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Cluster Synthesis. 22. Synthesis and Structural Characterization of $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ Containing an Interstitial Hydride Ligand and $Ru_5(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ Containing a Quadruply Bridging (Dimethylamino)carbyne Ligand

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The reaction of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (1) with $Ru(CO)_5$ at 68 °C yielded the two higher nuclearity cluster complexes $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (**2**, 28%) and $Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (**3**, 35%). Compound **2** was obtained from **3** in 63% yield by reaction with $Ru(CO)_5$. Compounds **2** and **3** were characterized by IR and ^1H NMR spectroscopy. Compound **2** was also characterized by a single-crystal X-ray diffraction analysis. The structural characterization of **3** was achieved via its bis(dimethylphenyl)phosphine derivative $Ru_4(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (**4**). For **2**: space group $P2_1/c$, $a = 14.590$ (1) Å, $b = 9.845$ (2) Å, $c = 22.381$ (3) Å, $\beta = 90.122$ (9)°, $V = 3214$ (1) Å^3, $Z = 4$. The structure was solved by direct methods and was refined (4777) reflections to $R = 0.025$ and $R_w = 0.023$. The molecule consists of a capped octahedral cluster of seven ruthenium atoms with the hydride (located and refined) on the interior of the octahedron. It appears that the hydride ligand does not lie in the exact center of the octahedron but is displaced slightly toward the capping metal atom. This hydride does exhibit the usual low-field ^1H NMR shift, δ 11.42. For **4**: space group $P2_1/c$, $a = 15.607$ (6) Å, $b = 12.255$ (3) Å, $c = 20.608$ (9) Å, $\beta = 106.27$ (3)°, $V = 3783$ (2) Å^3, $Z = 4$. The structure was solved by direct methods and was refined (3123 reflections) to $R = 0.035$ and $R_w = 0.035$. The molecule consists of a capped butterfly tetrahedron of five metal atoms with a quadruply briding (dimethylamino)carbyne ligand, C–N = 1.43 (1) Å, lying in the fold of the butterfly.

Introduction

Although there are a large number and variety of high nuclearity osmium carbonyl cluster complexes,[1] there are relatively few examples of ruthenium carbonyl cluster complexes that contain more than six metal atoms.[2-7] We have recently found that ruthenium pentacarbonyl is a very effective reagent for the enlargement of small ruthenium cluster complexes that contain sulfido ligands.[6-10] We have also discovered that bridging (dialkylamino)carbyne ligands can stabilize higher nuclearity ruthenium carbonyl cluster complexes.[10]

In this report, the results of our efforts to combine the cluster stabilization properties of the (dialkylamino)carbyne ligand with the cluster enlargement ability of ruthenium pentacarbonyl for the preparation of some new and unusual higher nuclearity clusters of ruthenium with bridging dimethylaminocarbyne ligands are described.

Experimental Section

General Data. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were stored over 4-Å molecular sieves. All chromatographic separations were performed in air. TLC separations were performed on plates (0.25 mm Kieselgel 60 F_{254}, E. Merck West Germany). IR spectra were recorded on a Nicolet 5 DXB FT–IR spectrophotometer. ^1H NMR spectra were obtained on a Brüker AM-300 spectrometer operating at 300 MHz. Mass spectra were obtained on a VG Model 70SQ spectrometer at 120 °C with electron-impact ionization at 70 eV. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$[10] and $Ru(CO)_5$[11] were prepared by the published procedures. Percent yields for all reactions were calculated on the basis of the amount of starting material consumed in the reaction.

Reaction of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (1) with $Ru(CO)_5$. 1 (100 mg, 0.120 mmol) was dissolved in 40 mL of hexane, and the solution was brought to reflux. A solution of $Ru(CO)_5$ (0.470 mmol) in hexane (100 mL) was added dropwise to the refluxing solution over a period of 3 h. The dark brown solution obtained was concentrated to a volume of ~50 mL and was then chromatographed over a Florisil column. Elution with hexane yielded 51 mg of $Ru_3(CO)_{12}$. Elution with a hexane/CH_2Cl_2 (9/1) solvent mixture yielded 40 mg of unreacted **1**. Elution with a hexane/CH_2Cl_2 (7/3) solvent mixture yielded 18 mg of $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (**2**, 28%) as a dark brown band and 16 mg of $Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$, (**3**, 35%) as a dark green band. Compounds **2** and **3** were further purified by TLC using a hexane/CH_2Cl_2 (7/3) solvent mixture.

When the reaction was performed in refluxing heptane solvent, the yield of **2** increased to 50% and the yield of **3** decreased to 30%. Small amounts of compounds **2** and **3** were also obtained in the preparation of **1**.[10] For **2**: IR (ν(CO), cm^{-1}, in hexane) 2094 (w), 2064 (vs), 2038 (s), 2024 (w), 2018 (w), 2012 (w), 2006 (w), 1966 (w); ^1H NMR (δ in $CDCl_3$) 11.42 (s, 1 H), 3.95 (s, 6 H). Anal. Calcd: C, 20.37; H, 0.54; N, 1.08. Found: C, 19.95; H, 0.61; N, 0.73. For **3**: IR (ν(CO), cm^{-1}, in hexane) 2098 (m), 2059 (s), 2038 (s), 2028 (vs), 2013 (vs), 1996 (m), 1978 (s), 1959 (m), 1872 (m), 1821 (s); ^1H NMR (δ in $CDCl_3$) 3.45 (s, 3 H), –22.05 (s, 1 H); mass spectrum for ^{104}Ru, m/e 956 – 28x,x = 0–14 ([M$^+$] – 14CO). Anal. Calcd: C, 21.40; H, 0.73; N, 1.46. Found: C, 22.60; H, 0.99; N, 1.56.

Reaction of 3 with $Ru(CO)_5$. **3** (16 mg, 0.017 mmol) was dissolved in 20 mL of hexane at reflux. A hexane solution (20

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mL) of $Ru(CO)_5$ (0.051 mmol) was added dropwise to the refluxing solution of **3** over a period of 30 min. During this time, the solution changed from dark green to dark brown. The solution was then chromatographed over a Florisil column. Elution with hexane gave 4 mg of $Ru_3(CO)_{12}$. Elution with a hexane/CH_2Cl_2 (65/35) solvent mixture gave, in order of elution, 7.5 mg of **2** (63%) and 8 mg of unreacted **3**. Further purification of both compounds was accomplished by TLC using a hexane/CH_2Cl_2 (7/3) solvent mixture.

Reaction of 3 with Dimethylphenylphosphine **3** (10 mg, 0.010 mmol) was dissolved in 20 mL of $CHCl_3$. Dimethylphenylphosphine (3.0 μL, 0.020 mmol) was added to the solution via syringe. The solution turned to light green. Removal of the solvent and chromatography of the light green residue by TLC using a hexane/CH_2Cl_2 (8/2) solvent mixture gave 9 mg of $Ru_5(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(PMe_2Ph)_2(\mu\text{-}H)$ (**4**, 77%). For **4**: IR (ν(CO), (cm^{-1} in $CHCl_3$) 2045 (w), 2018 (vs), 1995 (s), 1959 (w), 1794 (w), 1729 (w); ^1H NMR (δ in $CDCl_3$) 7.1–7.9 (m, 10 H), 2.96 (s, 3 H), 2.60 (s, 3 H), 2.11 (d, br, $J_{P\text{-}H}$ = 9 Hz, 3 H), 2.06 (d, br, $J_{P\text{-}H}$ = 9 Hz, 3 H), 1.82 (d, $J_{P\text{-}H}$ = 9.5 Hz, 6 H), −21.14 (s, 1 H).

Reaction of 1 with $Ru_3(CO)_{12}$. **1** (35 mg, 0.054 mmol) and 35 mg of $Ru_3(CO)_{12}$ (0.054 mmol) were dissolved in 50 mL of octane. The solution was refluxed for 30 min during which time the solution turned dark brown. The solvent was removed in vacuo. The dark brown residue was dissolved in a minimum of CH_2Cl_2 and was chromatographed by TLC using a hexane/CH_2Cl_2 (7/3) solvent mixture. This yielded only $Ru_3(CO)_{12}$ (20 mg), unreacted **1** (10 mg), and considerable amount of uncharacterizable material.

Crystallographic Analyses. Dark brown crystals of **2** were obtained by slow evaporation of solvent from a hexane/CH_2Cl_2 (3/7) solvent mixture at 5 °C. Dark green crystals of **4** were obtained by slow evaporation of solvent from a hexane/$CHCl_3$ (2/8) 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_α 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 Station, 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 $\sum_{hkl} w(|F_o| - F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = (F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o)^2]^{1/2}/Lp$.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified on the basis of the systematic absences observed during the collection of data. The coordinates of the heavy atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The interstitial hydride ligand was located in a difference Fourier map and was successfully refined. The positions of the methyl hydrogen atoms were calculated by assuming idealized tetrahedral geometry about the carbon atoms and C–H = 0.95 Å. The contributions of the methyl hydrogen atoms were added to the structure factor (SF) calculations, but their positions were not refined.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified on the basis of the systematic absences observed during the collection of data. The coordinates of the heavy atoms were obtained by direct methods (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 and phenyl hydrogen atoms were calculated by assuming idealized tetrahedral and planar geometries. The contributions of the hydrogen atoms were added to the SF calculations, but their positions were not refined.

Table I. Crystallographic Data for Compounds 2 and 4

	2	4
	(A) Crystal Data	
formula	$Ru_7O_{19}NC_{22}H_7$	$Ru_5P_2O_{12}NC_{31}H_{29}$
temp (±3 °C)	23 °C	23 °C
space group	$P2_1/c$	$P2_1/c$
a (Å)	14.590 (1)	15.607 (6)
b (Å)	9.845 (2)	12.255 (3)
c (Å)	22.381 (3)	20.698 (9)
β (deg)	90.122 (9)	106.27 (3)
V (Å^3)	3214 (1)	3783 (2)
M_r	1296.7	1174.8
Z	4	4
ρ_{calcd}, g/cm^3	2.67	2.06
	(B) Measurement of Intensity Data	
radiation	Mo Kα (0.71069)	Mo Kα (0.71069)
monochromator	graphite	graphite
detector aperture (mm)		
horizontal	2.0	2.0
vertical	2.0	2.0
cryst size (mm)	0.09 × 0.27 × 0.37	plate (not measd)
reflctns measd	$h,k,\pm l$	$h,k,\pm l$
max 2θ (deg)	52	45
scan type	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ)°, A =	1.1	1.1
bkgd	$^1/_4$ scan time at each end of scan	$^1/_4$ scan time at each end of scan
ω-scan rate[a] (deg/min)	4.0	4.0
no. of reflctns measd	5785	5172
data used ($F^2 \geq 3.0\sigma(F^2)$)	4777	3123
	(C) Treatment of Data	
absorptn correctn	empirical	empirical
coeff (cm^{-1})	32.03	20.46
transmission coeff		
max	1.000	1.000
min	0.659	0.852
no. of variables (refined)	446	460
P factor	0.01	0.02
final residuals		
R_F	0.025	0.035
R_{wF}	0.023	0.035
goodness of fit indicator	1.56	1.21
largest shift/error value of final cycle	0.03	0.01
largest peak in final diff Fourier (e/Å^3)	0.26	0.60

[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.

Results

The reaction of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (**1**) with $Ru(CO)_5$ at 68 °C yielded the two higher nuclearity ruthenium carbonyl cluster complexes $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (**2**, 28%) and $Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (**3**, 35%). Compound **2** was characterized by IR and ^1H NMR spectroscopy and by a single-crystal X-ray diffraction analysis. Compound **3** was characterized by IR and ^1H NMR spectroscopy, by mass spectrometry, and by a single-crystal X-ray diffraction analysis of its bis(dimethylphenylphosphine) derivative $Ru_5(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (**4**).

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

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[12] *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 II. Positional Parameters and *B*(eq) for $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (2)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru(1)	0.65222 (3)	0.14105 (5)	0.07288 (2)	2.39 (2)
Ru(2)	0.78555 (3)	0.14808 (5)	−0.01386 (2)	2.71 (2)
Ru(3)	0.65564 (3)	0.34895 (4)	0.16279 (2)	2.52 (2)
Ru(4)	0.68563 (3)	0.06673 (4)	0.19280 (2)	2.18 (2)
Ru(5)	0.80272 (3)	0.32857 (4)	0.08107 (2)	2.19 (2)
Ru(6)	0.83044 (3)	0.04683 (4)	0.10196 (2)	2.05 (2)
Ru(7)	0.83160 (3)	0.24061 (4)	0.20016 (2)	2.08 (2)
O(11)	0.5238 (3)	0.3380 (5)	0.0115 (2)	6.6 (3)
O(12)	0.4932 (3)	−0.0114 (5)	0.1282 (2)	5.7 (3)
O(13)	0.5997 (3)	−0.0852 (5)	−0.0119 (2)	5.6 (3)
O(21)	0.7777 (3)	−0.1090 (5)	−0.0878 (2)	5.3 (3)
O(22)	0.9659 (3)	0.2280 (5)	−0.0694 (2)	4.5 (2)
O(23)	0.6773 (3)	0.2903 (6)	−0.1098 (2)	6.9 (3)
O(31)	0.5899 (3)	0.5988 (5)	0.0945 (2)	5.3 (3)
O(32)	0.4583 (3)	0.2857 (5)	0.1865 (3)	6.8 (3)
O(33)	0.6624 (3)	0.5011 (6)	0.2802 (2)	6.5 (3)
O(41)	0.6732 (3)	−0.2393 (5)	0.1934 (2)	5.6 (3)
O(42)	0.5461 (3)	0.1006 (5)	0.2907 (2)	5.1 (2)
O(51)	0.7282 (3)	0.5190 (5)	−0.0142 (2)	5.5 (3)
O(52)	0.8387 (3)	0.5740 (4)	0.1601 (2)	4.2 (2)
O(53)	0.9991 (3)	0.3955 (5)	0.0501 (2)	5.0 (2)
O(61)	0.9222 (3)	−0.1311 (4)	0.1957 (2)	4.2 (2)
O(62)	0.7841 (4)	−0.2242 (5)	0.0453 (2)	6.5 (3)
O(63)	1.0215 (3)	0.0896 (4)	0.0528 (2)	4.0 (2)
O(71)	0.8582 (3)	0.4166 (5)	0.3087 (2)	5.2 (2)
O(72)	1.0368 (3)	0.2020 (5)	0.1925 (2)	4.8 (2)
N(1)	0.8172 (3)	0.0253 (5)	0.2974 (2)	3.0 (2)
C(1)	0.7894 (3)	0.0882 (5)	0.2500 (2)	2.4 (2)
C(2)	0.7684 (4)	−0.0881 (6)	0.3252 (3)	4.3 (3)
C(3)	0.9057 (4)	0.0582 (7)	0.3259 (3)	4.9 (3)
C(11)	0.5715 (4)	0.2646 (7)	0.0349 (3)	4.0 (3)
C(12)	0.5599 (4)	0.0458 (7)	0.1208 (3)	3.9 (3)
C(13)	0.6268 (4)	0.0013 (7)	0.0172 (3)	3.7 (3)
C(21)	0.7808 (4)	−0.0139 (7)	−0.0598 (2)	3.5 (3)
C(22)	0.8978 (4)	0.1970 (6)	−0.0481 (2)	3.3 (3)
C(23)	0.7181 (4)	0.2373 (7)	−0.0740 (3)	4.0 (3)
C(31)	0.6160 (4)	0.5044 (6)	0.1185 (3)	3.5 (3)
C(32)	0.5337 (4)	0.3067 (6)	0.1784 (3)	4.7 (4)
C(33)	0.6621 (4)	0.4414 (7)	0.2362 (3)	3.9 (3)
C(41)	0.6779 (4)	−0.1241 (6)	0.1927 (3)	3.3 (3)
C(42)	0.5984 (4)	0.0890 (6)	0.2529 (3)	3.1 (3)
C(51)	0.7534 (4)	0.4450 (6)	0.0204 (3)	3.4 (3)
C(52)	0.8181 (4)	0.4711 (6)	0.1402 (2)	3.1 (3)
C(53)	0.9261 (4)	0.3637 (6)	0.0593 (2)	3.1 (3)
C(61)	0.8848 (4)	−0.0608 (6)	0.1639 (2)	2.8 (3)
C(62)	0.7971 (4)	−0.1197 (6)	0.0641 (3)	3.6 (3)
C(63)	0.9474 (4)	0.0759 (6)	0.0685 (2)	2.9 (3)
C(71)	0.8455 (4)	0.3524 (6)	0.2668 (2)	3.1 (3)
C(72)	0.9600 (4)	0.2183 (5)	0.1952 (2)	2.8 (3)
H	0.751 (3)	0.186 (5)	0.131 (2)	4 (1)
H(21)	0.7797	−0.0951	0.3682	5.0
H(22)	0.8015	−0.1795	0.3053	5.0
H(23)	0.7196	−0.1246	0.3175	5.0
H(31)	0.9310	0.0173	0.3604	5.0
H(32)	0.9119	−0.0561	0.3309	5.0
H(33)	0.9408	0.1384	0.3106	5.0

angles are listed in Tables III and IV. The cluster consists of seven metal atoms arranged in the form of a capped octahedron with a hydride ligand on the interior of the octahedron. The ruthenium–ruthenium bond distances span a wide range, 2.7371 (6) –2.9417 (6) Å. The shortest metal–metal bond Ru(4)–Ru(7) is bridged by the carbon atom C(1) of the (dimethylamino)carbyne ligand. The Ru–C distances to the carbyne ligand, Ru(4)–C(1) = 1.992 (5) Å and Ru(7)–C(1) = 1.969 (5) Å, are similar to those observed in the compounds $Ru_3(CO)_{10}(\mu_3\text{-}CNMe_2)(\mu\text{-}H)$,[13] $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}CNMe_2)$ (**5**),[10] and $Ru_6(C)(CO)_{14}(\mu\text{-}CNMe_2)_2$.[10] The distances Ru(1)–Ru(2) = 2.7522 (7) Å and Ru(2)–Ru(5) = 2.7806 (7) Å to the capping atom Ru(2) are the next shortest metal–metal bonds. Structural studies of osmium cluster complexes have shown the metal–metal bonds to capping $Os(CO)_3$ groups are usually shorter than those in the cluster. Except for the short Ru(4)–Ru(7) bond, Ru–Ru bonds in the octahedral Ru_6 group are similar to those in the cluster anion $[Ru_6(CO)_{18}(\mu_6\text{-}H)]^-$ (**6**)[17] which also contains an interstitial hydride ligand. Due to the high quality of this structure, the interstitial hydride ligand was easily located and refined. An interesting feature is that the hydride ligand apparently does not lie exactly in the center of the octahedron, as it does in **6**[18] but appears to be shifted toward the capped triangular face Ru(1), Ru(5), and Ru(6). The distances Ru(1)–H = 1.98 (5) Å, Ru(5)–H = 1.94 (5) Å, and Ru(6)–H = 1.90 (5) Å are all shorter than the distances to

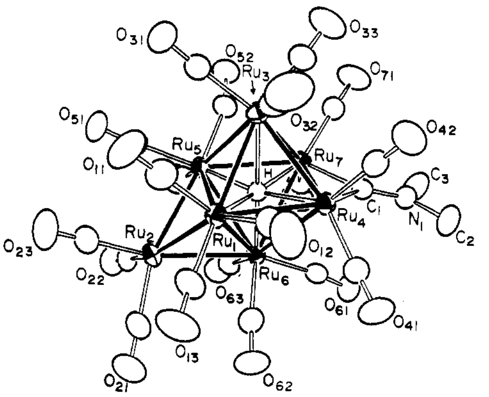

Figure 1. An ORTEP diagram of $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (**2**) showing 50% probability thermal ellipsoids.

Table III. Intramolecular Distances (Å) for $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (2)[a]

Ru(1)–C(13)	1.893 (6)	Ru(5)–C(53)	1.899 (6)
Ru(1)–C(11)	1.893 (7)	Ru(5)–C(51)	1.915 (6)
Ru(1)–C(12)	1.962 (6)	Ru(5)–C(52)	1.942 (6)
Ru(1)–Ru(2)	2.7522 (7)	Ru(5)–Ru(7)	2.8333 (7)
Ru(1)–Ru(4)	2.8231 (7)	Ru(5)–Ru(6)	2.8418 (8)
Ru(1)–Ru(6)	2.8352 (6)	Ru(6)–C(63)	1.887 (6)
Ru(1)–Ru(3)	2.8705 (7)	Ru(6)–C(62)	1.908 (6)
Ru(1)–Ru(5)	2.8743 (7)	Ru(6)–C(61)	1.915 (6)
Ru(2)–C(22)	1.873 (6)	Ru(6)–Ru(7)	2.9105 (7)
Ru(2)–C(23)	1.884 (6)	Ru(7)–C(71)	1.864 (6)
Ru(2)–C(21)	1.899 (6)	Ru(7)–C(72)	1.890 (6)
Ru(2)–Ru(5)	2.7806 (7)	Ru(7)–C(1)	1.969 (5)
Ru(2)–Ru(6)	2.8521 (7)	N(1)–C(1)	1.292 (6)
Ru(3)–C(32)	1.860 (6)	N(1)–C(2)	1.464 (7)
Ru(3)–C(33)	1.880 (6)	N(1)–C(3)	1.476 (7)
Ru(3)–C(31)	1.911 (6)	Ru(1)–H	1.980 (5)
Ru(3)–Ru(5)	2.8296 (7)	Ru(3)–H	2.250 (5)
Ru(3)–Ru(4)	2.8916 (8)	Ru(4)–H	2.060 (5)
Ru(3)–Ru(7)	2.9016 (6)	Ru(5)–H	1.940 (5)
Ru(4)–C(42)	1.866 (6)	Ru(6)–H	1.900 (5)
Ru(4)–C(41)	1.882 (6)	Ru(7)–H	2.020 (5)
Ru(4)–C(1)	1.992 (5)	Ru(4)–C(12)	2.448 (6)
Ru(4)–Ru(7)	2.7371 (6)	Ru(7)–C(52)	2.643 (6)
Ru(4)–Ru(6)	2.9417 (6)		

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

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Table IV. Intramolecular Bond Angles (deg) for $Ru_7(CO)_{19}(\mu\text{-}CNMe_2)(\mu_6\text{-}H)$ (2)[a]

C(13)–Ru(1)–Ru(2)	72.0 (2)	Ru(1)–Ru(3)–Ru(7)	87.37 (2)	C(63)–Ru(6)–Ru(1)	133.6 (2)
C(13)–Ru(1)–Ru(4)	118.1 (2)	Ru(4)–Ru(3)–Ru(7)	56.39 (1)	C(63)–Ru(6)–Ru(5)	85.1 (2)
C(13)–Ru(1)–Ru(6)	95.2 (2)	C(42)–Ru(4)–C(41)	94.4 (2)	C(63)–Ru(6)–Ru(2)	78.0 (2)
C(13)–Ru(1)–Ru(3)	169.5 (2)	C(42)–Ru(4)–C(1)	92.5 (2)	C(63)–Ru(6)–Ru(7)	101.4 (2)
C(13)–Ru(1)–Ru(5)	131.1 (2)	C(42)–Ru(4)–Ru(7)	114.5 (2)	C(63)–Ru(6)–Ru(4)	156.3 (2)
C(11)–Ru(1)–Ru(2)	96.1 (2)	C(42)–Ru(4)–Ru(1)	122.5 (2)	C(62)–Ru(6)–C(61)	87.2 (2)
C(11)–Ru(1)–Ru(4)	134.4 (2)	C(42)–Ru(4)–Ru(3)	87.2 (2)	C(62)–Ru(6)–Ru(1)	86.9 (2)
C(11)–Ru(1)–Ru(6)	151.9 (2)	C(42)–Ru(4)–Ru(6)	176.1 (2)	C(62)–Ru(6)–Ru(5)	136.8 (2)
C(11)–Ru(1)–Ru(3)	82.3 (2)	C(42)–Ru(4)–C(1)	98.8 (2)	C(62)–Ru(6)–Ru(2)	80.7 (2)
C(11)–Ru(1)–Ru(5)	95.2 (2)	C(41)–Ru(4)–Ru(7)	132.1 (2)	C(62)–Ru(6)–Ru(7)	154.1 (2)
C(12)–Ru(1)–Ru(2)	152.2 (2)	C(41)–Ru(4)–Ru(1)	104.3 (2)	C(62)–Ru(6)–Ru(4)	100.5 (2)
C(12)–Ru(1)–Ru(4)	58.3 (2)	C(42)–Ru(4)–Ru(3)	161.8 (2)	C(61)–Ru(6)–Ru(1)	136.5 (2)
C(12)–Ru(1)–Ru(6)	110.4 (2)	C(41)–Ru(4)–Ru(6)	88.6 (2)	C(61)–Ru(6)–Ru(5)	135.9 (2)
C(12)–Ru(1)–Ru(3)	88.2 (2)	C(1)–Ru(4)–Ru(7)	45.9 (1)	C(61)–Ru(6)–Ru(2)	160.9 (1)
C(12)–Ru(1)–Ru(5)	142.9 (2)	C(1)–Ru(4)–Ru(1)	135.5 (1)	C(61)–Ru(6)–Ru(7)	79.3 (2)
Ru(2)–Ru(1)–Ru(4)	123.79 (2)	C(1)–Ru(4)–Ru(3)	99.3 (1)	C(61)–Ru(6)–Ru(4)	80.4 (1)
Ru(2)–Ru(1)–Ru(6)	61.37 (2)	C(1)–Ru(4)–Ru(6)	84.6 (1)	Ru(1)–Ru(6)–Ru(5)	60.84 (2)
Ru(2)–Ru(1)–Ru(3)	117.73 (2)	Ru(7)–Ru(4)–Ru(1)	91.60 (2)	Ru(1)–Ru(6)–Ru(2)	57.88 (2)
Ru(2)–Ru(1)–Ru(5)	59.19 (2)	Ru(7)–Ru(4)–Ru(3)	61.99 (2)	Ru(1)–Ru(6)–Ru(7)	87.86 (2)
Ru(4)–Ru(1)–Ru(6)	62.65 (2)	Ru(7)–Ru(4)–Ru(6)	61.54 (2)	Ru(1)–Ru(6)–Ru(4)	58.47 (2)
Ru(4)–Ru(1)–Ru(3)	61.04 (2)	Ru(1)–Ru(4)–Ru(3)	60.29 (1)	Ru(5)–Ru(6)–Ru(2)	58.46 (2)
Ru(4)–Ru(1)–Ru(5)	88.60 (2)	Ru(1)–Ru(4)–Ru(6)	58.88 (2)	Ru(5)–Ru(6)–Ru(7)	59.00 (2)
Ru(6)–Ru(1)–Ru(3)	93.32 (2)	Ru(3)–Ru(4)–Ru(6)	90.69 (2)	Ru(5)–Ru(6)–Ru(4)	86.93 (2)
Ru(6)–Ru(1)–Ru(5)	59.69 (2)	C(53)–Ru(5)–C(51)	93.6 (2)	Ru(2)–Ru(6)–Ru(7)	117.27 (2)
Ru(3)–Ru(1)–Ru(5)	59.02 (2)	C(53)–Ru(5)–C(52)	86.3 (2)	Ru(2)–Ru(6)–Ru(4)	116.17 (2)
C(22)–Ru(2)–Ru(1)	156.2 (2)	C(53)–Ru(5)–Ru(2)	90.2 (2)	Ru(7)–Ru(6)–Ru(4)	55.77 (1)
C(22)–Ru(2)–Ru(5)	94.1 (2)	C(53)–Ru(5)–Ru(3)	151.0 (2)	C(71)–Ru(7)–C(72)	90.5 (2)
C(22)–Ru(2)–Ru(6)	105.2 (2)	C(53)–Ru(5)–Ru(7)	99.1 (2)	C(71)–Ru(7)–C(1)	91.7 (2)
C(23)–Ru(2)–Ru(1)	98.4 (2)	C(53)–Ru(5)–Ru(6)	94.9 (2)	C(71)–Ru(7)–Ru(4)	120.1 (2)
C(23)–Ru(2)–Ru(5)	107.1 (2)	C(53)–Ru(5)–Ru(1)	145.6 (2)	C(71)–Ru(7)–Ru(5)	126.0 (2)
C(23)–Ru(2)–Ru(6)	158.6 (2)	C(51)–Ru(5)–C(52)	95.4 (2)	C(71)–Ru(7)–Ru(3)	96.2 (2)
C(21)–Ru(2)–Ru(1)	109.6 (2)	C(51)–Ru(5)–Ru(2)	78.9 (2)	C(71)–Ru(7)–Ru(6)	172.6 (2)
C(21)–Ru(2)–Ru(5)	162.5 (2)	C(51)–Ru(5)–Ru(3)	97.5 (2)	C(72)–Ru(7)–C(1)	104.8 (2)
C(21)–Ru(2)–Ru(6)	101.9 (2)	C(51)–Ru(5)–Ru(7)	154.7 (2)	C(72)–Ru(7)–Ru(4)	134.0 (2)
Ru(1)–Ru(2)–Ru(5)	62.60 (2)	C(51)–Ru(5)–Ru(6)	138.9 (2)	C(72)–Ru(7)–Ru(5)	97.2 (2)
Ru(1)–Ru(2)–Ru(6)	60.75 (2)	C(51)–Ru(5)–Ru(1)	93.1 (2)	C(72)–Ru(7)–Ru(3)	154.5 (2)
Ru(5)–Ru(2)–Ru(6)	60.58 (2)	C(52)–Ru(5)–Ru(2)	173.1 (2)	C(72)–Ru(7)–Ru(6)	83.3 (1)
C(32)–Ru(3)–Ru(5)	146.3 (2)	C(52)–Ru(5)–Ru(3)	66.1 (2)	C(1)–Ru(7)–Ru(4)	46.6 (1)
C(32)–Ru(3)–Ru(1)	87.5 (2)	C(52)–Ru(5)–Ru(7)	64.1 (2)	C(1)–Ru(7)–Ru(5)	136.0 (1)
C(32)–Ru(3)–Ru(4)	83.5 (2)	C(52)–Ru(5)–Ru(6)	125.2 (2)	C(1)–Ru(7)–Ru(3)	99.5 (1)
C(32)–Ru(3)–Ru(7)	135.2 (2)	C(52)–Ru(5)–Ru(1)	126.5 (2)	C(1)–Ru(7)–Ru(6)	85.8 (1)
C(33)–Ru(3)–Ru(5)	124.2 (2)	Ru(2)–Ru(5)–Ru(3)	118.16 (2)	Ru(4)–Ru(7)–Ru(5)	91.17 (2)
C(33)–Ru(3)–Ru(1)	163.4 (2)	Ru(2)–Ru(5)–Ru(7)	122.44 (2)	Ru(4)–Ru(7)–Ru(3)	61.62 (2)
C(33)–Ru(3)–Ru(4)	104.8 (2)	Ru(2)–Ru(5)–Ru(6)	60.95 (2)	Ru(4)–Ru(7)–Ru(6)	62.69 (2)
C(33)–Ru(3)–Ru(7)	83.3 (2)	Ru(2)–Ru(5)–Ru(1)	58.22 (2)	Ru(5)–Ru(7)–Ru(3)	59.11 (2)
C(31)–Ru(3)–Ru(5)	87.2 (2)	Ru(3)–Ru(5)–Ru(7)	61.65 (2)	Ru(5)–Ru(7)–Ru(6)	59.29 (2)
C(31)–Ru(3)–Ru(1)	101.7 (2)	Ru(3)–Ru(5)–Ru(6)	94.06 (2)	Ru(3)–Ru(7)–Ru(6)	91.12 (2)
C(31)–Ru(3)–Ru(4)	159.2 (2)	Ru(3)–Ru(5)–Ru(1)	60.43 (2)	C(1)–N(1)–C(2)	124.2 (5)
C(31)–Ru(3)–Ru(7)	135.2 (2)	Ru(7)–Ru(5)–Ru(6)	61.71 (1)	C(1)–N(1)–C(3)	121.5 (5)
Ru(5)–Ru(3)–Ru(1)	60.56 (2)	Ru(7)–Ru(5)–Ru(1)	88.61 (2)	C(2)–N(1)–C(3)	114.2 (5)
Ru(5)–Ru(3)–Ru(4)	88.13 (2)	Ru(6)–Ru(5)–Ru(1)	59.47 (2)	N(1)–C(1)–Ru(7)	137.1 (4)
Ru(5)–Ru(3)–Ru(7)	59.24 (2)	C(63)–Ru(6)–C(62)	100.6 (2)	N(1)–C(1)–Ru(4)	135.5 (4)
Ru(1)–Ru(3)–Ru(4)	58.67 (2)	C(63)–Ru(6)–C(61)	89.9 (2)	Ru(7)–C(1)–Ru(4)	87.4 (2)

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

the atoms Ru(3), Ru(4), and Ru(7), Ru(3)–H = 2.25 (5) Å, Ru(4)–H = 2.06 (5) Å, and Ru(7)–H = 2.02 (5) Å, although the the significance of the differences could be debated in view of the size of the estimated standard deviations, 0.05 Å. Unsymmetrically bonded μ_6-H ligands have been observed in the octahedral cavities of some high nuclearity nickel carbonyl cluster complexes.[19] An interesting feature of interstitial hydride ligands is that they occasionally exhibit very low-field resonance shifts in their ^{1}H NMR spectra (e.g., the shift position of the hydride ligand in 6 is +16.43 ppm). The hydride resonance of 2 also exhibits a very low-field shift value, δ 11.42. The C(1)–N(1) distance in the (dimethylamino)carbyne ligand is characteristically short, 1.292 (6) Å.[10,13] The molecule contains an approximate plane of symmetry that passes through the carbyne ligand; thus, the methyl groups are equivalent, δ 3.95. Compound 2 contains 19 carbonyl ligands distributed about the cluster as shown in Figure 1. All the carbonyl ligands are of a linear terminal type, except for C(12)–O(12) and C(52)–O(52) which are semibridging ligands, Ru(4)···C(12) = 2.448 (6) and Ru(7)···C(52) = 2.643 (6) Å.

The molecular formula for 3, $Ru_5(CO)_{14}(\mu\text{-}CNMe_2)(\mu\text{-}H)$, was obtained from the parent ion observed in its mass spectrum, *m/e* 956 for ^{104}Ru. The isotope distribution pattern is consistent with the presence of five ruthenium atoms. Peaks due to the loss of each of the 14 carbonyl ligands were prominently displayed. The ^{1}H NMR spectrum showed resonances at 3.45 (6 H) and −22.05 (1 H) ppm due to the methyl groups on the carbyne ligand and the hydride ligand, respectively. Numerous attempts to obtain single crystals of 3 for a crystallographic structural analysis were unsuccessful. Therefore, the bis(phosphine) derivative 4 was prepared. Crystals of 4 suitable for a crystallographic analysis were obtained, and the analysis was performed. An ORTEP drawing of the molecular structure of 4 is shown in Figure 2. Final positional parameters are listed in Table V. Selected interatomic

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[19] Broach, R. W.; Dahl, L.; Longoni, G.; Chini, P.; Schultz, A. J.; Williams, J. M., *Adv. Chem. Ser.* 1978, *No. 167*, 93.

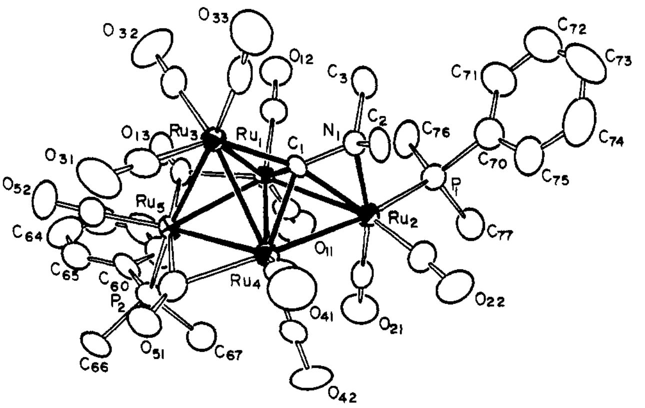


Figure 2. An ORTEP diagram of $Ru_5(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (4) showing 50% probability thermal ellipsoids.

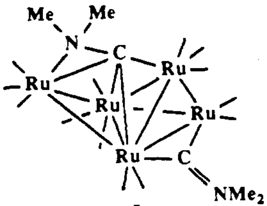
Table V. Positional Parameters for $Ru_5(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (4)

atom	x	y	z	B(eq), Å^2
Ru(1)	0.79196 (6)	0.19621 (7)	0.92909 (4)	2.02 (4)
Ru(2)	0.72569 (6)	0.06704 (7)	0.81199 (4)	2.21 (4)
Ru(3)	0.68650 (6)	0.10204 (7)	1.00598 (4)	2.24 (4)
Ru(4)	0.60287 (6)	0.16838 (7)	0.87162 (4)	2.10 (4)
Ru(5)	0.67247 (6)	0.32502 (7)	0.96947 (4)	2.21 (4)
P(1)	0.8454 (2)	−0.0053 (3)	0.7789 (2)	2.8 (1)
P(2)	0.6657 (2)	0.4996 (2)	0.9272 (2)	2.6 (1)
O(11)	0.8828 (6)	0.3349 (8)	0.8453 (4)	5.6 (5)
O(12)	0.9672 (5)	0.1121 (7)	1.0134 (4)	4.3 (4)
O(13)	0.8684 (5)	0.3623 (7)	1.0489 (4)	4.2 (4)
O(21)	0.7190 (6)	0.2611 (7)	0.7222 (4)	5.2 (5)
O(22)	0.5805 (6)	−0.0410 (7)	0.7041 (4)	4.7 (4)
O(31)	0.5304 (6)	0.1680 (8)	1.0597 (5)	5.8 (5)
O(32)	0.8340 (6)	0.145 (1)	1.1346 (4)	6.5 (5)
O(33)	0.6702 (7)	−0.1305 (7)	1.0530 (5)	6.0 (5)
O(41)	0.4374 (6)	0.0304 (7)	0.8451 (5)	5.0 (4)
O(42)	0.5157 (7)	0.2631 (9)	0.7331 (5)	6.0 (5)
O(51)	0.4671 (5)	0.3155 (7)	0.9193 (4)	3.5 (4)
O(52)	0.6435 (6)	0.4131 (8)	1.0967 (4)	4.8 (4)
N(1)	0.7236 (5)	−0.0455 (7)	0.8905 (4)	2.1 (4)
C(1)	0.7068 (7)	0.0580 (8)	0.9166 (5)	2.0 (4)
C(2)	0.6507 (8)	−0.1266 (9)	0.8765 (5)	3.1 (5)
C(3)	0.8069 (7)	−0.101 (1)	0.9294 (5)	2.9 (5)
C(11)	0.8476 (7)	0.280 (1)	0.8762 (6)	2.9 (5)
C(12)	0.8992 (7)	0.140 (1)	0.9796 (6)	2.8 (5)
C(13)	0.8076 (8)	0.326 (1)	1.0085 (5)	2.7 (5)
C(21)	0.7216 (8)	0.188 (1)	0.7571 (5)	3.1 (5)
C(22)	0.6398 (8)	−0.001 (1)	0.7443 (6)	2.9 (5)
C(31)	0.5888 (8)	0.146 (1)	1.0404 (6)	3.8 (6)
C(32)	0.7778 (8)	0.131 (1)	1.0863 (6)	3.5 (6)
C(33)	0.6788 (9)	−0.046 (1)	1.0325 (6)	3.6 (6)
C(41)	0.5024 (8)	0.081 (1)	0.8560 (6)	3.3 (5)
C(42)	0.5516 (7)	0.232 (1)	0.7857 (6)	3.1 (5)
C(51)	0.5402 (8)	0.293 (1)	0.9224 (5)	2.8 (5)
C(52)	0.6521 (7)	0.381 (1)	1.0476 (6)	3.0 (5)

Table VI. Intramolecular Distances (Å) for $Ru_5(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (4)[a]

Ru(1)–C(12)	1.84 (1)	Ru(3)–Ru(4)	2.829 (2)
Ru(1)–C(11)	1.88 (1)	Ru(4)–C(41)	1.85 (1)
Ru(1)–C(1)	2.12 (1)	Ru(4)–C(42)	1.90 (1)
Ru(1)–C(13)	2.24 (1)	Ru(4)–C(1)	2.12 (1)
Ru(1)–Ru(5)	2.744 (1)	Ru(4)–C(51)	2.22 (1)
Ru(1)–Ru(2)	2.828 (2)	Ru(4)–Ru(5)	2.776 (2)
Ru(1)–Ru(3)	2.831 (2)	Ru(5)–C(52)	1.86 (1)
Ru(1)–Ru(4)	2.876 (2)	Ru(5)–C(13)	2.04 (1)
Ru(2)–C(22)	1.84 (1)	Ru(5)–C(51)	2.06 (1)
Ru(2)–C(21)	1.86 (1)	Ru(5)–P(2)	2.301 (3)
Ru(2)–N(1)	2.133 (8)	P(1)–C(77)	1.79 (1)
Ru(2)–C(1)	2.26 (1)	P(1)–C(76)	1.81 (1)
Ru(2)–P(1)	2.336 (3)	P(1)–C(70)	1.83 (1)
Ru(2)–Ru(4)	2.837 (2)	P(2)–C(67)	1.80 (1)
Ru(3)–C(32)	1.89 (1)	P(2)–C(66)	1.80 (1)
Ru(3)–C(33)	1.91 (1)	P(2)–C(60)	1.81 (1)
Ru(3)–C(31)	1.93 (1)	N(1)–C(1)	1.43 (1)
Ru(3)–C(1)	2.03 (1)	N(1)–C(2)	1.48 (1)
Ru(3)–Ru(5)	2.826 (1)	N(1)–C(3)	1.49 (1)

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



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distances and angles are listed in Tables V and VI, respectively. The molecule consists of a cluster of five ruthenium atoms arranged in the form of a capped butterfly tetrahedron. A quadruply bridging (dimethylamino)carbyne ligand, $CNMe_2$, lies in the fold of the butterfly. Compound 4 is structurally similar to the pentaruthenium bis(dimethylamino)carbyne cluster complex 5.[10] The shortest metal–metal bonds in 4 are the two CO-bridged bonds, Ru(1)–Ru(5) = 2.744 (1) Å and Ru(4)–Ru(5) = 2.776 (2) Å, to the capping metal atom Ru(5). The nonbridged bond Ru(3)–Ru(5) is significantly longer, 2.826 (1) Å. The bonds around the periphery of the butterfly are very similar, range 2.828 (2) –2.837 (2) Å, and are similar to those in 5. The hinge bond Ru(1)–Ru(4) is the longest in the molecule, 2.876 (2) Å, and is believed to be bridged by a hydride ligand; see below. The carbyne ligand exhibits the quadruply bridging coordination mode that was also found in 1[10] and 5. The carbon atom is asymmetrically bonded to the four metal atoms, range 2.03 (1) –2.26 (1) Å, with the longest bond to the metal atom Ru(2) that also contains a bond to the nitrogen atom, Ru(2)–N(1) = 2.133 (8) Å. The quadruply bridging (dimethylamino)carbyne ligands in 1 and 5 are bonded similarly. The C(1)–N(1) distance of 1.43 (1) Å is significantly longer than that of *edge-bridging* aminocarbyne ligands[13] but is similar to the C–N distances of 1.435 (7) and 1.434 (6) Å found for the quadruply bridging ligands in 1 and 5, respectively.[10] Compound 4 contains a hydride ligand as indicated by its high-field NMR shift, δ −21.14. The position of this ligand was not established directly from the structural analysis, but an examination of the structure suggests that the probable site is a bridging position across the Ru(1)–Ru(4) bond. The reasons for this assignment are as follows: (1) the long length of the Ru(1)–Ru(4) bond (the longest in the molecule) (bridging hydride ligands are known to cause an elongation of metal–metal bonds),[13] (2) large Ru–Ru–C angles to the CO ligands, Ru(4)–Ru(1)–C(11) = 114.5 (3)° and Ru(1)–Ru(4)–C(42) = 116.8 (3)°, compared to those in 5; and (3) the bridging hydride ligand in 1 was found at the corresponding site in the structural analysis of that compound.[10] Compound 4 contains 12 carbonyl ligands. Two of these, C(13)–O(13) and C(51)–O(51), are bridging ligands. All the others are terminal ligands distributed as shown in Figure 2. Compound 4 contains two PMe_2Ph ligands. These are coordinated Ru(2), Ru(2)–P(1) = 2.336 (3) Å, and the capping atom Ru(5), Ru(5)–P(2) = 2.301 (3) Å. They exhibit no unusual bonding distortions.

The ^1H NMR spectrum of 4 shows separate resonances for the two methyl groups on the nitrogen atom of the carbyne ligand. This is consistent with the solid-state structure of the molecule that contains no symmetry. Likewise the diastereotopic methyl groups on one of the phosphine ligands appear as separate doublets (at 300 MHz) although there are slightly broader than usual. The methyl groups of the second phosphine ligand appear as

Scheme I

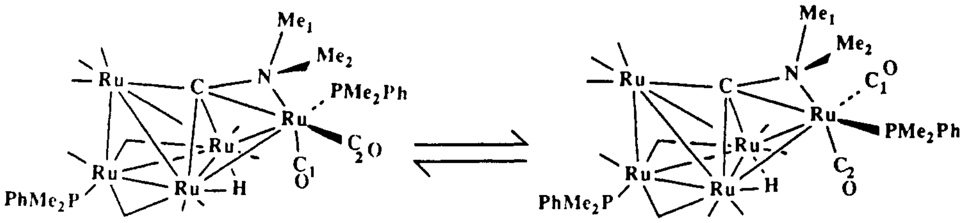

Table VII. Intramolecular Bond Angles (deg) for $Ru_5(CO)_{12}(PMe_2Ph)_2(\mu_4\text{-}\eta^2\text{-}CNMe_2)(\mu\text{-}H)$ (4)[a]

C(12)–Ru(1)–Ru(5)	129.1 (3)	C(41)–Ru(4)–Ru(1)	149.5 (3)
C(12)–Ru(1)–Ru(2)	109.3 (3)	C(42)–Ru(4)–Ru(5)	111.7 (4)
C(12)–Ru(1)–Ru(3)	96.3 (3)	C(42)–Ru(4)–Ru(3)	172.2 (4)
C(12)–Ru(1)–Ru(4)	148.8 (3)	C(42)–Ru(4)–Ru(2)	86.3 (3)
C(11)–Ru(1)–Ru(5)	109.0 (3)	C(42)–Ru(4)–Ru(1)	116.8 (3)
C(11)–Ru(1)–Ru(2)	85.9 (4)	C(1)–Ru(4)–Ru(5)	91.6 (3)
C(11)–Ru(1)–Ru(3)	169.7 (3)	C(1)–Ru(4)–Ru(3)	45.6 (3)
C(11)–Ru(1)–Ru(4)	114.5 (3)	C(1)–Ru(4)–Ru(2)	51.8 (3)
C(1)–Ru(1)–Ru(5)	92.3 (3)	C(1)–Ru(4)–Ru(1)	47.4 (3)
C(1)–Ru(1)–Ru(2)	52.0 (3)	C(51)–Ru(4)–Ru(5)	47.0 (3)
C(1)–Ru(1)–Ru(3)	45.6 (3)	C(51)–Ru(4)–Ru(3)	83.1 (3)
C(1)–Ru(1)–Ru(4)	47.2 (3)	C(51)–Ru(4)–Ru(2)	160.6 (3)
C(13)–Ru(1)–Ru(5)	46.9 (3)	C(51)–Ru(4)–Ru(1)	105.1 (3)
C(13)–Ru(1)–Ru(2)	163.2 (3)	Ru(5)–Ru(4)–Ru(3)	60.56 (4)
C(13)–Ru(1)–Ru(3)	80.9 (3)	Ru(5)–Ru(4)–Ru(2)	116.31 (5)
C(13)–Ru(1)–Ru(4)	105.9 (3)	Ru(5)–Ru(4)–Ru(1)	58.08 (4)
Ru(5)–Ru(1)–Ru(2)	117.62 (5)	Ru(3)–Ru(4)–Ru(2)	96.65 (5)
Ru(5)–Ru(1)–Ru(3)	60.90 (4)	Ru(3)–Ru(4)–Ru(1)	59.49 (4)
Ru(5)–Ru(1)–Ru(4)	59.14 (4)	Ru(2)–Ru(4)–Ru(1)	59.35 (4)
Ru(2)–Ru(1)–Ru(3)	96.80 (5)	C(52)–Ru(5)–Ru(1)	140.4 (3)
Ru(2)–Ru(1)–Ru(4)	59.64 (4)	C(52)–Ru(5)–Ru(4)	139.2 (3)
Ru(3)–Ru(1)–Ru(4)	59.44 (4)	C(52)–Ru(5)–Ru(3)	98.2 (4)
C(22)–Ru(2)–Ru(1)	156.1 (3)	C(13)–Ru(5)–C(51)	168.0 (5)
C(22)–Ru(2)–Ru(4)	95.2 (3)	C(13)–Ru(5)–Ru(1)	53.5 (3)
C(21)–Ru(2)–Ru(1)	90.8 (3)	C(13)–Ru(5)–Ru(4)	116.2 (3)
C(21)–Ru(2)–Ru(4)	90.1 (3)	C(13)–Ru(5)–Ru(3)	84.5 (3)
N(1)–Ru(2)–Ru(1)	78.1 (2)	C(51)–Ru(5)–Ru(1)	115.0 (3)
N(1)–Ru(2)–Ru(4)	78.4 (2)	C(51)–Ru(5)–Ru(4)	52.2 (3)
C(1)–Ru(2)–P(1)	126.0 (3)	C(51)–Ru(5)–Ru(3)	86.1 (3)
C(1)–Ru(2)–Ru(1)	47.7 (3)	P(2)–Ru(5)–Ru(1)	112.54 (8)
C(1)–Ru(2)–Ru(4)	47.4 (2)	P(2)–Ru(5)–Ru(4)	113.64 (9)
P(1)–Ru(2)–Ru(1)	109.27 (9)	P(2)–Ru(5)–Ru(3)	172.54 (9)
P(1)–Ru(2)–Ru(4)	170.22 (9)	Ru(1)–Ru(5)–Ru(4)	62.79 (4)
Ru(1)–Ru(2)–Ru(4)	61.00 (4)	Ru(1)–Ru(5)–Ru(3)	61.06 (4)
C(32)–Ru(3)–Ru(5)	92.1 (4)	Ru(4)–Ru(5)–Ru(3)	60.66 (4)
C(32)–Ru(3)–Ru(4)	146.3 (4)	C(1)–N(1)–C(2)	117.2 (8)
C(32)–Ru(3)–Ru(1)	90.1 (4)	C(1)–N(1)–C(3)	115.3 (8)
C(33)–Ru(3)–Ru(5)	171.5 (4)	C(1)–N(1)–Ru(2)	75.9 (5)
C(33)–Ru(3)–Ru(4)	120.3 (4)	C(2)–N(1)–C(3)	107.8 (8)
C(33)–Ru(3)–Ru(1)	129.9 (3)	C(2)–N(1)–Ru(2)	117.5 (6)
C(31)–Ru(3)–Ru(5)	79.6 (4)	C(3)–N(1)–Ru(2)	120.5 (6)
C(31)–Ru(3)–Ru(4)	94.9 (3)	N(1)–C(1)–Ru(3)	132.1 (7)
C(31)–Ru(3)–Ru(1)	137.5 (4)	N(1)–C(1)–Ru(4)	126.9 (7)
C(1)–Ru(3)–Ru(5)	92.1 (3)	N(1)–C(1)–Ru(1)	125.3 (7)
C(1)–Ru(3)–Ru(4)	48.3 (3)	N(1)–C(1)–Ru(2)	66.2 (5)
C(1)–Ru(3)–Ru(1)	48.4 (3)	Ru(3)–C(1)–Ru(4)	86.1 (4)
Ru(5)–Ru(3)–Ru(4)	58.78 (3)	Ru(3)–C(1)–Ru(1)	86.0 (4)
Ru(5)–Ru(3)–Ru(1)	58.04 (3)	Ru(3)–C(1)–Ru(2)	161.6 (5)
Ru(4)–Ru(3)–Ru(1)	61.07 (4)	Ru(4)–C(1)–Ru(1)	85.4 (4)
C(41)–Ru(4)–Ru(5)	131.8 (4)	Ru(4)–C(1)–Ru(2)	80.7 (3)
C(41)–Ru(4)–Ru(3)	98.0 (4)	Ru(1)–C(1)–Ru(2)	80.3 (3)
C(41)–Ru(4)–Ru(2)	108.3 (4)		

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

a single doublet. The existence of exchange averaging was suspected and confirmed by a DNMR study. At -8 °C at 80 MHz in $CDCl_3$, the methyl groups on the nitrogen atom appear as a singlet at 2.93 ppm and a poorly resolved doublet at 2.53 ppm due to a long-range coupling, J_{P-H} = 2.1 Hz, to one of the phosphine ligands. The diastereotopic methyl groups of one of the phosphine ligands appear as two doublets, δ = 2.11, J_{P-H} = 9.1 Hz and δ = 2.06, J_{P-H} = 9.8 Hz. The methyl groups on the second phosphine appear as a single doublet at 1.82 (J_{P-H} = 9.4 Hz). As the temperature is raised, the resonances of the inequivalent methyl groups on the phosphine ligand and the nitrogen atom broaden and coalesce, T_c = 14 °C. The methyl groups on the nitrogen atom also broaden and coalesce: T_c = 46 °C; ΔG^*_{319} = 15.9 kcal/mol. The methyl groups of both phosphine ligands appear as a sharp doublets at 46 °C. The fast-exchange limit for the methyl groups on the nitrogen atom could not be obtained in $CDCl_3$ solvent. The most likely exchange process is one that involves a rotation of the phosphine ligand and two carbonyl ligands about a pseudothreefold axis on Ru(2) (Scheme I). Examples of this process have been observed in other phosphine-substituted ruthenium clusters.[20]

The presence of the two absorptions in the IR spectrum of **3** at 1872 and 1821 cm^{-1} can be attributed to bridging carbonyl ligands and suggests that the structure of **3** is similar to that of **4**. When treated with $Ru(CO)_5$ in a refluxing hexane solution, compound **3** was converted to **2** in 63% yield. This suggests that **3** is an intermediate in the formation of **2**. This is further supported by an unsuccessful attempt to obtain **2** from **1** in one step by adding a triruthenium grouping generated from $Ru_3(CO)_{12}$.

Discussion

The results of this study are summarized in Scheme II. When heated to 68 °C in the presence of $Ru(CO)_5$, the metal nuclearity of compound **1** is increased by 1, by the addition of a $Ru(CO)_3$ group to one of the closed triangular triruthenium faces to yield **3**. It is believed that this takes place via the formation of unsaturated intermediates such as $Ru(CO)_4$ formed by the decarbonylation of $Ru(CO)_5$. Interactions of the $Ru(CO)_4$ fragment with the oxygen atoms of suitably positioned carbonyl ligands in **1** may precede the formation of the metal–metal bonds. Evidence for such interactions was recently obtained by an analysis of the products formed from the reaction of $Mo_2Ru(CO)_7Cp_2(\mu_3\text{-}S)$ with $Ru(CO)_5$.[9] Compound **3** is electron-precise, although by this information, one of the metal–metal bonds to the capping $Ru(CO)_3$ group would have to be regarded as a donor–acceptor bond. Compound **3** contains a total of 74 cluster valence electrons and also obeys the polyhedral skeletal electron pair (PSEP) bonding theory as extended to condensed polyhedra by Mingos.[21]

The reaction of **1** with $Ru(CO)_5$ also yielded the heptaruthenium complex **2** by the addition of three ruthenium-containing groups. Compound **3** appears to be an intermediate in the formation of **2** since **2** could be made from **3** by reaction with additional $Ru(CO)_5$, and it could not be made by the addition of a performed triruthenium group (i.e. $Ru_3(CO)_{12}$) to **1**. Curiously, we have obtained no evidence for the existence of any stable hexaruthenium species in this transformation. The cluster of metal atoms

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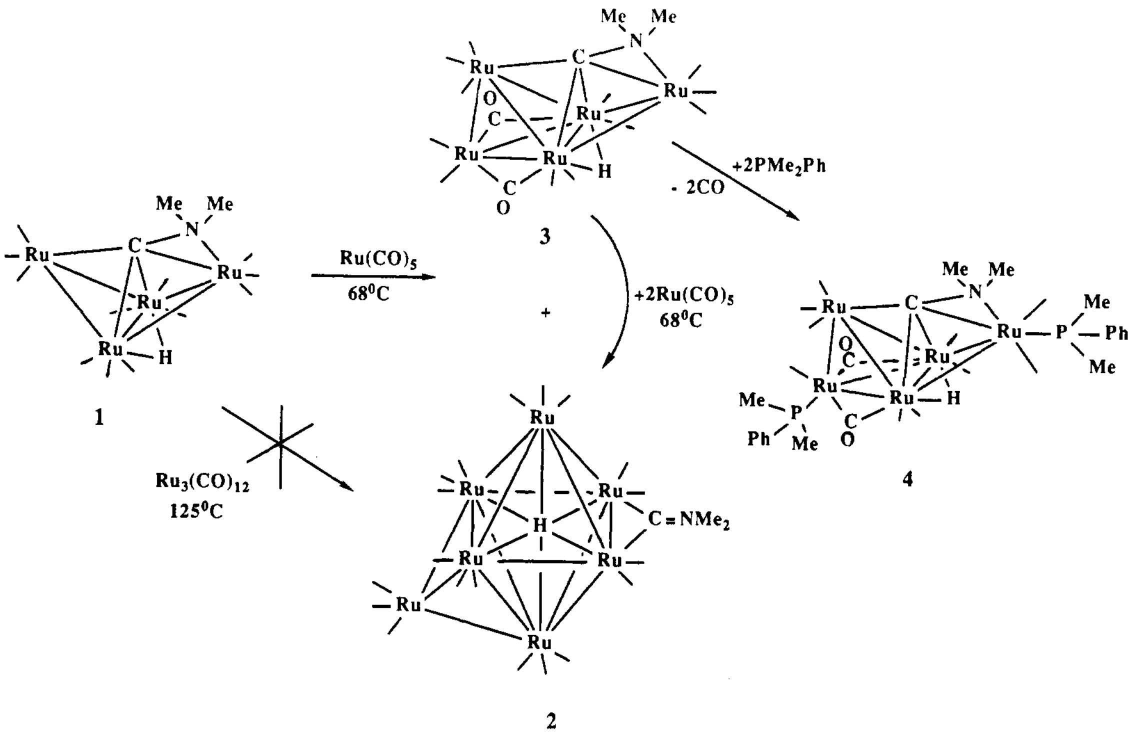
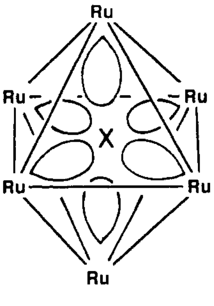
[20] Rosenberg, E.; Thorsen, C. B.; Milone, L.; Aime, S., Inorg. Chem. **1985**, *24*, 231.

[21] Mingos, D. M. P. *Acc. Chem. Res.* **1984** *17*, 311.

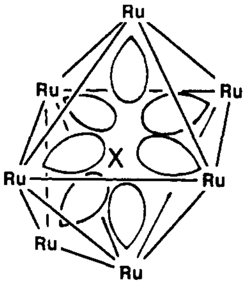
Scheme II



in 2 has adopted a capped octahedral shape. The hydride ligand lies in the interior of the octahedron but appears to be shifted off center in the direction of the site of the capping atom. Certainly, a better analysis (probably by using neutron data) will be necessary to determine the significance of this shift; however, a very simple consideration of the orbitals involved in the bonding does suggest that a shift toward the capping site should be expected. The form of the bonding orbitals for an octahedral cluster of metal atoms is well-known.[22] The only orbital of bonding significance on the hydrogen atom is the 1s orbital, and it is totally symmetric. Accordingly, there is only one cluster orbital to which it can form a bonding interaction, and that is the totally symmetric one A which consists of six atomic orbitals directed toward the center of the octahedron. Experimentally, it has been found that interstitial hydride ligands in octahedral M_6 clusters lie in the center of the octahedral cavity. Mingos et al. have provided an analysis of the effect of capping atoms on the bonding of clusters.[23] The principal effect is a simple stabilization of the bonding orbitals of the parent cluster. However, the symmetric orbital of the capped cluster B does contain an orbital contribution from the capping atom. Thus, the center of gravity X of the complete orbital will be displaced toward the capping atom. The degree to which this perturbation will result in a shifting of the hydride ligand has yet to be ascertained, but the direction will surely be toward the capping atom. Overall, compound 2 contains a total of 98 cluster valence electrons and is thus in accord with the bonding requirements of the PSEP bonding theory.[21]



A



B

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Registry No. 1, 112139-08-9; 2, 115511-90-5; 3, 115461-84-2; 4, 115461-85-3; $Ru(CO)_5$, 16406-48-7; $Ru_3(CO)_{12}$, 15243-33-1.

Supplementary Material Available: Tables of C–C and C–O distances, phosphine carbon and hydrogen atom positional parameters for 4, and anisotropic thermal parameters for both structural analyses (7 pages); listings of observed and calculated structure factor amplitudes (53 pages). Ordering information is given on any current masthead page.

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(22) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, 1980.

(23) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* 1977, 610.