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An Unusual Electron-Rich Carbido Platinum–Ruthenium Cluster from the Reaction of Diphenylacetylene with $PtRu_5(CO)_{16}(\mu_6\text{-}C)$. Synthesis and Crystallographic Characterizations of $PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)$ and $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)_2(\mu_6\text{-}C)$

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The new compound $PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)$, **2**, was isolated in 37% yield from the reaction of $PtRu_5(CO)_{16}(\mu_6\text{-}C)$, **1**, with diphenylacetylene in the presence of UV irradiation. A minor product $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)_2(\mu_6\text{-}C)$, **3**, was also obtained in 7% yield. Compound **3** was obtained in a better yield (35%) from the reaction of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$ with PhC_2Ph. Compounds **2** and **3** were characterized by single crystal X-ray diffraction analyses. In **2**, the five ruthenium atoms are arranged in the form of a square pyramid with the carbido carbon atom located in the center of the square face. The platinum atom caps one Ru_3 triangle. There is a triply bridging PhC_2Ph ligand on one of the $PtRu_2$ triangular groupings and an edge bridging PhC_2Ph ligand across the bond between the platinum atom and the ruthenium atom at the apex of the square pyramid. The molecule contains a total of 88 valence electrons which is two more than predicted for a capped square pyramidal cluster. Two of the ruthenium–ruthenium bonds in the cluster were found to be unusually long (≥3.00 Å). Compound **3** contains an octahedral cluster of six ruthenium atoms with the two diphenylacetylene ligands bridging two triruthenium triangles. The carbido carbon atom is located in the center of the octahedron. When treated with CO, **2** was converted back to **1** in 36% yield. Crystal data for **2**: space group $P2_1/n$, $a = 19.586$ (5) Å, $b = 12.073$ (2) Å, $c = 36.467$ (6) Å, $\beta = 97.26$ (2)°, $Z = 8$, 5664 reflections, $R = 0.031$; for **3**: space group $P\bar{1}$, $a = 11.2374$ (6) Å, $b = 19.962$ (2) Å, $c = 9.782$ (1) Å, $\alpha = 96.532$ (8)°, $\beta = 99.470$ (7)°, $\gamma = 96.770$ (6)°, $Z = 2$, 3194 reflections, $R = 0.025$.

Introduction

Alkynes are effective and widely utilized ligands in metal carbonyl cluster complexes.[1] They typically adopt triply bridging coordinations at trinuclear metal centers. To date, there have been only a few examples of cluster complexes that contain both carbido ligands and alkyne ligands.[2,3] We have recently prepared the new carbide-containing mixed metal complex $PtRu_5(CO)_{16}(\mu_6\text{-}C)$, **1**,[4] and have now investigated its reaction with PhC_2Ph in the presence of UV irradiation. We have found a pattern of multiple substitution that is combined with a transformation of the octahedral cluster of **1** into a square pyramidal platinum-capped pentaruthenium cluster in the major product.

Experimental Section

General Procedures. All reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over molecular sieves and deoxygenated by purging with nitrogen prior to use. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. A Brüker AM-300 FT-NMR spectrometer was used to obtain ^1H NMR spectra. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ. TLC separations were performed by using silica gel (60 Å, F_{254}) on plates (Whatman 0.25 mm) under air. $PtRu_5(CO)_{16}(\mu_6\text{-}C)$,[4] and $Ru_6(CO)_{17}(\mu_6\text{-}C)$[5] were prepared by previously reported procedures. PhC_2Ph was purchased from Aldrich and was used without further purification. UV irradiations were performed externally on reaction solutions in Pyrex glassware by using a high pressure mercury lamp (360 W) purchased from Gates Co., Hempstend, NY.

Reaction of $PtRu_5(CO)_{16}(\mu_6\text{-}C)$, 1, with Diphenylacetylene, PhC_2Ph. A 16.6-mg amount of **1** (0.0143 mmol) and a 5.1-mg amount of PhC_2Ph (0.029 mmol) were dissolved in 60 mL of CH_2Cl_2. The solution was irradiated with a slow purge of nitrogen at 25 °C for 14 h. The solvent was removed by rotary evaporation. The residue was redissolved in a minimum amount of CH_2Cl_2 and separated by TLC using a CH_2Cl_2/hexane (1/4) elution solvent mixture. This yielded in the order of elution: 1.5 mg of unreacted **1**, a trace amount of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$,[3] 1.3 mg of red-brown $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)_2(\mu_6\text{-}C)$, **3**, 7% yield, and 7.5 mg of purple $PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)$, **2**, 37% yield. IR ($\nu$CO cm^{-1} in hexane) for **2**: 2087(s), 2061(s), 2055(vs), 2033(s), 2027(m), 2016(w), 2002(w), 1983(w), 1979(w), 1948(vw); and for **3**: 2081(m), 2049(s), 2030(vs), 1998(w), 1986(w), 1979(sh). ^1H NMR (δ in $CDCl_3$) for **2**: 7.06–7.37 (m, Ph); for **3**: 7.02–7.20 (m, Ph). Anal. Calcd (found) for **2**: C%, 35.20 (34.39), H%, 1.41 (1.31); for **3**: C%, 37.67 (37.49), H%, 1.51 (1.46).

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Synthesis of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$. A 30.0-mg amount of $Ru_6(CO)_{17}(\mu_6\text{-}C)$ (0.0258 mmol) and a 9.1-mg amount of PhC_2Ph (0.051 mmol) were dissolved in 80 mL of CH_2Cl_2. This solution was then irradiated under a slow purge of nitrogen at 25 °C for 13 h. The solvent was removed by rotary evaporation and the residue was separated by TLC. This yielded 15.6 mg of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$, 46%. This compound was spectroscopically (IR and ^1H NMR) identical to a compound with the same formula reported by Drake, et al.[3] prepared by different method. Compound **3** was also obtained from this reaction in 12% yield.

Synthesis of $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)_2(\mu_6\text{-}C)$, 3. A 15.0-mg amount of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$ (0.0120 mmol) and a 5.0-mg amount of PhC_2Ph (0.028 mmol) were dissolved in 70 mL CH_2Cl_2. This solution was irradiated for 20 h at 25 °C. After separation by TLC, 5.7 mg of **3**, 35% yield, was obtained, and 3.6 mg of unreacted **2** was recovered in the order of elution.

Reaction of 2 with Carbon Monoxide. A 10.0-mg amount of **2** (0.00862 mmol) was dissolved in 20 mL of hexane. This solution was then heated to reflux (68 °C) under a slow purge of CO for 1 h. The solvent was removed in vacuum and the residue was separated by TLC by using a CH_2Cl_2/hexane (3/7) solvent mixture to elute 2.9 mg of **1**, 36%, and 0.6 mg of unreacted **2** in the order of elution.

Crystallographic Analysis. Crystals of **2** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 10 °C. Crystals of **3** were grown by slow evaporation of solvent from a solution in CH_2Cl_2/hexane (4/1) solvent at 10 °C. The crystals used for data collection were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained through the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Lorentz/polarization (Lp) and absorption corrections were applied to the data for each analysis. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/n$ for **2** was identified uniquely based on the systematic absences observed during the collection of data. Compound **3** crystallized in the triclinic crystal system. The space group of $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Each structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The positions of the hydrogen atoms in both structures were calculated by using idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **2** crystallized with two independent molecules in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **3**, the carbon atoms on the phenyl ring were refined with isotropic thermal parameters. All the other non-hydrogen atoms were refined anisotropically. Crystallographic data are listed in Table I for both structural analyses.

Results and Discussion

Table I. Crystal Data for Compounds 2 and 3

	2	3
formula	$PtRu_5O_{13}C_{42}H_{20}$	$Ru_6O_{13}C_{42}H_{20}$
fw	1433.05	1339.03
crystal system	monoclinic	triclinic
lattice parameters:		
a (Å)	19.586(5)	11.2374(6)
b (Å)	12.073(2)	19.962(2)
c (Å)	36.467(6)	9.782(1)
α (deg)	90.0	96.532(8)
β (deg)	97.26(2)	99.470(7)
γ (deg)	90.0	96.770(6)
V (Å^3)	8554(5)	2129.3(3)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	8	2
ρcalcd (g/cm^3)	2.23	2.09
μ (Mo Kα) (cm^{-1}	50.44	20.98
temp (°C)	20	20
no. of obsd rflns ($I > 3\sigma$)	5664	3194
residuals: *R*, R_w	0.031, 0.030	0.025, 0.031

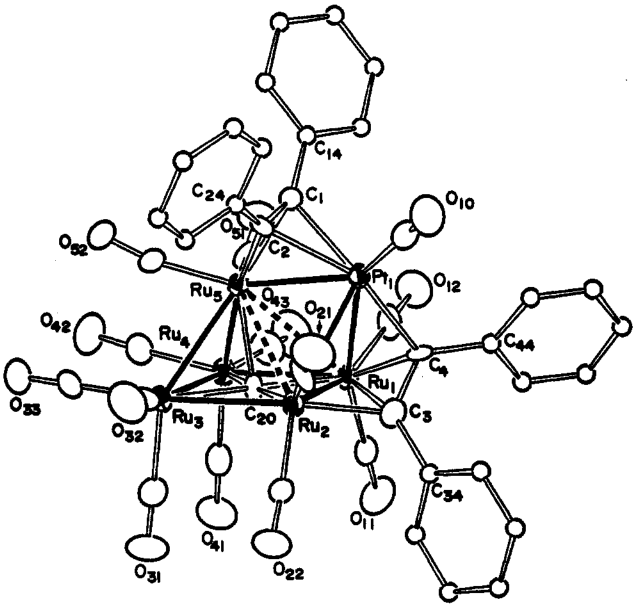

Figure 1. An ORTEP drawing of $PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)$, **2**.

When a solution of compound **1** and PhC_2Ph in hexane solvent was irradiated, the compound $PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)$, **2**, was formed in 37% yield. A minor product $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)_2(\mu_6\text{-}C)$, **3**, was also obtained in 7% yield. Compound **3** was subsequently obtained in a better yield (35%) from the reaction of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$ with PhC_2Ph in the presence of UV irradiation. Compounds **2** and **3** were characterized by X-ray diffraction analyses. Crystals of **2** contain two structurally similar independent molecules in the asymmetric crystal unit. An ORTEP drawing of one of these is shown in Figure 1. Selected final atomic positional parameters are listed in Table II. Selected interatomic bond distances and angles are listed in Tables III and IV. The molecule consists of square pyramidal cluster of five ruthenium atoms with the platinum carbonyl group capping a triangular triruthenium grouping, Ru(1)–Ru(2)–Ru(5). The carbido ligand occupies an interstitial position in the base of the square pyramid as found in other pentametallic carbido carbonyl cluster complexes.[2] A triply bridging PhC_2Ph ligand occupies the Pt(1)–Ru(1)–Ru(2) triangular grouping, and an edge bridging PhC_2Ph ligand bridges the Pt(1)–Ru(5) bond between the platinum atom and the apex of the square pyramid. The latter has the commonly observed perpendicular bridging

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

Table II. Positional Parameters and B_{eq} Values for $PtRu_5C(CO)_{13}(PhC_2Ph)_2$, 2

atom	*x*	*y*	*z*	B_{eq},^{a} Å^2	atom	*x*	*y*	*z*	B_{eq},^{a} Å^2
Pt(1A)	0.04478(03)	0.08216(05)	0.379808(15)	2.73(3)	O(52B)	1.1172(06)	0.1464(09)	0.1151(03)	6.3(7)
Pt(1B)	0.84866(03)	0.07646(05)	0.127600(15)	3.10(3)	C(1A)	0.1244(06)	0.1867(11)	0.4091(04)	2.9(7)
Ru(1A)	0.07734(05)	−0.14148(09)	0.40231(03)	2.67(5)	C(1B)	0.9448(06)	0.1841(10)	0.1332(04)	2.5(7)
Ru(1B)	0.86935(05)	−0.14185(09)	0.10091(03)	2.80(5)	C(2A)	0.1386(06)	0.1860(10)	0.3747(03)	2.2(6)
Ru(2A)	0.10047(05)	−0.08566(10)	0.33372(03)	2.85(5)	C(2B)	0.9161(06)	0.1821(11)	0.0994(03)	2.6 (7)
Ru(2B)	0.92667(05)	−0.10178(10)	0.17010(03)	2.85(5)	C(3A)	0.0048(07)	−0.1313(12)	0.3499(04)	3.5(7)
Ru(3A)	0.25098(06)	−0.10579(10)	0.35508(03)	3.13(6)	C(3B)	0.8234(06)	−0.1418(12)	0.1540(04)	3.3(7)
Ru(3B)	1.06793(05)	−0.11665(09)	0.14603(03)	2.90(5)	C(4A)	−0.0153(07)	−0.0580(10)	0.3754(04)	2.8(7)
Ru(4A)	0.22164(06)	−0.16705(10)	0.42858(03)	3.20(6)	C(4B)	0.7896(06)	−0.0626(12)	0.1301(04)	3.6(7)
Ru(4B)	0.99889(06)	−0.16090(10)	0.07243(03)	3.02(6)	C(10A)	−0.0188(08)	0.1895(13)	0.3577(04)	4.0(9)
Ru(5A)	0.18221(05)	0.04097(09)	0.39930(03)	2.61(5)	C(10B)	0.7951(08)	0.1848(15)	0.1484(05)	6(1)
Ru(5B)	0.97744(05)	0.03858(09)	0.10807(03)	2.57(5)	C(11A)	0.0674(07)	−0.2936(13)	0.4093(04)	3.6(8)
O(10A)	−0.0517(06)	0.2490(10)	0.3408(03)	6.5(7)	C(11B)	0.8170(07)	−0.1013(13)	0.0537(05)	4.3(8)
O(10B)	0.7717(07)	0.2504(11)	0.1641(04)	9(1)	C(12A)	0.0514(07)	−0.1091(13)	0.4498(04)	4.3(8)
O(11A)	0.0612(06)	−0.3861(09)	0.4141(03)	6.8(7)	C(12B)	0.8553(08)	−0.2935(14)	0.0895(05)	4.7(9)
O(11B)	0.7870(06)	−0.0725(11)	0.0274(03)	7.3(7)	C(20A)	0.1652(06)	−0.1232(11)	0.3793(03)	2.8(6)
O(12A)	0.0368(06)	−0.0892(10)	0.4785(03)	6.8(7)	C(20B)	0.9709(06)	−0.1280(10)	0.1232(03)	2.4(6)
O(12B)	0.8476(06)	−0.3833(10)	0.0840(04)	8.0(8)	C(21A)	0.0695(07)	0.0223(14)	0.2974(04)	4.5(9)
O(21A)	0.0470(06)	0.0913(10)	0.2785(03)	6.7(7)	C(21B)	0.9148(08)	−0.0109(14)	0.2113(05)	4.4(9)
O(21B)	0.9047(07)	0.0456(12)	0.2347(03)	8.4(8)	C(22A)	0.1017(07)	−0.1923(12)	0.2970(04)	3.5(8)
O(22A)	0.1049(06)	−0.2567(10)	0.2749(03)	6.7(7)	C(22B)	0.9471(07)	−0.2220(14)	0.2023(04)	3.7(8)
O(22B)	0.9632(06)	−0.2939(10)	0.2208(03)	6.7(7)	C(31A)	0.2572(08)	−0.2491(14)	0.3342(05)	4.9(9)
O(31A)	0.2613(06)	−0.3332(10)	0.3206(04)	8.1(8)	C(31B)	1.1606(08)	−0.0990(12)	0.1331(04)	4.1(8)
O(31B)	1.2130(05)	−0.918(09)	0.1243(03)	5.5(6)	C(32A)	0.2440(08)	−0.0349(13)	0.3087(05)	4.7(9)
O(32A)	0.2440(06)	0.0032(11)	0.2798(03)	6.9(7)	C(32B)	1.0930(07)	−0.0521(13)	0.1922(05)	4.7(9)
O(32B)	1.1130(07)	−0.0151(12)	0.2208(03)	8.3(8)	C(33A)	0.3512(08)	−0.0885(12)	0.3642(04)	4.1(8)
O(33A)	0.4083(06)	−0.0794(10)	0.3690(03)	6.9(7)	C(33B)	1.0866(08)	−0.2613(15)	0.1645(05)	5(1)
O(33B)	1.0968(07)	−0.3475(10)	0.1761(03)	7.3(8)	C(41A)	0.2305(08)	−0.3205(15)	0.4190(04)	4.7(9)
O(41A)	0.2340(07)	−0.4113(10)	0.4117(04)	10(1)	C(41B)	1.0132(08)	−0.3152(14)	0.0785(04)	4.1(8)
O(41B)	1.0211(06)	−0.4089(10)	0.0826(04)	8.0(8)	C(42A)	0.3180(08)	−0.1416(12)	0.4425(04)	4.5(8)
O(42A)	0.3746(06)	−0.1231(10)	0.4510(03)	7.4(7)	C(42B)	1.0850(08)	−0.1344(12)	0.0552(04)	3.7(8)
O(42B)	1.1366(06)	−0.1111(10)	0.0452(03)	6.4(7)	C(43A)	0.1994(09)	−0.1960(13)	0.4778(05)	5(1)
O(43A)	0.1867(07)	−0.2143(12)	0.5064(04)	8.8(9)	C(43B)	0.9467(08)	−0.1812(14)	0.0256(05)	4.9(9)
O(43B)	0.9157(07)	−0.1916(12)	−0.0034(03)	8.4(8)	C(51A)	0.1996(07)	0.0223(12)	0.4517(04)	3.6(8)
O(51A)	0.2011(05)	0.0487(08)	0.4827(03)	5.2(6)	C(51B)	0.9738(07)	0.0302(12)	0.0545(04)	3.6(8)
O(51B)	0.9647(06)	0.0666(09)	0.0256(03)	6.3(6)	C(52A)	0.2697(07)	0.0958(12)	0.3953(04)	3.4(7)
O(52A)	0.3204(05)	0.1445(08)	0.3962(03)	5.1(6)	C(52B)	1.0675(08)	0.0949(13)	0.1150(05)	4.8(9)

^{a} $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i{}^*a_j{}^*\vec{a}_i\vec{a}_j$, see Fischer, R. X.; Tillmanns, E., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988,** *C44*, 775.

Table III. Intramolecular Distances for 2^a

atom	atom	distance	atom	atom	distance
Pt(1A)	Ru(1A)	2.870(1)	Ru(2A)	C(3A)	2.11(1)
Pt(1A)	Ru(2A)	2.930(1)	Ru(2A)	C(20A)	2.01(1)
Pt(1A)	Ru(5A)	2.741(1)	Ru(2B)	Ru(3B)	3.012(2)
Pt(1A)	C(1A)	2.18(1)	Ru(2B)	Ru(5B)	3.090(2)
Pt(1A)	C(2A)	2.25(1)	Ru(2B)	C(3B)	2.09(1)
Pt(1A)	C(4A)	2.06(1)	Ru(2B)	C(20B)	2.04(1)
Pt(1B)	Ru(1B)	2.856(1)	Ru(3A)	Ru(4A)	2.907(2)
Pt(1B)	Ru(2B)	2.961(1)	Ru(3A)	Ru(5A)	2.847(2)
Pt(1B)	Ru(5B)	2.745(1)	Ru(3A)	C(20A)	2.00(1)
Pt(1B)	C(1B)	2.28(1)	Ru(3B)	Ru(4B)	2.898(2)
Pt(1B)	C(2B)	2.18(1)	Ru(3B)	Ru(5B)	2.820(2)
Pt(1B)	C(4B)	2.05(1)	Ru(3B)	C(20B)	1.98(1)
Ru(1A)	Ru(2A)	2.684(2)	Ru(4A)	Ru(5A)	2.799(2)
Ru(1A)	Ru(4A)	2.884(2)	Ru(4A)	C(20A)	2.06(1)
Ru(1A)	Ru(5A)	3.023(2)	Ru(4B)	Ru(5B)	2.793(2)
Ru(1A)	C(3A)	2.24(1)	Ru(4B)	C(20B)	2.04(1)
Ru(1A)	C(4A)	2.20(1)	Ru(5A)	C(1A)	2.15(1)
Ru(1A)	C(20A)	2.02(1)	Ru(5A)	C(2A)	2.10(1)
Ru(1B)	Ru(2B)	2.673(2)	Ru(5A)	C(20A)	2.12(1)
Ru(1B)	Ru(4B)	2.870(2)	Ru(5B)	C(1B)	2.12(1)
Ru(1B)	Ru(5B)	3.026(2)	Ru(5B)	C(2B)	2.11(1)
Ru(1B)	C(3B)	2.23(1)	Ru(5B)	C(20B)	2.09(1)
Ru(1B)	C(4B)	2.21(1)	C(1A)	C(2A)	1.32(2)
Ru(1B)	C(20B)	2.06(1)	C(1B)	C(2B)	1.29(2)
Ru(2A)	Ru(3A)	2.962(2)	C(3A)	C(4A)	1.38(2)
Ru(2A)	Ru(5A)	3.107(2)	C(3B)	C(4B)	1.40(2)
			O	C(av)	1.13(2)

^{a} Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

mode,[7] while the former exhibits the usual μ_3-$\|$ coordination mode.[1] The molecule contains thirteen linear, terminal carbonyl ligands distributed among the six metal atoms as shown in Figure 1. Interestingly, compound 2 contains a total of 88 valence electrons which is two more than that predicted for a capped square pyramidal cluster according to the skeletal electron pair theory.[8] It was observed that two ruthenium–ruthenium bonds in each cluster in the crystal are unusually long, Ru(1A)–Ru(5A) = 3.023 (2) Å,

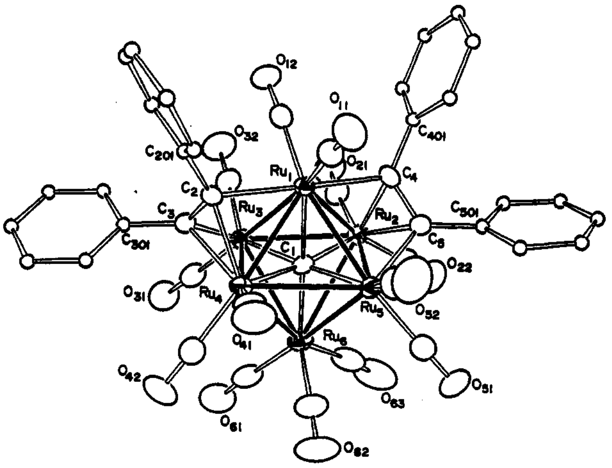

Figure 2. An ORTEP diagram of $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)_2(\mu_6\text{-}C)$, 3.

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(7) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858, and references therein. (b) Hoffman, D. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1982**, 1471. (c) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1973**, *12*, 323.

(8) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapt. 2.

Table IV. Intramolecular Bond Angles for 2[a]

atom	atom	atom	angle	atom	atom	atom	angle
Pt(1A)	Ru(1A)	Ru(4A)	111.64(4)	Ru(4A)	Ru(5A)	Ru(2A)	86.71(5)
Ru(2A)	Ru(1A)	Ru(4A)	93.60(5)	Ru(5B)	Ru(3B)	Ru(2B)	86.71(4)
Pt(1B)	Ru(1B)	Ru(4B)	111.55(5)	Ru(4B)	Ru(5B)	Ru(2B)	87.08(4)
Ru(2B)	Ru(1B)	Ru(4B)	94.07(5)	Ru(1A)	C(20A)	Ru(2A)	83.5(5)
Pt(1A)	Ru(2A)	Ru(3A)	109.65(4)	Ru(1A)	C(20A)	Ru(4A)	90.0(5)
Ru(1A)	Ru(2A)	Ru(3A)	90.80(5)	Ru(1A)	C(20A)	Ru(5A)	93.6(5)
Ru(2A)	Ru(3A)	Ru(4A)	87.55(5)	Ru(2A)	C(20A)	Ru(3A)	95.1(5)
Ru(1A)	Ru(4A)	Ru(3A)	88.05(5)	Ru(2A)	C(20A)	Ru(5A)	97.4(5)
Ru(1B)	Ru(4B)	Ru(3B)	88.88(5)	Ru(3A)	C(20A)	Ru(4A)	91.4(5)
Pt(1A)	Ru(5A)	Ru(3A)	119.03(5)	Ru(3A)	C(20A)	Ru(5A)	87.1(5)
Pt(1A)	Ru(5A)	Ru(4A)	118.44(5)	Ru(4A)	C(20A)	Ru(5A)	84.0(5)
Pt(1B)	Ru(5B)	Ru(3B)	121.64(5)	Ru(1B)	C(20B)	Ru(2B)	81.5(4)
Pt(1B)	Ru(5B)	Ru(4B)	117.49(5)	Ru(1B)	C(20B)	Ru(4B)	89.0(5)
Pt(1A)	C(1A)	Ru(5A)	78.6(4)	Ru(1B)	C(20B)	Ru(5B)	93.6(5)
Pt(1B)	C(1B)	Ru(5B)	77.2(4)	Ru(2B)	C(20B)	Ru(3B)	97.1(5)
Pt(1A)	C92A)	Ru(5A)	78.0(4)	Ru(2B)	C(20B)	Ru(5B)	96.8(5)
Pt(1B)	C(2B)	Ru(5B)	79.5(4)	Ru(3B)	C(20B)	Ru(4B)	92.4(5)
Ru(1B)	Ru(2B)	Ru(3B)	90.34(5)	Ru(3B)	C(20B)	Ru(5B)	87.5(5)
Ru(3A)	Ru(5A)	Ru(1A)	86.52(5)	Ru(4B)	C(20B)	Ru(5B)	85.1(5)
Ru(3B)	Ru(5B)	Ru(1B)	87.33(5)	M	C(av)	O	177(2)

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

Table V. Positional Parameters and B_{eq} Values for $Ru_6C(CO)_{13}(\mu_3\text{-}PhC_2Ph)$, 3

atom	x	y	z	B(eq),[a] Å^2
Ru(1)	–0.05075(05)	0.29327(03)	0.18869(06)	2.47(2)
Ru(2)	–0.18321(05)	0.20324(03)	0.32410(06)	2.84(3)
Ru(3)	0.04520(05)	0.28741(03)	0.47262(06)	2.55(3)
Ru(4)	0.16878(05)	0.24371(03)	0.26351(06)	2.59(3)
Ru(5)	–0.05907(05)	0.15160(03)	0.11898(06)	2.83(3)
Ru(6)	0.05106(06)	0.13987(03)	0.39959(06)	3.17(3)
O(11)	–0.0654(06)	0.3114(03)	–0.1183(07)	5.9(3)
O(12)	–0.1268(05)	0.4312(03)	0.2810(06)	5.4(3)
O(21)	–0.2915(06)	0.2936(03)	0.5268(07)	6.7(3)
O(22)	–0.3618(06)	0.0910(03)	0.3901(07)	6.9(3)
O(31)	0.2079(06)	0.2877(03)	0.7506(06)	6.7(3)
O(32)	–0.0601(06)	0.4063(03)	0.6029(07)	6.7(3)
O(41)	0.2641(06)	0.2146(03)	–0.0078(07)	6.0(3)
O(42)	0.4014(06)	0.2017(03)	0.4107(08)	7.4(4)
O(51)	–0.1298(06)	–0.0016(03)	0.0803(07)	6.0(3)
O(52)	–0.0159(07)	0.1474(04)	–0.1795(07)	7.7(4)
O(61)	0.2241(08)	0.1371(04)	0.6693(08)	8.9(4)
O(62)	0.1806(07)	0.0360(04)	0.2560(07)	7.7(4)
O(63)	–0.1263(07)	0.0341(04)	0.4852(10)	11.0(5)
C(1)	–0.0042(06)	0.2174(03)	0.2970(07)	2.8(3)
C(2)	0.1397(06)	0.3488(03)	0.2556(07)	2.4(3)
C(3)	0.1801(06)	0.3433(03)	0.3947(07)	2.5(3)
C(4)	–0.2387(06)	0.2415(04)	0.1310(07)	2.8(3)
C(5)	–0.2369(06)	0.1724(04)	0.0910(07)	3.0(3)
C(11)	–0.0584(07)	0.3058(04)	–0.0038(09)	3.7(4)
C(12)	–0.1013(07)	0.3796(04)	0.2445(08)	3.5(4)
C(21)	–0.2438(07)	0.2613(04)	0.4543(09)	4.2(4)
C(22)	–0.2940(08)	0.1331(05)	0.3637(09)	4.5(4)
C(31)	0.1452(08)	0.2866(04)	0.6468(09)	3.9(4)
C(32)	–0.0228(07)	0.3598(04)	0.5566(08)	3.8(4)
C(41)	0.2266(07)	0.2259(04)	0.0933(09)	4.0(4)
C(42)	0.3113(08)	0.2165(04)	0.3562(09)	4.3(4)
C(51)	–0.1014(07)	0.0563(05)	0.0939(08)	3.9(4)
C(52)	–0.0304(08)	0.1493(04)	–0.0671(10)	4.8(4)
C(61)	0.1582(10)	0.1395(04)	0.5685(10)	5.4(4)
C(62)	0.1310(09)	0.0756(05)	0.3055(09)	5.2(4)
C(63)	–0.0639(09)	0.0768(05)	0.4534(11)	6.3(5)

[a] See footnote a, Table II.

Table VI. Intramolecular Distances for 3[a]

atom	atom	distance	atom	atom	distance
Ru(1)	Ru(2)	2.7857(8)	Ru(3)	C(1)	2.043(7)
Ru(1)	Ru(3)	2.8299(9)	Ru(3)	C(3)	2.073(6)
Ru(1)	Ru(4)	2.7832(8)	Ru(4)	Ru(5)	3.0071(9)
Ru(1)	Ru(5)	2.8195(8)	Ru(4)	Ru(6)	2.8946(9)
Ru(1)	C(1)	2.015(7)	Ru(4)	C(1)	2.042(7)
Ru(1)	C(2)	2.248(7)	Ru(4)	C(2)	2.170(6)
Ru(1)	C(4)	2.193(7)	Ru(4)	C(3)	2.219(7)
Ru(2)	Ru(3)	2.9534(9)	Ru(5)	Ru(6)	2.8666(9)
Ru(2)	Ru(5)	2.7971(9)	Ru(5)	C(1)	2.017(7)
Ru(2)	Ru(6)	3.0714(8)	Ru(5)	C(5)	2.069(7)
Ru(2)	C(1)	2.062(7)	Ru(6)	C(1)	2.040(7)
Ru(2)	C(4)	2.143(7)	C(2)	C(3)	1.38(1)
Ru(2)	C(5)	2.254(7)	C(4)	C(5)	1.39(1)
Ru(3)	Ru(4)	2.7726(8)	O	C(av)	1.14(1)
Ru(3)	Ru(6)	2.9616(8)			

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

Ru(2A)–Ru(5A) = 3.107 (2) Å, Ru(1B)–Ru(5B) = 3.026 (2) Å, Ru(2B)–Ru(5B) = 3.090 (2) Å. The Ru – Ru bond distances in the parent molecule $Ru_5(CO)_{15}(\mu_5\text{-}C)$ all lie in the range 2.800 (2)–2.882 (2) Å.[9] These long distances in **2** could be a consequence of bond weakening due to the presence of two excess electrons in the complex. We are unaware of any previous reports of 88 electron cluster complexes having the capped square pyramidal geometry.[8] When **2** was treated with CO (1 atm/68 °C), the alkyne ligands were displaced and the platinum atom was shifted back to its original position capping the $Ru_4(C)$ face to reform **1** in 35% yield.

An ORTEP drawing of the molecular structure of the minor product **3** is shown in Figure 2. Selected final atomic positional parameters are listed in Table V. Selected interatomic bond distances and angles are listed in Tables VI and VII. This molecule consists of an octahedral cluster of six ruthenium atoms with an interstitial carbido ligand and two triply bridging PhC_2Ph ligands on two of the triangular triruthenium faces. If it were not for presence of three carbonyl ligands on the metal atom Ru(6), the complex **3** would contain a 2-fold rotation axis that would pass along the Ru(1)–Ru(6) vector. The cluster of compound **3** is structurally very similar to the clusters of the two monoalkyne $Ru_6(C)$ cluster complexes, $Ru_6(CO)_{15}(\mu_3\text{-}HC_2Ph)(\mu_6\text{-}C)$ and $Ru_6(CO)_{15}(\mu_3\text{-}MeC_2Ph)(\mu_6\text{-}C)$, that were recently reported.[3] It seemed likely that a monoalkyne complex would provide a more efficient synthetic route to **3**, and this was independently confirmed through the reaction of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$ with PhC_2Ph. Recently, a series of monoalkyne complexes, $Ru_6(CO)_{15}(\mu_3\text{-}RC_2R')(\mu_6\text{-}C)$, R = R′ = H; R = R′ = Me; R =

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[9] Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* 1983, 277.

Table VII. Intramolecular Bond Angles for 3[a]

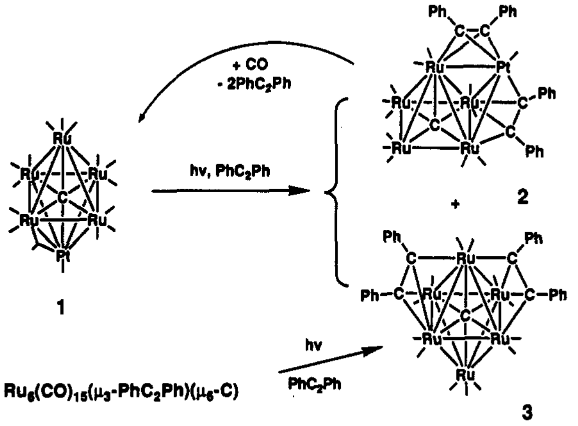
atom	atom	atom	angle	atom	atom	atom	angle
Ru(2)	Ru(1)	Ru(4)	94.70(2)	Ru(1)	C(1)	Ru(4)	86.6(3)
Ru(3)	Ru(1)	Ru(5)	91.85(3)	Ru(1)	C(1)	Ru(5)	88.7(3)
Ru(3)	Ru(2)	Ru(5)	89.74(2)	Ru(2)	C(1)	Ru(3)	92.0(3)
Ru(1)	Ru(3)	Ru(6)	88.80(2)	Ru(2)	C(1)	Ru(5)	86.6(3)
Ru(2)	Ru(3)	Ru(4)	91.28(2)	Ru(2)	C(1)	Ru(6)	97.0(3)
Ru(1)	Ru(4)	Ru(6)	91.08(2)	Ru(3)	C(1)	Ru(4)	85.5(3)
Ru(3)	Ru(4)	Ru(5)	89.11(2)	Ru(3)	C(1)	Ru(6)	93.0(3)
Ru(1)	Ru(5)	Ru(6)	90.93(3)	Ru(4)	C(1)	Ru(5)	95.6(3)
Ru(2)	Ru(5)	Ru(4)	89.69(2)	Ru(4)	C(1)	Ru(6)	90.3(3)
Ru(3)	Ru(6)	Ru(5)	88.26(2)	Ru(5)	C(1)	Ru(6)	89.9(3)
Ru(1)	C(1)	Ru(2)	86.2(3)	Ru	C(av)	O	177(1)
Ru(1)	C(1)	Ru(3)	88.4(3)				

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

R′ = Et; R = R′ = Ph; R, R′ = H, Ph; R, R′ = Me, Ph were reported.[5]

A summary of the results of this study are shown in Scheme I. Irradiation of 1 in the presence of PhC_2Ph led to the loss of three carbonyl ligands, the addition of two PhC_2Ph ligands, and a shift of the Pt(CO) grouping to form the compound 2. The cluster was transformed into a capped square pyramid. Johnson and Lewis have reported that the addition of alkynes to $Os_6(CO)_{17}(NCMe)$ also causes rearrangements of the cluster geometry to that of capped square pyramids.[10] In 2 the PhC_2Ph ligands serve as four electron donors, and there is an increase by two in the number of valence electrons to 88. Structurally, it was observed that two of the ruthenium–ruthenium bonds in the cluster are unusually long. This could be a consequence of selective bond weakening due to the presence of the two excess electrons in the complex. When 2 was treated with CO, the alkyne ligands were displaced and the platinum atom was shifted back to the position across the $Ru_4(C)$ square face to reform 1.

Scheme I



A small amount of the hexaruthenium complex 3 was also formed in the reaction of 1 with PhC_2Ph. Evidently, the UV irradiation caused some cluster fragmentation and the stable product 3 was subsequently assembled. In view of the obvious stability of 3, we devised a more efficient route to it via the reaction of $Ru_6(CO)_{15}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$ with PhC_2Ph. Compounds 2 and 3 are the first examples of carbide containing metal carbonyl cluster complexes that have two alkyne ligands.

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Supplementary Material Available: Tables of phenyl ring and hydrogen atom parameters and anisotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

OM920705C

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[10] Gomez-Sal, M. P.; Johnson, B. F. G.; Kamarudin, R. A.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1622.