (2)
C11	Ru1	Ru3	77.4 (2)	C41	Ru4	Ru3	108.5 (2)
C11	Ru1	Ru2	170.1 (2)	C41	Ru4	Ru1	148.0 (2)
C11	Ru1	Ru4	110.1 (2)	C42	Ru4	Ru2	165.6 (2)
C13	Ru1	Ru3	161.8 (2)	C42	Ru4	Ru3	70.4 (2)
C13	Ru1	Ru2	88.2 (2)	C42	Ru4	Ru1	107.2 (2)
C13	Ru1	Ru4	108.7 (2)	C43	Ru4	Ru2	96.0 (2)
C1	Ru1	Ru3	44.1 (1)	C43	Ru4	Ru3	156.2 (2)
C1	Ru1	Ru2	53.5 (1)	C43	Ru4	Ru1	110.6 (2)
C1	Ru1	Ru4	48.7 (1)	C1	Ru4	Ru2	53.4 (1)
Ru3	Ru1	Ru2	96.77 (2)	C1	Ru4	Ru3	43.9 (1)
Ru3	Ru1	Ru4	60.11 (1)	C1	Ru4	Ru1	49.1 (1)
Ru2	Ru1	Ru4	60.03 (2)	Ru2	Ru4	Ru3	96.31 (2)
C23	Ru2	Ru1	92.0 (2)	Ru2	Ru4	Ru1	59.79 (1)
C23	Ru2	Ru4	88.5 (2)	Ru3	Ru4	Ru1	59.64 (2)
C22	Ru2	Ru1	165.0 (2)	C1	N1	Ru2	77.7 (2)
C22	Ru2	Ru4	105.1 (2)	C2	N1	Ru2	119.2 (3)
C21	Ru2	Ru1	98.4 (2)	C3	N1	Ru2	120.1 (3)
C21	Ru2	Ru4	158.6 (2)	N1	C1	Ru3	135.5 (3)
N1	Ru2	Ru1	78.8 (1)	N1	C1	Ru4	125.5 (3)
N1	Ru2	Ru4	78.8 (1)	N1	C1	Ru1	124.3 (3)
C1	Ru2	Ru1	48.6 (1)	N1	C1	Ru2	65.1 (2)
C1	Ru2	Ru4	48.1 (1)	Ru3	C1	Ru4	86.8 (2)
Ru1	Ru2	Ru4	60.18 (2)	Ru3	C1	Ru1	85.9 (2)
C33	Ru3	Ru1	98.9 (2)	Ru3	C1	Ru2	159.4 (2)
C33	Ru3	Ru4	149.8 (2)	Ru4	C1	Ru1	82.2 (2)
C31	Ru3	Ru1	153.7 (2)	Ru4	C1	Ru2	78.5 (1)
C31	Ru3	Ru4	99.8 (2)	Ru1	C1	Ru2	78.0 (1)
C1	Ru3	Ru1	50.0 (1)	Ru1	H1	Ru4	113 (3)
C1	Ru3	Ru4	49.3 (1)	H1	Ru1	C12	176 (2)
C32	Ru3	Ru1	104.3 (2)	H1	Ru4	C41	171 (1)

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

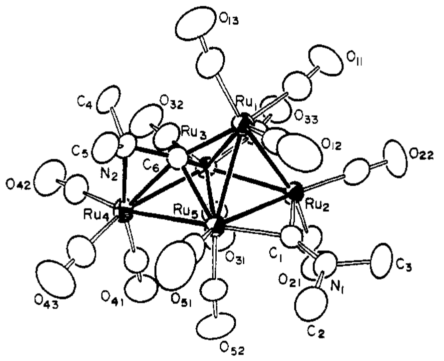

Figure 2. An ORTEP drawing of $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and B(eq) for $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3)

atom	x	y	z	B(eq), Å^2
Ru1	0.014 181 (51)	0.361 864 (41)	0.222 471 (52)	2.68 (2)
Ru2	0.103 040 (50)	0.203 454 (43)	0.231 587 (50)	2.64 (2)
Ru3	−0.125 541 (51)	0.174 952 (41)	0.103 094 (49)	2.49 (2)
Ru4	−0.339 244 (51)	0.137 434 (43)	0.243 826 (54)	2.88 (2)
Ru5	−0.096 675 (49)	0.198 164 (41)	0.367 784 (48)	2.36 (2)
O11	0.240 38 (55)	0.440 93 (45)	0.060 75 (57)	6.2 (3)
O12	0.148 99 (59)	0.450 70 (44)	0.469 89 (55)	6.8 (3)
O13	−0.044 03 (64)	0.548 74 (47)	0.172 51 (76)	8.5 (4)
O21	0.130 97 (61)	0.003 53 (47)	0.233 22 (59)	6.7 (3)
O22	0.379 27 (51)	0.288 39 (51)	0.194 16 (63)	7.1 (3)
O31	−0.147 33 (55)	−0.040 19 (41)	0.080 81 (56)	5.7 (3)
O32	−0.299 71 (61)	0.150 49 (48)	−0.132 19 (55)	6.9 (3)
O33	0.081 08 (53)	0.236 91 (43)	−0.082 91 (49)	5.3 (3)
O41	−0.367 41 (55)	−0.077 52 (42)	0.256 41 (57)	5.9 (3)
O42	−0.563 37 (57)	0.086 91 (48)	0.054 51 (63)	7.2 (3)
O43	−0.482 11 (66)	0.120 83 (54)	0.480 71 (68)	8.3 (4)
O51	−0.158 71 (62)	0.276 80 (56)	0.613 19 (54)	7.7 (4)
O52	−0.149 05 (61)	−0.006 23 (45)	0.461 10 (65)	7.3 (3)
N1	0.160 53 (49)	0.222 43 (43)	0.513 47 (50)	3.3 (2)
N2	−0.280 95 (47)	0.294 08 (39)	0.228 72 (49)	2.8 (2)
C1	0.087 75 (58)	0.214 06 (46)	0.411 25 (60)	2.6 (3)
C2	0.117 34 (74)	0.223 07 (65)	0.640 90 (66)	4.8 (4)
C3	0.293 17 (66)	0.235 35 (64)	0.506 91 (73)	4.8 (4)
C4	−0.316 64 (65)	0.333 41 (55)	0.110 72 (68)	3.7 (3)
C5	−0.297 07 (67)	0.352 03 (54)	0.337 79 (67)	3.7 (3)
C6	−0.165 23 (56)	0.273 83 (46)	0.229 73 (56)	2.5 (3)
C11	0.159 29 (77)	0.406 75 (60)	0.123 12 (77)	4.4 (4)
C12	0.100 52 (72)	0.417 17 (55)	0.376 03 (77)	4.0 (3)
C13	−0.031 55 (73)	0.475 68 (64)	0.188 35 (83)	4.9 (4)
C21	0.120 92 (71)	0.079 13 (65)	0.231 94 (69)	4.1 (4)
C22	0.273 75 (76)	0.256 42 (60)	0.209 00 (69)	4.2 (4)
C31	−0.140 07 (69)	0.039 42 (57)	0.089 17 (65)	3.5 (3)
C32	−0.236 29 (77)	0.163 63 (59)	−0.042 79 (76)	4.4 (4)
C33	0.017 36 (71)	0.217 16 (55)	−0.000 21 (71)	3.8 (3)
C41	−0.353 13 (68)	0.003 99 (62)	0.251 93 (71)	3.9 (3)
C42	−0.479 93 (73)	0.106 08 (59)	0.125 12 (79)	4.4 (4)
C43	−0.430 10 (77)	0.128 61 (64)	0.391 27 (84)	4.9 (4)
C51	−0.135 47 (69)	0.246 42 (61)	0.520 76 (73)	4.2 (4)
C52	−0.134 08 (70)	0.069 77 (65)	0.426 13 (69)	4.1 (3)
C61	0.564 82 (97)	0.323 28 (80)	0.7479 (10)	7.2 (3)
C62	0.595 37 (98)	0.395 26 (86)	0.6737 (10)	7.6 (3)
C63	0.5350 (12)	0.461 93 (96)	0.6779 (12)	10.1 (3)
C64	0.4450 (11)	0.447 76 (91)	0.7737 (12)	9.0 (3)
C65	0.4247 (11)	0.367 38 (92)	0.8499 (11)	8.6 (3)
C66	0.4859 (11)	0.308 06 (85)	0.8288 (11)	8.1 (3)

structure. The coordinates of the heavy atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the methyl hydrogen atoms were calculated by assuming idealized tetrahedral geometry. The contributions of the hydrogen atoms were added to the SF calculations, but their positions were not refined. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure.

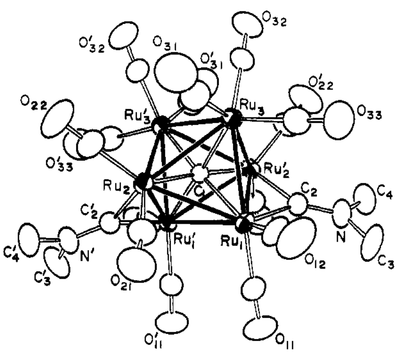

Figure 3. An ORTEP drawing of $Ru_6C(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4) showing 50% probability thermal ellipsoids.

Table VI. Intramolecular Distances (Å) for $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3)[a]

atom	atom	dist	atom	atom	dist
Ru1	C12	1.872 (8)	Ru5	C6	2.114 (6)
Ru1	C13	1.920 (9)	O11	C11	1.137 (8)
Ru1	C11	1.927 (9)	O12	C12	1.128 (8)
Ru1	C6	2.012 (6)	O13	C13	1.127 (9)
Ru1	Ru2	2.7941 (9)	O21	C21	1.136 (9)
Ru1	Ru5	2.812 (1)	O22	C22	1.149 (8)
Ru1	Ru3	2.864 (1)	O31	C31	1.127 (8)
Ru2	C22	1.857 (8)	O32	C32	1.133 (8)
Ru2	C21	1.875 (9)	O33	C33	1.141 (8)
Ru2	C1	1.925 (6)	O41	C41	1.137 (8)
Ru2	Ru5	2.7204 (9)	O42	C42	1.130 (8)
Ru2	Ru3	2.7665 (9)	O43	C43	1.127 (9)
Ru3	C32	1.911 (8)	O51	C51	1.141 (8)
Ru3	C31	1.912 (8)	O52	C52	1.128 (8)
Ru3	C33	1.931 (8)	N1	C1	1.307 (8)
Ru3	C6	2.107 (6)	N1	C3	1.456 (8)
Ru3	Ru5	2.804 (1)	N1	C2	1.457 (8)
Ru3	Ru4	2.8062 (9)	N2	C6	1.435 (7)
Ru4	C41	1.887 (8)	N2	C5	1.465 (8)
Ru4	C43	1.893 (9)	N2	C4	1.478 (8)
Ru4	C42	1.904 (8)	C61	C66	1.24 (1)
Ru4	N2	2.149 (5)	C61	C62	1.28 (1)
Ru4	C6	2.289 (6)	C62	C63	1.36 (1)
Ru4	Ru5	2.8352 (9)	C63	C64	1.44 (1)
Ru5	C51	1.877 (8)	C64	C65	1.39 (1)
Ru5	C52	1.886 (9)	C65	C66	1.29 (1)
Ru5	C1	2.053 (6)			

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

Results

When compound 1 was heated to 185 °C for 30 min in the absence of solvent, three new compounds, $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (2 6%)), $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3 (5%)), and $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4 (6%)), were obtained. When pyrolyzed in nonane solvent at 150 °C for 1 h, the yield of 2 was almost zero (just a trace), and the yields of 3 and 4 were not greatly changed (7% and 6%, respectively). However, very small amounts of compounds believed to be higher nuclearity species were also obtained. Most of the material obtained from these reactions proved to be uncharacterizable decomposition under both sets of conditions. When 1 was allowed to react with $Ru(CO)_5$ in a refluxing hexane solution, compound 2 was obtained in 60% yield. The yields of the uncharacterized "higher" nuclearity species were slightly increased. These compounds are now undergoing further study. Compounds 2, 3, and 4 were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.

Table VII. Intramolecular Bond Angles (deg) for $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (3)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C12	Ru1	C13	92.8 (3)	C33	Ru3	Ru4	172.1 (2)	C6	Ru5	Ru2	92.3 (2)
C12	Ru1	C11	95.0 (3)	C33	Ru3	Ru1	78.7 (2)	C6	Ru5	Ru3	48.3 (2)
C12	Ru1	C6	117.2 (3)	C6	Ru3	Ru2	91.2 (2)	C6	Ru5	Ru1	45.5 (2)
C12	Ru1	Ru2	92.3 (2)	C6	Ru3	Ru5	48.5 (2)	C6	Ru5	Ru4	52.7 (2)
C12	Ru1	Ru5	83.8 (2)	C6	Ru3	Ru4	53.3 (2)	Ru2	Ru5	Ru3	60.08 (2)
C12	Ru1	Ru3	140.8 (2)	C6	Ru3	Ru1	44.6 (2)	Ru2	Ru5	Ru1	60.65 (2)
C13	Ru1	C11	92.3 (3)	Ru2	Ru3	Ru5	58.46 (2)	Ru2	Ru5	Ru4	118.95 (3)
C13	Ru1	C6	93.2 (3)	Ru2	Ru3	Ru4	118.37 (3)	Ru3	Ru5	Ru1	61.32 (3)
C13	Ru1	Ru2	169.7 (3)	Ru2	Ru3	Ru1	59.48 (2)	Ru3	Ru5	Ru4	59.68 (2)
C13	Ru1	Ru5	131.5 (3)	Ru5	Ru3	Ru4	60.71 (2)	Ru1	Ru5	Ru4	97.59 (3)
C13	Ru1	Ru3	120.6 (2)	Ru5	Ru3	Ru1	59.47 (3)	C1	N1	C3	121.6 (6)
C11	Ru1	C6	146.9 (3)	Ru4	Ru3	Ru1	97.06 (3)	C1	N1	C2	123.2 (6)
C11	Ru1	Ru2	78.3 (2)	C41	Ru4	C43	90.7 (3)	C3	N1	C2	115.2 (6)
C11	Ru1	Ru5	136.2 (2)	C41	Ru4	C42	91.4 (3)	C6	N2	C5	116.0 (5)
C11	Ru1	Ru3	102.9 (2)	C41	Ru4	N2	167.4 (3)	C6	N2	C4	116.0 (5)
C6	Ru1	Ru2	92.4 (2)	C41	Ru4	C6	129.9 (3)	C6	N2	Ru4	76.5 (3)
C6	Ru1	Ru5	48.6 (2)	C41	Ru4	Ru3	90.6 (2)	C5	N2	C4	109.5 (5)
C6	Ru1	Ru3	47.3 (2)	C41	Ru4	Ru5	91.5 (2)	C5	N2	Ru4	117.5 (4)
Ru2	Ru1	Ru5	58.06 (2)	C43	Ru4	C42	96.6 (4)	C4	N2	Ru4	118.2 (4)
Ru2	Ru1	Ru3	58.53 (2)	C43	Ru4	N2	97.8 (3)	N1	C1	Ru2	136.5 (5)
Ru5	Ru1	Ru3	59.21 (2)	C43	Ru4	C6	117.1 (3)	N1	C1	Ru5	137.2 (5)
C22	Ru2	C21	88.1 (3)	C43	Ru4	Ru3	156.5 (3)	Ru2	C1	Ru5	86.2 (3)
C22	Ru2	C1	105.2 (3)	C43	Ru4	Ru5	96.9 (3)	N2	C6	Ru1	132.1 (4)
C22	Ru2	Ru5	149.1 (2)	C42	Ru4	N2	96.8 (3)	N2	C6	Ru3	125.1 (4)
C22	Ru2	Ru3	140.3 (2)	C42	Ru4	C6	122.5 (3)	N2	C6	Ru5	127.1 (4)
C22	Ru2	Ru1	105.4 (2)	C42	Ru4	Ru3	106.8 (2)	N2	C6	Ru4	65.9 (3)
C21	Ru2	C1	95.7 (3)	C42	Ru4	Ru5	166.1 (2)	Ru1	C6	Ru3	88.1 (2)
C21	Ru2	Ru5	108.6 (2)	N2	Ru4	C6	37.6 (2)	Ru1	C6	Ru5	85.9 (2)
C21	Ru2	Ru3	105.2 (2)	N2	Ru4	Ru3	78.0 (1)	Ru1	C6	Ru4	162.0 (3)
C21	Ru2	Ru1	166.0 (2)	N2	Ru4	Ru5	78.3 (1)	Ru3	C6	Ru5	83.3 (2)
C1	Ru2	Ru5	48.8 (2)	C6	Ru4	Ru3	47.5 (1)	Ru3	C6	Ru4	79.2 (2)
C1	Ru2	Ru3	110.3 (2)	C6	Ru4	Ru5	47.2 (2)	Ru5	C6	Ru4	80.1 (2)
C1	Ru2	Ru1	84.5 (2)	Ru3	Ru4	Ru5	59.61 (2)	O11	C11	Ru1	172.8 (7)
Ru5	Ru2	Ru3	61.47 (2)	C51	Ru5	C52	92.9 (3)	O12	C12	Ru1	177.8 (8)
Ru5	Ru2	Ru1	61.29 (2)	C51	Ru5	C1	99.4 (3)	O13	C13	Ru1	171.8 (8)
Ru3	Ru2	Ru1	61.99 (2)	C51	Ru5	C6	103.2 (3)	O21	C21	Ru2	179.3 (8)
C32	Ru3	C31	92.6 (3)	C51	Ru5	Ru2	141.1 (2)	O22	C22	Ru2	179.3 (7)
C32	Ru3	C33	90.4 (3)	C51	Ru5	Ru3	150.4 (2)	O31	C31	Ru3	179.3 (8)
C32	Ru3	C6	105.3 (3)	C51	Ru5	Ru1	106.8 (3)	O32	C32	Ru3	174.5 (7)
C32	Ru3	Ru2	155.5 (2)	C51	Ru5	Ru4	98.4 (2)	O33	C33	Ru3	164.4 (7)
C32	Ru3	Ru5	145.5 (2)	C52	Ru5	C1	86.1 (3)	O41	C41	Ru4	176.8 (7)
C32	Ru3	Ru4	86.1 (2)	C52	Ru5	C6	139.1 (3)	O42	C42	Ru4	179.6 (8)
C32	Ru3	Ru1	121.6 (2)	C52	Ru5	Ru2	98.2 (2)	O43	C43	Ru4	177.3 (8)
C31	Ru3	C33	93.9 (3)	C52	Ru5	Ru3	105.1 (2)	O51	C51	Ru5	179.2 (8)
C31	Ru3	C6	139.6 (3)	C52	Ru5	Ru1	158.3 (2)	O52	C52	Ru5	175.9 (7)
C31	Ru3	Ru2	85.9 (2)	C52	Ru5	Ru4	88.2 (2)	C66	C61	C62	127 (1)
C31	Ru3	Ru5	97.9 (2)	C1	Ru5	C6	126.7 (2)	C61	C62	C63	119 (1)
C31	Ru3	Ru4	93.3 (2)	C1	Ru5	Ru2	44.9 (2)	C62	C63	C64	115 (1)
C31	Ru3	Ru1	144.7 (2)	C1	Ru5	Ru3	105.0 (2)	C65	C64	C63	119 (1)
C33	Ru3	C6	121.3 (3)	C1	Ru5	Ru1	81.8 (2)	C66	C65	C64	118 (1)
C33	Ru3	Ru2	65.3 (2)	C1	Ru5	Ru4	161.5 (2)	C61	C66	C65	122 (1)
C33	Ru3	Ru5	121.2 (2)								

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

An ORTEP drawing of the molecular structure of 2 is shown in Figure 1. Final crystallographic positional parameters are listed in Table II. Intramolecular bond distances and selected bond angles are listed in Tables III and IV, respectively. Intramolecular bond distances and selected bond angles are listed in Tables III and IV, respectively. The molecule consists of a "butterfly" tetrahedron of four ruthenium atoms. The Ru–Ru bonding distances are all very similar to those found in 1, and all lie in the narrow range of 2.8131 (7)–2.830 (1) Å.[13] The longest bond Ru(1)–Ru(4) contains a bridging hydride ligand that was both located and refined in the analysis. Its ^1H NMR signal occurs at δ −22.56. The Ru–H distances of 1.67 (5) and 1.72 (5) Å are also similar to those found in 1, 1.80 (3)–1.93 (5) Å. The most interesting ligand in 2 is the quadruply bridging(dimethylamino)carbyne ligand, C(1), N(1), C(2), C(3). The carbyne carbon atom C(1) is bonded to all four ruthenium atoms while the nitrogen atom N(1) is bonded only to Ru(2), Ru(2)–N(1) = 2.149 (4) Å. The Ru–C(1) distances exhibit considerable variation, 1.964 (5)–2.316 (5) Å, with the longest bond being to the N-bonded metal atom Ru(2) and the shortest bond to Ru(3). The Ru–C distances to the "hinge" atoms Ru(1) and Ru(4) are similar, 2.161 (5) and 2.146 (5) Å. The Ru–C distances to the edge-bridging $C{=}NMe_2$ ligand in 1 are 2.018 (5)–2.039 (4) Å. The C(1)–N(1) distance of 1.434 (6) Å is only slightly shorter than a C–N single bond (e.g., N(1)–C(2) = 1.486 (7) Å and N(1)–C(3) = 1.487 (6) Å. This distance is significantly longer than C–N distance in 1, 1.279 (5) Å[1.280 (6) Å].[13] The C–N distance found in terminally coordinated aminocarbyne ligands usually lies somewhere between these values (e.g., $[W(O\text{-}t\text{-}Bu)_3(CNMe_2)]_2$, 1.34 (2) Å,[14] $Cr(CO)_4Br(CNEt_2)$, 1.29 (1) Å[15]).

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[13] Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

[14] Chisholm, M. H.; Huffman, J. L.; Marchant, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 6162.

Table VIII. Positional Parameters and *B*(eq) for $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1	0.372008 (30)	0.090858 (19)	0.236831 (25)	2.31 (1)
Ru2	0.514776 (29)	0.167113 (20)	0.113834 (23)	2.41 (1)
Ru3	0.377671 (31)	0.253896 (19)	0.231795 (26)	2.55 (1)
O11	0.37081 (36)	−0.07921 (20)	0.25117 (34)	5.8 (2)
O12	0.13759 (34)	0.08074 (25)	0.11892 (32)	6.1 (2)
O21	0.38698 (38)	0.06310 (25)	−0.02964 (29)	5.9 (2)
O22	0.56570 (49)	0.27754 (27)	−0.03163 (32)	7.6 (3)
O31	0.31607 (44)	0.32400 (28)	0.04232 (31)	7.4 (3)
O32	0.40340 (39)	0.40422 (22)	0.33163 (31)	5.7 (2)
O33	0.12772 (39)	0.23604 (29)	0.25633 (46)	9.0 (3)
N	0.26607 (36)	0.08325 (23)	0.41388 (30)	3.8 (2)
C1	1/2	0.17084 (32)	1/4	2.1 (2)
C2	0.34246 (37)	0.10511 (25)	0.36579 (31)	2.8 (2)
C3	0.16432 (49)	0.04027 (37)	0.37531 (44)	5.5 (3)
C4	0.27774 (56)	0.09703 (37)	0.51324 (42)	5.4 (3)
C11	0.37370 (40)	−0.01517 (27)	0.24509 (34)	3.4 (2)
C12	0.22576 (46)	0.08515 (28)	0.16350 (38)	3.8 (2)
C21	0.43097 (45)	0.10254 (30)	0.02679 (36)	3.8 (2)
C22	0.54843 (51)	0.23590 (31)	0.02273 (37)	4.3 (2)
C31	0.34444 (48)	0.29175 (33)	0.10938 (40)	4.4 (2)
C32	0.39274 (44)	0.34768 (29)	0.29477 (37)	3.7 (2)
C33	0.22102 (47)	0.24126 (31)	0.24607 (50)	5.1 (3)

Each metal atom contains three linear terminal carbonyl ligands. Overall, the molecule possesses an approximate symmetry plane that passes through the atoms Ru(2), Ru(3), C(1), and N(1). Compound **2** contains 62 valence electrons and is thus electron-precise.

An ORTEP drawing of the molecular structure of **3** is shown in Figure 2. Final crystallographic positional parameters are listed in Table V. Intramolecular bond distances and selected bond angles are listed in Tables VI and VII, respectively. Compound **3** consists of five metal atoms arranged in the form of a cluster that can be described as a capped butterfly tetrahedron. A quadruply bridging (dimethylamino)carbyne ligand C(6), N(2), C(4), C(5) lies in the fold of the butterfly, and an edge-bridging (dimethylamino)carbyne bridges the Ru(2)–Ru(5) bond to the capping metal atom Ru(2). The metrical parameters of the edge-bridging carbyne ligand are very similar to those found in **1**,[13] C(1)–N(1) = 1.307 (8) Å. The nitrogen atom N(1) is planar. The dimensions of the quadruply bridging carbyne ligand are similar to those of the quadruply bridging carbyne ligand in **2**, C(6)–N(2) = 1.435 (7) Å. There is a significant asymmetry in the bonding of the carbon atom C(6) to the metal atoms that is very similar to that observed in **2**. The metal–metal bond distances span a significant range, 2.7204 (9)–2.864 (1) Å. The shortest bonds involve the capping atom Ru(2), and the shortest of these contains the edge-bridging (dimethylamino)carbyne ligand. Like **2**, all the metal atoms in **3** obey the 18-electron rule although the Ru(2)–Ru(3) bond must be regarded as a donor–acceptor bond from Ru(3) to Ru(2). Such heteropolar bonding is a characteristic feature of capping groups derived from the iron subgroup.[16]

An ORTEP drawing of **4** is shown in Figure 3. Final crystallographic positional parameters are listed in Table VIII. Intramolecular bond distances and selected bond angles are listed in Tables IX and X, respectively. The molecule consists of an octahedral cluster of six ruthenium atoms that contains a carbido carbon atom C(1) in the center. Overall, the molecule contains a twofold rotational symmetry that is crystallographically imposed. The Ru–Ru bond distances span a considerable range, 2.7290 (8)–2.9771 (8) Å, but this variation is similar to that found in other Ru_6 carbido cluster complexes.[17] The shortest metal–metal bond is Ru(1)–Ru(2′)[Ru(1′)–Ru(2)], and this contains an edge-bridging (dimethylamino)carbyne, C(2), N, C(3), C(4). The Ru–C(2) distances, 1.995 (5) and 1.984 (5) Å, and the C(2)–N distance of 1.287 (6) Å are similar to those of the edge-bridging (dimethylamino)carbyne ligands found in **1** and **3**. The methyl groups are chemically inequivalent, and these exhibit separate resonances in the ^1H NMR spectrum, δ 3.80 (s, 6 H) and 3.89 (s, 6 H).

Table IX. Intramolecular Distances (Å) for $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4)[a]

atom	atom	dist	atom	atom	dist
Ru1	C12	1.875 (6)	Ru3	C33	1.897 (6)
Ru1	C11	1.878 (5)	Ru3	C31	1.898 (6)
Ru1	C2	1.995 (5)	Ru3	C1	2.040 (4)
Ru1	C1	2.049 (4)	Ru3	Ru3′	2.834 (1)
Ru1	Ru2′	2.7290 (8)	O11	C11	1.136 (5)
Ru1	Ru3	2.8833 (9)	O12	C12	1.134 (6)
Ru1	Ru1′	2.966 (1)	O21	C21	1.140 (6)
Ru1	Ru2	2.9971 (8)	O22	C22	1.128 (6)
Ru2	C21	1.870 (5)	O31	C31	1.140 (6)
Ru2	C22	1.896 (5)	O32	C32	1.134 (6)
Ru2	C2	1.984 (5)	O33	C33	1.133 (6)
Ru2	C1	2.0357 (5)	N	C2	1.287 (6)
Ru2	Ru3′	2.8562 (7)	N	C3	1.451 (7)
Ru2	Ru3	2.9735 (8)	N	C4	1.464 (7)
Ru3	C32	1.892 (5)			

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

Discussion

The pyrolysis of **1** has yielded three new higher nuclearity clusters of ruthenium that contain (dimethylamino)carbyne ligands. Two of these, **2** and **3**, contain the first examples of quadruply bridging (dimethylamino)carbyne ligands. An important effect of this coordination mode upon the ligand is the elongation of the C–N bond. A similar lengthening effect was observed on the C–O bond of the quadruply bridging methoxycarbyne ligand in the compound $Fe_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}COMe)(\mu\text{-}H)$.[18] This is believed to have a significant effect on the reactivity of the methoxycarbyne ligand.[18] The effect that this elongation might have on the reactivity of the (dimethylamino)carbyne ligand has not yet been studied.

The formations of **2** and **3** are believed to be the result of the coupling of fragments of **1** produced by the high temperatures with unfragmented molecules of **1**; see Scheme I. Rupture of the two unsupported Ru–Ru bonds in **1** should yield $Ru(CO)_4$ and $Ru_2(CO)_6(\mu\text{-}CNMe_2)H$ fragments. The combination of $Ru(CO)_4$ with **1** accompanied by the loss of two CO ligands should yield **2**. This is supported by the observation that much higher yields (60%) of **2** were obtained when **1** was allowed to react with $Ru(CO)_5$. To form **3**, the combination of the Ru_2 fragment with **1** must include the loss of four CO groups plus the two hydride ligands, presumably in the form of H_2.

We have shown previously the importance of sulfido ligands in the systematic preparation of higher nuclearity

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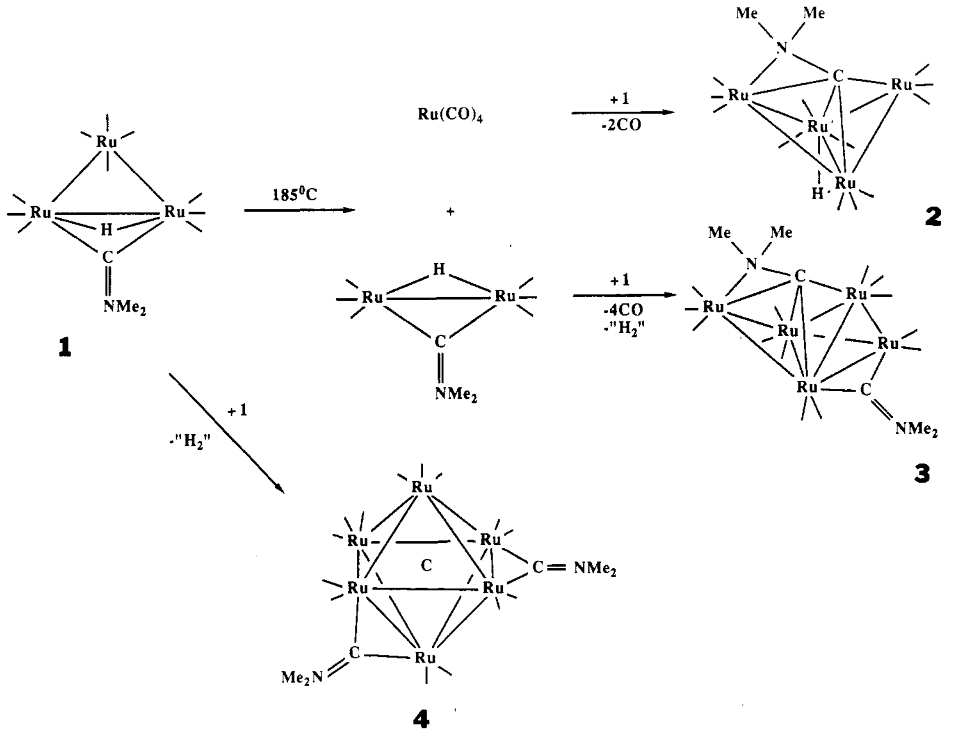
Table X. Intramolecular Bond Angles (deg) for $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$ (4)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C12	Ru1	C11	89.0 (2)	C22	Ru2	Ru3′	95.7 (2)	C1	Ru3	Ru2′	45.45 (2)
C12	Ru1	C2	105.6 (2)	C22	Ru2	Ru3	105.9 (2)	C1	Ru3	Ru1	45.3 (1)
C12	Ru1	C1	132.9 (2)	C22	Ru2	Ru1	157.0 (2)	C1	Ru3	Ru2	43.09 (2)
C12	Ru1	Ru2	140.3 (2)	C2′	Ru2	C1	94.2 (2)	Ru3	Ru3	Ru2	63.01 (2)
C12	Ru1	Ru3	93.5 (1)	C2	Ru2	Ru1	46.9 (1)	Ru3′	Ru3	Ru1	91.26 (1)
C12	Ru1	Ru1′	152.7 (2)	C2′	Ru2	Ru3′	85.6 (1)	Ru3′	Ru3	Ru2	58.86 (2)
C12	Ru1	Ru2	103.2 (1)	C2′	Ru2	Ru3	136.1 (1)	Ru2′	Ru3	Ru1	56.78 (2)
C11	Ru1	C2	93.8 (2)	C2′	Ru2	Ru1	101.7 (1)	Ru2′	Ru3	Ru2	88.51 (2)
C11	Ru1	C1	133.0 (2)	C1	Ru2	Ru1′	48.3 (1)	Ru1	Ru3	Ru2	61.08 (2)
C11	Ru1	Ru2	116.2 (2)	C1	Ru2	Ru3′	45.6 (1)	C2	N	C3	123.0 (5)
C11	Ru1	Ru3	177.3 (2)	C1	Ru2	Ru3	43.2 (1)	C2	N	C4	122.4 (5)
C11	Ru1	Ru1′	89.5 (1)	C1	Ru2	Ru1	43.4 (1)	C3	N	C4	114.5 (4)
C11	Ru1	Ru2	119.3 (1)	Ru1	Ru2	Ru3	62.11 (2)	Ru2	C1	Ru2	176.3 (3)
C2	Ru1	C1	93.5 (1)	Ru1	Ru2	Ru3′	91.47 (2)	Ru2	C1	Ru3	93.7 (1)
C2	Ru1	Ru2	46.5 (1)	Ru1	Ru2	Ru1	62.46 (3)	Ru2′	C1	Ru3	89.0 (1)
C2	Ru1	Ru3	84.6 (1)	Ru3	Ru2	Ru3′	58.13 (3)	Ru2	C1	Ru1	93.6 (1)
C2	Ru1	Ru1′	101.8 (1)	Ru3	Ru2	Ru1	88.94 (2)	Ru2′	C1	Ru1	83.8 (1)
C2	Ru1	Ru2	136.0 (1)	Ru3′	Ru2	Ru1	57.97 (2)	Ru2	C1	Ru3′	89.0 (1)
C1	Ru1	Ru2′	47.87 (2)	C32	Ru3	C33	93.7 (2)	Ru2′	C1	Ru3′	93.7 (1)
C1	Ru1	Ru3	45.0 (1)	C32	Ru3	C31	98.2 (2)	Ru2	C1	Ru1′	83.8 (1)
C1	Ru1	Ru1′	43.6 (1)	C32	Ru3	C1	123.9 (2)	Ru2′	C1	Ru1′	93.6 (1)
C1	Ru1	Ru2	43.04 (2)	C32	Ru3	Ru3	84.0 (2)	Ru3′	C1	Ru3	88.0 (2)
Ru2	Ru1	Ru3	61.11 (2)	C32	Ru3	Ru2′	95.1 (2)	Ru3	C1	Ru1	89.68 (3)
Ru2′	Ru1	Ru1′	62.87 (2)	C32	Ru3	Ru1	149.7 (2)	Ru3′	C1	Ru1	176.6 (2)
Ru2	Ru1	Ru2′	90.88 (2)	C32	Ru3	Ru2	136.0 (2)	Ru3	C1	Ru1′	176.6 (2)
Ru3	Ru1	Ru1′	88.64 (1)	C33	Ru3	C31	95.3 (3)	Ru3′	C1	Ru1′	89.68 (3)
Ru3	Ru1	Ru2′	60.96 (1)	C33	Ru3	C1	125.1 (2)	Ru1	C1	Ru1	92.8 (2)
Ru1′	Ru1	Ru2	54.67 (2)	C33	Ru3	Ru3′	161.7 (2)	N	C2	Ru2′	136.8 (4)
C21	Ru2	C22	93.2 (2)	C33	Ru3	Ru2′	99.3 (2)	N	C2	Ru1	136.6 (4)
C21	Ru2	C2′	96.0 (2)	C33	Ru3	Ru1	81.5 (2)	Ru2′	C2	Ru1	86.6 (2)
C21	Ru2	C1	124.9 (2)	C33	Ru3	Ru2	129.0 (2)	O11	C11	Ru1	177.4 (5)
C21	Ru2	Ru1	112.4 (2)	C31	Ru3	C1	114.2 (2)	O12	C12	Ru1	179.1 (5)
C21	Ru2	Ru3′	170.5 (2)	C31	Ru3	Ru3	103.0 (2)	O21	C21	Ru2	174.8 (5)
C21	Ru2	Ru3	116.0 (2)	C31	Ru3	Ru2′	159.6 (2)	O22	C22	Ru2	178.3 (6)
C21	Ru2	Ru1	81.5 (2)	C31	Ru3	Ru1	112.0 (2)	O31	C31	Ru3	168.7 (6)
C22	Ru2	C2′	101.2 (2)	C31	Ru3	Ru2	71.2 (2)	O32	C32	Ru3	178.7 (5)
C22	Ru2	C1	137.1 (2)	C1	Ru3	Ru3	46.0 (1)	O33	C33	Ru3	177.6 (6)
C22	Ru2	Ru1	138.9 (2)								

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

Scheme I



clusters of osmium.[19] Perhaps, the (dimethylamino)carbyne ligand plays a similar role in the assembly of these higher clusters of ruthenium. This is strongly suggested by the observation that the ligand can adopt the quadruply bridging bonding mode.

The formation of 4 may occur by a process that is independent of the formation of 2 and 3. The metal nuclearity suggests that it is formed by a combination of two formula equivalents of 1 that is accompanied by the appropriate loss of CO groups and the hydride ligands. The source of the carbido carbon atom in 4 has not been determined; however, it was shown that the carbido ligand in Ru$_6$(C)(CO)$_{17}$, obtained from the pyrolysis of Ru$_3$(CO)$_{12}$, was derived from a CO ligand.[20] It seems reasonable to assume that the carbido ligand in 4 was also derived from CO.

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Registry No. **1**, 59532-85-3; **2**, 112139-08-9; **3**, 112139-10-3; **4**, 112139-09-0; Ru(CO)$_5$, 16406-48-7.

Supplementary Material Available: Tables of positional parameters of the hydrogen atoms for 3 and 4 and anisotropic thermal parameters (*U* values) for all three structural analyses (7 pages); listings of structure factor amplitudes for all three structural analyses (63 pages). Ordering information is given on any current masthead page.

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Metal Atom Synthesis of Metallaboron Clusters. 10.[1] Synthesis and Structural Characterization of (η^6-Arene)thiaferraborane Clusters

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The reactions of thermally generated iron atoms with toluene and *nido*-7-SB$_{10}$H$_{12}$ or *nido*-6-SB$_9$H$_{11}$ were found to give the first examples of (η^6-arene)thiametallaborane complexes, *closo*-2-[η^6-C$_6$H$_5$CH$_3$]-2,1-FeSB$_{10}$H$_{10}$ (I) and *nido*-8-[η^6-C$_6$H$_5$CH$_3$]-8,7-FeSB$_9$H$_{11}$ (II), in high yield. The sandwich structures of I and II were confirmed by single-crystal X-ray crystallographic studies. Crystal data for I: space group *Pbca*; $Z = 8$; $a = 16.338$ (2) Å, $b = 14.429$ (4) Å, $c = 11.760$ (2) Å; $V = 2772.4$ Å^3. The structure was refined to a final R of 0.040 and R_w of 0.048 for the 1417 reflections that had $F_o^2 > 3\sigma(F_o^2)$. Crystal data for II: space group $P2_1/n$; $Z = 4$; $a = 8.736$ (2) Å, $b = 13.919$ (1) Å, 11.807 (2) Å; $\beta = 105.76$ (2)°; $V = 1381.9$ Å^3. The structure was refined to a final R of 0.063 and R_w of 0.089 for the 2587 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

As part of our interest in the synthesis and structural characterization of new types of hybrid main group–transition metal clusters, we have explored new routes to metallathiaborane clusters. We have previously demonstrated that metal atom techniques can be used to generate a number of new metallathiaborane cage systems including (η-C$_5$H$_5$)$_2$Co$_2$S$_2$B$_5$H$_5$,[2] (η-C$_5$H$_5$)$_2$Co$_2$SB$_5$H$_7$,[2] (η-C$_5$H$_5$)CoS$_2$B$_6$H$_8$,[2] and (η-C$_5$H$_5$)$_2$Co$_2$S$_2$B$_2$H$_2$.[3] These complexes were obtained from reactions involving the reactive small cage borane, pentaborane(9); however, we have recently begun to investigate the synthesis of new types of larger cage metallathiaborane clusters.

The *nido*-thiaborane clusters 7-SB$_{10}$H$_{12}$ and 6-SB$_9$H$_{11}$ were originally reported by Muetterties[4] in 1967. Although both compounds can be obtained in reasonable yields, the chemistry of these two clusters has not been as extensively developed as their carborane analogues. For example, studies of the transition-metal chemistry of these cage systems have led to the isolation of only a limited number of different types of compounds, including bis(thiaborane) sandwich complexes[4,5] as well as complexes having either cyclopentadienyl[4,6] or phosphine[7-12] metal ligands.

One area of recent interest in polyhedral boron cluster chemistry has been the synthesis and properties of (η^6-

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