1248 *Organometallics* **1993**, *12*, 1248-1256

Cluster Synthesis. 41. New Platinum–Ruthenium Cluster Complexes from the Reaction of PhC≡CPh with $Pt_2Ru_4(CO)_{18}$. Synthesis and Structural Characterizations of $Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$, $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$, $Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$, $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$, and $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$(dppe)

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The reaction of $Pt_2Ru_4(CO)_{18}$ (**1**) with diphenylacetylene, PhC_2Ph, in refluxing heptane (97 °C) yielded two new compounds, $Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**2**, 6%) and $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**3**, 27%). Both compounds **2** and **3** were characterized by IR, proton NMR, and single-crystal X-ray diffraction analyses. Compound **2** contains five metal atoms, two platinum and three ruthenium, which are arranged in a distorted square-pyramidal structure. Compound **3** consists of a six-metal Pt_3Ru_3 octahedral cluster that is capped by three ruthenium atoms. There is a Ru–Ru bond between two of the capping ruthenium atoms. When **3** was treated with CO at 25 °C, two new compounds, $Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**4**, 16%) and $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**5**, 20%), were obtained. Compound **4** consists of a square-pyramidal Pt_2Ru_3 cluster that has a ruthenium group bridging the Pt–Pt axial-basal edge. Compound **5** exhibits a novel cluster that has a central triplatinum cluster with diruthenium groupings bridging each Pt–Pt edge and a triply bridging alkyne on each $PtRu_2$ triangle. The molecule could be viewed as an assembly derived of three $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ groupings. Compound **5** was converted back to **3** (94%) by heating in a hexane solution. Upon reaction with 1,2-bis(diphenylphosphino)ethane (dppe), it was converted into 3 equiv of the new complex $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$(dppe) (**6**) in 10% yield. When compound **5** was treated with CO prior to the addition of dppe, compound **6** was obtained in a much better yield (46%). Crystal data for **2**: space group $P\bar{1}$, $a = 13.219(3)$ Å, $b = 13.262(3)$ Å, $c = 13.126(3)$ Å, $\alpha = 102.75(2)°$, $\beta = 96.69(2)°$, $\gamma = 85.59(2)°$, $Z = 2$, 3659 reflections, $R = 0.024$. Crystal data for **3**: space group $P\bar{1}$, $a = 15.218(2)$ Å, $b = 15.444(3)$ Å, $c = 14.464(3)$ Å, $\alpha = 94.48(2)°$, $\beta = 100.29(1)°$, $\gamma = 87.55(2)°$, $Z = 2$, 4722 reflections, $R = 0.040$. Crystal data for **4**: space group $P2_1/c$, $a = 16.381(2)$ Å, $b = 10.715(2)$ Å, $c = 23.987(2)$ Å, $\beta = 90.215(7)°$, $Z = 4$, 3179 reflections, $R = 0.022$. Crystal data for **5**: space group $P\bar{1}$, $a = 14.866(2)$ Å, $b = 17.507(5)$ Å, $c = 13.597(3)$ Å, $\alpha = 102.50(2)°$, $\beta = 93.31(1)°$, $\gamma = 100.86(2)°$, $Z = 2$, 4943 reflections, $R = 0.033$. Crystal data for **6**: space group *Pbcn*, $a = 23.103(2)$ Å, $b = 21.930(4)$ Å, $c = 20.663(2)$ Å, $Z = 8$, 3721 reflections, $R = 0.042$.

Introduction

Studies of coordination and reactivity of alkynes in transition metal cluster complexes have been of interest because it is believed that these small molecules may serve as models for understanding some aspects of the adsorption and reactivity of small molecules on metal surfaces.[1,2] We have recently reported that synthesis and structural characterization of the new platinum–ruthenium carbonyl cluster complex $Pt_2Ru_4(CO)_{18}$ (**1**).[3] We have found that **1** readily reacts with a variety of small molecules: hydrogen,[4] 1,5-cyclooctadiene (COD),[5] 1,2-bis(diphenylphosphino)ethane (dppe),[3b] and even other metal carbonyl complexes[6] to produce interesting new platinum–ruthenium cluster complexes. Compound **1** has a open puckered raft structure which can be viewed as a dimer of the unknown species $[PtRu_2(CO)_9]$. Our investigations have shown that **1** can be symmetrically split to form a $PtRu_2$ trinuclear cluster (e.g. $PtRu_2(CO)_8$(dppe)) or condensed to form higher nuclearity species derived from the combination of three $PtRu_2$ groupings (e.g. $Pt_3Ru_6(CO)_{21}(\mu\text{-}H)_3(\mu_3\text{-}H)$).[4] We have now expanded our studies of **1** to include the reaction with diphenylacetylene, PhC_2Ph. The principal product is the compound $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}$

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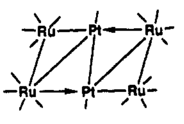
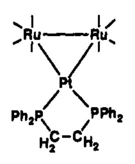
Table I. Crystal Data of Compounds 2–6

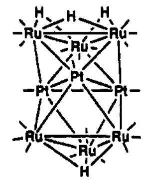
	2	**3**	**4**	**5**	**6**
formula	$Pt_2Ru_3O_8C_{50}H_{30}$	$Pt_3Ru_6O_{14}C_{56}H_{30}\cdot 1.5C_6H_{14}$	$Pt_2Ru_4O_{14}C_{42}H_{20}$	$Pt_3Ru_6O_{18}C_{60}H_{30}$	$PtRu_2P_2O_6C_{46}H_{34}\cdot CH_3CO_2C_2H_5\cdot 0.5C_7H_{16}$
formula weight	1452.17	2247.80	1543.07	2230.58	1280.16
crystal system	triclinic	triclinic	monoclinic	triclinic	orthorhombic
lattice parameters					
a (Å)	13.219(2)	15.218(2)	16.381(2)	14.866(2)	23.103(2)
b (Å)	13.262(3)	15.444(3)	10.715(2)	17.507(5)	21.930(4)
c (Å)	13.126(3)	14.464(3)	23.987(2)	13.597(3)	20.663(2)
α (deg)	102.75(2)	94.48(2)	90.0	102.50(2)	90.0
β (deg)	96.69(2)	100.29(1)	90.215(7)	93.31(1)	90.0
γ (deg)	85.59(2)	87.55(2)	90.0	100.86(2)	90.0
V (Å^3)	2226(1)	3333(2)	4210(1)	3375(1)	10469(4)
space group	$P\bar{1}$(no. 2)	$P\bar{1}$(no. 2)	$P2_1/c$(no. 14)	$P\bar{1}$(no. 2)	$Pbcn$(no. 60)
Z value	2	2	4	2	8
ρ_{calc} (g/cm^3)	2.17	2.24	2.43	2.19	1.62
μ (Mo Kα) cm^{-1})	73.58	76.91	81.29	75.99	33.62
temperature (°C)	20	23	20	20	20
$2\theta_{max}$ (°)	40.0	42.0	40.0	40.1	41.0
no. obs ($I > 3\sigma$)	3659	4722	3179	4943	3721
residuals: R, R_w	0.024; 0.029	0.040; 0.040	0.022; 0.023	0.033; 0.049	0.042; 0.051



$Pt_2Ru_4(CO)_{18}$, 1



$PtRu_2(CO)_8(dppe)$



$Pt_3Ru_6(CO)_{21}(H)_4$

$PhC_2Ph)_3$, **3**. Its formula suggests that it is also derived from the combination of three $PtRu_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ groupings. Compound **3** adds CO to yield two products: the smaller cluster $PtRu_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**4**) and a more opened form of **3**, $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**5**). Compound **5** reacts with dppe to yield the expected trinuclear grouping $PtRu_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ in the isolable complex $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(dppe)$ (**6**). A portion of this work has been previously published.[3a]

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent-grade solvents were dried over molecular sieves and were 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). $Pt_2Ru_4(CO)_{18}$ and $PtRu_2(CO)_8(dppe)$ were prepared by previously reported procedures.[3] PhC_2Ph and 1,2-bis(diphenylphosphino)ethane (dppe) were purchased from Aldrich and were used without further purification.

Reaction of $Pt_2Ru_4(CO)_{18}$ (1) with Diphenylacetylene. In a typical reaction, a 30.0-mg amount of **1** (0.023 mmol) and 10.0 mg of PhC_2Ph (0.056 mmol) were dissolved in 40 mL of heptane at 40–50 °C. The solution was then heated to reflux (97 °C) for 10 min. After cooling to 25 °C, the solvent was removed on a rotary evaporator and the residue was separated by TLC. The following products were separated in order of elution by using a CH_2Cl_2/hexane (3/7) solvent mixture: a trace amount of $Ru_3(CO)_{12}$; a trace amount of unreacted **1**; 0.6 mg of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$,[7] 3%; 2.1 mg of $Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**2**, 6%); 8.7 mg of $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**3**, 27%); 2.2 mg of an unknown purple compound; and 3.3 mg of an unknown brown compound. All attempts to obtain crystals of the latter two compounds have been unsuccessful. IR (νCO in hexane) for **2**: 2063 (m), 2038 (m), 2025 (vs), 2010, (s), 1988 (m), 1976 (m), 1965 (w). IR (νCO in hexane) for **3**: 2058 (m), 2040 (vs), 2024 (s), 2018 (s), 2001 (s), 1979 (w), 1970 (w), 1962 (w), 1944 (vw), 1897 (vw, Br), 1886 (sh). IR for unknown purple compound: 2063 (m), 2019 (vs), 1988 (w), 1970 (m), 1963 (m); for unknown brown compound: 2049 (s), 2041 (vs), 2033 (s) 2023(s), 2014 (m), 2007 (s), 1986 (w). ^1H NMR (δ in $CDCl_3$) for **2**: 6.7–7.5 (m, Ph). ^1H NMR (δ in $CDCl_3$) for **3**: 6.2–8.0 (m, Ph). Anal. Calcd (found) for **2**: C, 41.36 (41.66); H, 2.08 (1.81). Anal. Calcd (found) for **3**: C, 31.75 (32.68); H, 1.43 (1.88).

Reaction of 3 with CO. **3** (15.9 mg, 0.0075 mmol) was dissolved in 25 mL of hexane, and CO was purged through the solution slowly at 25 °C for 15 min. The solvent was removed by rotary evaporation, and the residue was separated by TLC plates using a CH_2Cl_2/hexane (1/4) solvent mixture. This yielded in order of elution: 2.8 mg of $Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**4**, 16%), 3.6 mg of $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**5**, 20%), and 6.0 mg of a brown compound **X**. Numerous attempts to obtain crystals of compound **X** were unsuccessful. IR (νCO, cm^{-1} in hexane) for **4**: 2085 (w), 2059 (vs), 2044 (s), 2025 (m), 1996 (sh), 1993 (w), 1986 (w). IR (νCO, cm^{-1} in hexane) for **5**: 2080 (m), 2066 (s), 2057 (vs), 2052 (vs), 2040 (s), 2012 (m), 2004 (m), 1999 (m), 1991 (m), 1978 (w); for **X**: 2065 (w), 2049 (m), 2040 (sh), 2034 (s), 2024 (vs), 2008 (m), 2001 (m), 1990 (w), 1984 (w), 1961 (vw), 1952 (vw). ^1H NMR (δ in $CDCl_3$) for **4**: 7.1–7.7 (m, Ph). ^1H NMR (δ in $CDCl_3$) for **5**: 7.1–7.6 (m, Ph). Anal. Calcd (found) for **4**: C, 32.69 (32.74); H, 1.31 (1.27). Anal. Calcd (found) for **5**: C, 32.31 (32.52); H, 1.36 (1.18).

Reaction of X with CO. **X** (7.0 mg) was allowed to react with CO (1 atm) in 20 mL of hexane at 25 °C for 45 min. The solvent was removed on a rotary evaporator, and the residue was separated by TLC. This yielded 0.8 mg of **4**, 1.4 mg of **5**, and 3.6 mg of unreacted **X**.

Reaction of X with CO and dppe in Two Steps. **X** (6.5 mg) was dissolved in 20 mL of hexane, and CO was allowed to purge through this solution slowly at 25 °C for 60 min. A 3.0-mg sample of dppe was then added to the resulting solution, and the mixture was stirred for an additional 50 min; 3.6 mg of **6** was isolated by TLC.

Pyrolysis of 5 at 68 °C. An 8.5-mg amount of **5** (0.0040) mmol) dissolved in 20 mL of hexane was heated to reflux under a slow purge of nitrogen for 30 min. The color of the solution changed from brown to green during this time. The solvent was removed by rotary evaporation, and the product was separated by TLC to yield 7.6 mg of **3**, 94%.

Reaction of 5 with CO. An 8.4-mg amount of **5** (0.0037 mmol) in 20 mL of hexane was allowed to react with CO (1 atm) at 25 °C for 1 h. At this time, the IR spectrum showed absorptions at 2101 (w), 2073 (m), 2057 (vs), 2042 (m), 2024 (sh), 2019 (m), 2008 (w), 2001 (m), 1993 (w), 1978 (w) that we attribute these to

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Table II. Positional Parameters and *B*(eq) Values for $Pt_2Ru_3(CO)_8(C_2Ph_2)_3$, 2

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.22008(03)	0.08356(03)	0.34394(03)	2.62(2)
Pt(2)	0.39940(03)	0.20572(03)	0.35745(03)	3.07(2)
Ru(1)	0.20037(06)	0.29784(06)	0.36250(06)	2.79(3)
Ru(2)	0.10343(06)	0.17606(06)	0.19297(05)	2.41(3)
Ru(3)	0.30171(06)	0.12517(06)	1.17123(06)	2.61(3)
O(10)	0.2560(08)	–0.0442(07)	0.5108(06)	7.8(5)
O(11)	0.1298(07)	0.5212(06)	0.4182(06)	6.7(4)
O(12)	0.2988(06)	0.3304(06)	0.5880(06)	4.9(4)
O(20)	0.5445(07)	0.1757(08)	0.5419(07)	8.6(6)
O(21)	–0.0159(06)	–0.0176(07)	0.1512(06)	6.1(4)
O(22)	–0.0567(07)	0.2658(07)	0.0490(07)	7.0(5)
O(31)	0.4377(06)	0.1164(06)	0.0012(06)	5.2(4)
O(32)	0.1769(05)	–0.0273(06)	0.0069(06)	4.9(4)
C(1)	0.2228(08)	0.2818(07)	0.1879(07)	3.1(4)
C(2)	0.3144(07)	0.2997(07)	0.2551(07)	2.9(4)
C(3)	0.1036(07)	0.1926(07)	0.4105(07)	2.7(4)
C(4)	0.0470(07)	0.2366(07)	0.3341(07)	3.1(4)
C(5)	0.3340(07)	–0.0007(07)	0.2556(07)	2.9(4)
C(6)	0.4202(07)	0.0558(06)	0.2627(07)	2.6(4)
C(10)	0.2381(08)	0.0040(08)	0.4485(09)	4.3(5)
C(11)	0.1582(08)	0.4367(09)	0.3954(07)	4.2(5)
C(12)	0.2692(08)	0.3165(07)	0.4997(09)	3.3(5)
C(20)	0.4900(09)	0.1877(08)	0.4724(10)	4.7(6)
C(21)	0.0278(08)	0.0578(09)	0.1675(07)	3.7(5)
C(22)	0.0053(09)	0.2313(08)	0.1042(09)	4.3(5)
C(31)	0.3869(08)	0.1213(07)	0.0649(08)	3.5(5)
C(32)	0.2099(08)	0.0400(08)	0.0718(08)	3.6(5)

Table III. Intramolecular Distances[a] for 2

Pt(1)–Pt(2)	2.9396(9)	Ru(1)–C(4)	2.20(1)
Pt(1)–Ru(1)	2.793(1)	Ru(2)–Ru(3)	2.688(1)
Pt(1)–Ru(2)	2.807(1)	Ru(2)–C(1)	2.21(1)
Pt(1)–Ru(3)	2.797(1)	Ru(2)–C(4)	2.051(9)
Pt(1)–C(3)	2.154(9)	Ru(2)–C(32)	2.58(1)
Pt(1)–C(5)	2.107(9)	Ru(3)–C(1)	2.229(9)
Pt(2)–Ru(1)	2.816(1)	Ru(3)–C(2)	2.343(9)
Pt(2)–Ru(3)	2.666(1)	Ru(3)–C(5)	2.189(9)
Pt(2)–C(2)	2.19(1)	Ru(3)–C(6)	2.14(1)
Pt(2)–C(6)	2.116(8)	C(1)–C(2)	1.42(1)
Ru(1)–Ru(2)	2.696(1)	C(3)–C(4)	1.39(1)
Ru(1)–C(1)	2.306(9)	C(5)–C(6)	1.40(1)
Ru(1)–C(2)	2.186(9)	M–C(av)	1.88(1)
Ru(1)–C(3)	2.198(9)	O–C(av)	1.15(1)

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

Table IV. Intramolecular Bond Angles[a] for 2

Pt(2)–Pt(1)–Ru(1)	58.78(3)	Pt(1)–Ru(1)–Ru(2)	61.49(3)
Pt(2)–Pt(1)–Ru(2)	95.20(3)	Pt(2)–Ru(1)–Ru(2)	100.70(4)
Pt(2)–Pt(1)–Ru(3)	55.32(2)	Pt(1)–Ru(2)–Ru(1)	60.94(3)
Ru(1)–Pt(1)–Ru(2)	57.57(3)	Pt(1)–Ru(2)–Ru(3)	61.14(3)
Ru(1)–Pt(1)–Ru(3)	73.24(3)	Ru(1)–Ru(2)–Ru(3)	76.52(4)
Ru(2)–Pt(1)–Ru(3)	57.32(3)	Pt(1)–Ru(3)–Pt(2)	65.06(3)
Pt(1)–Pt(2)–Ru(1)	58.00(3)	Pt(1)–Ru(3)–Ru(2)	61.53(3)
Pt(1)–Pt(2)–Ru(3)	59.62(3)	Pt(2)–Ru(3)–Ru(2)	104.91(4)
Ru(1)–Pt(2)–Ru(3)	74.86(3)	Ru(3)–C(32)–O(32)	162.4(9)
Pt(1)–Ru(1)–Pt(2)	63.22(3)	M–C(av)–O	176(1)

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

a species that we propose to be $PtRu_2(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$, 7. This compound was stable only under a CO atmosphere and could not be isolated. After removal of the CO atmosphere and solvent, only compounds 4 (0.6 mg, 10%), 2 (2.2 mg, 40%), 5 (2.0 mg), and **X** (1.1 mg) were isolated after separation by TLC.

Reaction of 5 with 1,2-Bis(diphenylphosphino)ethane (dppe). A 5.2-mg amount of 5 (0.0023 mmol) and a 2.8-mg amount of dppe (0.0070 mmol) were dissolved in 10 mL of CH_2Cl_2. The solution was stirred at 25 °C for 40 min. The solvent was removed by rotary evaporation, and the residue was separated by TLC using a CH_2Cl_2/hexane (3/7) solvent mixture. This yielded 1.2 mg of unreacted 5 (22%), 0.6 mg of red $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(dppe)$, 6 (10%), and traces of a few uncharacterizable products. IR (νCO, cm^{-1} in hexane) for 6: 2048 (s), 2016 (vs), 1979 (s), 1966 (m), 1949 (m). ^{1}H NMR (δ in CH_2Cl_2) for 6: 7.0–7.4 (m, Ph, 30 H), 2.2–2.4 (m, CH_2, 4 H, $^2J_{P-H}$ = 15.3 Hz). Anal. Calcd (found) for 6: C, 48.55 (48.38); H, 2.66 (2.51).

Table V. Positional Parameters and *B*(eq) Values for $Pt_3Ru_6(CO)_{14}(PhCCPh)_3$, 3

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.28983(05)	0.23978(05)	0.53032(05)	3.43(3)
Pt(2)	0.35536(05)	0.30192(04)	0.70801(05)	3.20(3)
Pt(3)	0.10855(05)	0.31485(05)	0.57947(05)	3.73(3)
Ru(1)	0.16444(10)	0.33172(10)	0.41884(1)	3.82(7)
Ru(2)	0.21639(10)	0.19955(09)	0.69602(10)	3.65(7)
Ru(3)	0.25585(10)	0.40892(09)	0.58198(10)	3.42(7)
Ru(4)	0.19905(10)	0.37427(09)	0.74746(10)	3.62(7)
Ru(5)	0.14011(11)	0.15391(09)	0.49914(10)	4.12(7)
Ru(6)	0.37638(11)	0.12352(09)	0.65676(10)	4.04(7)
O(11)	0.2257(10)	0.4312(10)	0.2743(10)	7.4(4)
O(12)	–0.0271(12)	0.3622(11)	0.3182(12)	9.6(5)
O(21)	0.0945(11)	0.0509(11)	0.6884(11)	8.6(4)
O(22)	0.1010(10)	0.2388(09)	0.8460(10)	7.1(4)
O(31)	–0.0835(13)	0.2756(11)	0.5127(12)	9.9(5)
O(33)	0.3886(09)	0.4838(09)	0.4793(10)	6.7(3)
O(34)	0.1089(10)	0.5362(10)	0.5118(10)	7.1(4)
O(41)	0.2579(10)	0.4077(10)	0.9590(11)	8.2(4)
O(42)	0.0155(09)	0.4573(09)	0.7389(09)	6.5(3)
O(51)	–0.0459(11)	0.0875(10)	0.4664(11)	8.2(4)
O(52)	0.2095(10)	–0.0207(11)	0.4440(11)	8.3(4)
O(61)	0.3281(11)	–0.0648(12)	0.6393(12)	9.4(5)
O(62)	0.5712(11)	0.0731(10)	0.7061(11)	8.5(4)
O(63)	0.4294(10)	0.1080(10)	0.4655(11)	8.3(4)
C(1)	0.3454(10)	0.4339(10)	0.7138(11)	3.2(3)
C(2)	0.2639(11)	0.4808(10)	0.7188(11)	3.4(4)
C(3)	0.2397(11)	0.2186(11)	0.3866(11)	3.8(4)
C(4)	0.1515(11)	0.1908(11)	0.3713(11)	3.7(4)
C(5)	0.3166(11)	0.1441(11)	0.7882(11)	3.6(4)
C(6)	0.3812(11)	0.2046(11)	0.7898(11)	3.9(4)
C(11)	0.2051(12)	0.3899(12)	0.3299(13)	5.0(4)
C(12)	0.0477(15)	0.3519(14)	0.3562(15)	6.5(5)
C(21)	0.1447(14)	0.1047(14)	0.6823(14)	6.1(5)
C(22)	0.1473(13)	0.2480(13)	0.7896(14)	5.5(5)
C(31)	–0.0087(16)	0.2858(14)	0.5363(15)	6.8(6)
C(33)	0.3382(12)	0.4552(12)	0.5173(13)	4.8(4)
C(34)	0.1620(14)	0.4819(14)	0.5305(14)	5.9(5)
C(41)	0.2335(13)	0.3968(12)	0.8791(14)	5.3(5)
C(42)	0.0855(13)	0.4253(12)	0.7412(13)	4.7(4)
C(51)	0.0251(14)	0.1134(13)	0.4786(13)	5.4(5)
C(52)	0.1813(13)	0.0467(14)	0.4668(13)	5.4(5)
C(61)	0.3467(15)	0.0078(15)	0.6442(15)	6.6(5)
C(62)	0.4970(15)	0.0900(14)	0.6866(14)	6.2(5)
C(63)	0.3919(13)	0.1309(13)	0.5301(15)	6.0(5)

Reaction of 5 with a Combination of CO and dppe. An 8.6-mg amount of 5 (0.004 mmol) was dissolved in 20 mL of hexane, and CO was purged slowly through the solution at 25 °C for 60 min. A 6.0-mg portion of dppe (0.014 mmol) was then added, and the mixture solution was stirred for an additional 50 min. The solvent was removed by rotary evaporation, and the residue was separated by TLC. This yielded 2.1 mg of unreacted 5 (25%) and 6.0 mg of 6 (46%).

Reaction of $PtRu_2(CO)_8(dppe)$ with PhC_2Ph. A 13.5-mg amount of $PtRu_2(CO)_8(dppe)$ (0.013 mmol) was mixed with 6.0 mg of PhC_2Ph (0.034 mmol) in 15 mL of heptane. The solution was then heated to reflux (97 °C) for 4 h. The color of the solution changed from yellow to dark-red. After cooling, the solvent was removed by rotary evaporation and the residue was separated by TLC. This yielded 5.4 mg of 6 (36%) with 1.3 mg of unreacted $PtRu_2(CO)_8(dppe)$ (10%) recovered.

Crystallographic Analysis. Crystals of compound 2 suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution of ethyl acetate/ethanol (2/1) at 25 °C. Crystals of compound 3 were grown from a solution in hexane solvent by cooling to 10 °C. Crystals of compound 4 were grown from a solution in a CH_2Cl_2/hexane (1/2) solvent mixture by cooling to –20 °C. Crystals of compound 5 were grown from a solution in a CH_2Cl_2/hexane (1/1) solvent mixture by cooling to 10 °C. Crystals of compound 6 were grown in a solution of ethyl

Table VI. Intramolecular Distances[a] for 3

Pt(1)–C(3)	2.09(2)	Ru(2)–C(22)	1.95(2)
Pt(1)–C(63)	2.24(2)	Ru(2)–C(5)	2.04(2)
Pt(1)–Ru(5)	2.637(2)	Ru(2)–Ru(4)	2.757(2)
Pt(1)–Ru(1)	2.699(2)	Ru(2)–Ru(6)	2.788(2)
Pt(1)–Pt(2)	2.702(1)	Ru(2)–Ru(5)	2.920(2)
Pt(1)–Ru(3)	2.714(2)	Ru(3)–C(1)	2.15(2)
Pt(1)–Ru(6)	2.785(2)	Ru(3)–C(2)	2.18(2)
Pt(1)–Ru(2)	2.937(2)	Ru(3)–Ru(4)	2.782(2)
Pt(2)–C(6)	1.97(2)	Ru(4)–C(2)	2.06(2)
Pt(2)–C(1)	2.03(2)	Ru(4)–C(22)	2.30(2)
Pt(2)–Ru(2)	2.667(2)	Ru(5)–C(4)	2.02(2)
Pt(2)–Ru(4)	2.719(2)	Ru(6)–C(63)	1.90(2)
Pt(2)–Ru(3)	2.760(2)	Ru(6)–C(6)	2.20(2)
Pt(2)–Ru(6)	2.817(2)	Ru(6)–C(5)	2.24(2)
Pt(3)–Ru(1)	2.648(2)	C(1)–C(2)	1.42(2)
Pt(3)–Ru(4)	2.685(2)	C(3)–C(4)	1.40(2)
Pt(3)–Ru(3)	2.716(2)	C(5)–C(6)	1.38(2)
Pt(3)–Ru(5)	2.721(2)	O–C(av)	1.16(2)
Pt(3)–Ru(2)	2.817(2)	M–C(av)	1.85(2)
Ru(1)–Ru(3)	2.73(2)	Pt(1)–Pt(3)	3.124(1)
Ru(1)–C(3)	2.11(2)	Ru(1)–Ru(5)	3.125(2)
Ru(1)–C(4)	2.24(2)		

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

Table VII. Intramolecular Bond Angles[a] for 3

Ru(5)–Pt(1)–Ru(1)	71.70(5)	Ru(4)–Ru(2)–Ru(6)	122.25(7)
Ru(5)–Pt(1)–Pt(2)	118.75(5)	Ru(4)–Ru(2)–Ru(5)	113.25(7)
Ru(5)–Pt(1)–Ru(3)	109.73(6)	Ru(4)–Ru(2)–Pt(1)	90.51(6)
Ru(5)–Pt(1)–Ru(6)	92.87(5)	Ru(6)–Ru(2)–Pt(3)	123.81(5)
Ru(1)–Pt(1)–Pt(2)	120.52(5)	Ru(6)–Ru(2)–Ru(5)	86.96(6)
Ru(1)–Pt(1)–Ru(6)	163.66(5)	Pt(1)–Ru(3)–Pt(3)	70.24(4)
Ru(1)–Pt(1)–Ru(2)	108.23(5)	Pt(1)–Ru(3)–Ru(4)	94.80(6)
Ru(3)–Pt(1)–Ru(6)	122.80(5)	Pt(3)–Ru(3)–Pt(2)	90.41(5)
Ru(3)–Pt(1)–Ru(2)	86.03(5)	Ru(1)–Ru(3)–Pt(2)	117.35(5)
Ru(2)–Pt(2)–Ru(3)	90.62(5)	Ru(1)–Ru(3)–Ru(4)	116.39(7)
Pt(1)–Pt(2)–Ru(4)	96.57(4)	Pt(3)–Ru(4)–Pt(2)	91.99(5)
Ru(4)–Pt(2)–Ru(6)	122.61(5)	Ru(2)–Ru(4)–Ru(3)	88.32(6)
Ru(3)–Pt(2)–Ru(6)	119.93(5)	Pt(1)–Ru(5)–Pt(3)	71.32(4)
Ru(1)–Pt(3)–Ru(4)	122.96(5)	Pt(3)–Ru(1)–Pt(1)	71.50(4)
Ru(1)–Pt(3)–Ru(5)	71.18(5)	O(63)–C(63)–Ru(6)	150(2)
Ru(1)–Pt(3)–Ru(2)	113.41(6)	O(63)–C(63)–Pt(1)	125(2)
Ru(4)–Pt(3)–Ru(5)	122.61(5)	O(22)–C(22)–Ru(2)	151(2)
Ru(3)–Pt(3)–Ru(5)	107.18(5)	O(22)–C(22)–Ru(4)	129(2)
Ru(3)–Pt(3)–Ru(2)	88.41(5)	Ru(2)–C(22)–Ru(4)	80.6(7)
Pt(2)–Ru(2)–Pt(3)	90.20(5)	Ru(6)–C(63)–Pt(1)	84.1(8)
Pt(2)–Ru(2)–Ru(5)	110.53(6)	M–C(av)–O	177(2)

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

Table VIII. Positional Parameters and *B*(eq) Values for $Pt_2Ru_4(CO)_{14}(C_2Ph_2)_2$, 4

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.16039(02)	0.12226(04)	0.912186(16)	2.27(2)
Pt(2)	0.28702(02)	0.22866(04)	0.874960(16)	2.12(2)
Ru(1)	0.15705(05)	0.19828(08)	0.79573(03)	2.22(4)
Ru(2)	0.28743(05)	−0.03619(08)	0.87000(03)	2.34(4)
Ru(3)	0.12867(05)	−0.05076(08)	0.82771(03)	2.37(4)
Ru(4)	0.19006(05)	0.35474(08)	0.94879(03)	2.71(4)
O(10)	−0.0084(05)	0.1072(09)	0.9574(03)	6.3(5)
O(11)	0.0820(05)	0.2145(08)	0.6793(03)	5.6(5)
O(12)	0.2178(05)	0.4630(07)	0.7790(03)	4.6(4)
O(13)	−0.0108(05)	0.2701(08)	0.8337(03)	5.0(5)
O(20)	0.4156(05)	0.4200(08)	0.8444(03)	5.4(5)
O(21)	0.2230(05)	−0.1535(07)	0.9738(03)	5.1(5)
O(22)	0.3170(05)	−0.3014(08)	0.8343(03)	5.2(5)
O(23)	0.4603(05)	−0.0236(08)	0.9214(04)	6.0(5)
O(31)	0.0456(05)	−0.1930(08)	0.9190(03)	6.1(5)
O(32)	−0.0317(05)	−0.0064(07)	0.7644(03)	4.8(4)
O(33)	0.1421(05)	−0.2938(08)	0.7642(03)	4.9(5)
O(41)	0.2848(05)	0.5897(08)	0.9763(04)	6.1(5)
O(42)	0.0756(06)	0.4049(09)	1.0434(04)	7.4(6)
O(43)	0.0783(06)	0.5110(09)	0.8712(03)	7.0(6)
C(1)	0.2336(05)	0.0222(09)	0.7832(04)	2.6(5)
C(2)	0.2890(05)	0.1195(09)	0.8000(04)	2.1(5)
C(3)	0.3028(06)	0.2408(09)	0.9609(04)	2.8(5)
C(4)	0.2381(05)	0.1796(09)	0.9826(04)	2.3(5)
C(10)	0.0565(07)	0.1055(11)	0.9420(04)	3.7(6)
C(11)	0.1127(06)	0.2013(10)	0.7221(05)	3.3(6)
C(12)	0.1958(06)	0.3651(11)	0.7870(04)	3.1(6)
C(13)	0.0534(07)	0.2406(10)	0.8222(04)	3.3(6)
C(20)	0.3716(06)	0.3447(11)	0.8565(04)	3.0(6)
C(21)	0.2412(07)	−0.0975(10)	0.9352(05)	3.7(6)
C(22)	0.3078(06)	−0.2017(12)	0.8471(04)	3.3(6)
C(23)	0.3952(07)	−0.0230(10)	0.9013(04)	3.2(6)
C(31)	0.0758(07)	−0.1368(10)	0.8863(05)	3.6(6)
C(32)	0.0288(07)	−0.0179(10)	0.7891(04)	3.2(6)
C(33)	0.1391(06)	−0.2026(11)	0.7881(04)	3.0(6)
C(41)	0.2482(07)	0.5026(12)	0.9667(05)	4.0(7)
C(42)	0.1193(07)	0.3845(11)	1.0076(05)	4.2(6)
C(43)	0.1203(07)	0.4468(11)	0.8977(05)	4.1(6)

acetate/heptane (1/1) by cooling to 10 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using 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.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Lorentz/polarization (Lp) and absorption corrections were applied to the data for each structure. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/L_p$.

All of the structures were solved by a combination of direct methods (MITHRIL) and difference Fourier analyses. The positions of the hydrogen atoms in all of the structures were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. Crystal data and results of the analyses are listed in Table I.

Compounds 2, 3, and 5 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure in each case. For compounds 2 and 5, all non-hydrogen atoms in the structures were refined with anisotropical thermal parameters. For 3, only the metal atoms were refined anisotropically. For 3, 1.5 molecules of hexane from the crystallization solvent were found cocrystallized in the lattice in the final stages of the analysis. These were included in the analysis and were satisfactorily refined.

Compound 4 crystallized in a monoclinic crystal system. From the systematic absences in the data the space group $P2_1/c$ was uniquely identified. All non-hydrogen atoms in this structure were refined anisotropically.

Compound 6 crystallized in the orthorhombic crystal system. The space group *Pbcn* was established on the basis of the systematic absences observed during the collection of data. All non-hydrogen atoms were refined with the anisotropical thermal parameters. In the final stages of the analysis, 1 molecule of ethyl acetate and 0.5 molecule of heptane cocrystallized from the crystallization solvent were found in the lattice. The heptane molecule was position about a crystallographic 2-fold rotation axis. These molecules did not define to a convergence and were included as fixed contributions on the final cycles of least-squares refinement.

Results and Discussion

Two new compounds, $Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (2) (6%) and $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$

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

Table IX. Intramolecular Distances[a] for 4

Pt(1)-Pt(2)	2.5325(6)	Ru(1)-C(1)	2.29(1)
Pt(1)-Ru(1)	2.9100(9)	Ru(1)-C(2)	2.322(9)
Pt(1)-Ru(2)	2.8727(9)	Ru(2)-Ru(3)	2.792(1)
Pt(1)-Ru(3)	2.7937(9)	Ru(2)-C(1)	2.343(9)
Pt(1)-Ru(4)	2.685(1)	Ru(2)-C(2)	2.367(9)
Pt(1)-C(4)	2.199(9)	Ru(3)-C(1)	2.17(1)
Pt(2)-Ru(1)	2.8671(9)	Ru(4)-C(3)	2.23(1)
Pt(2)-Ru(2)	2.840(1)	Ru(4)-C(4)	2.19(1)
Pt(2)-Ru(4)	2.7395(9)	C(1)-C(2)	1.44(1)
Pt(2)-C(2)	2.145(9)	C(3)-C(4)	1.35(1)
Pt(2)-C(3)	2.081(9)	M-C(av)	1.90(1)
Ru(1)-Ru(3)	2.816(1)	C-O(av)	1.14(1)

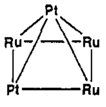
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles[a] for 4

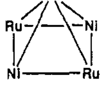
Pt(2)-Pt(1)-Ru(1)	63.13(2)	Ru(1)-Pt(2)-Ru(4)	93.07(3)
Pt(2)-Pt(1)-Ru(2)	63.03(2)	Ru(2)-Pt(2)-Ru(4)	121.41(2)
Pt(2)-Pt(1)-Ru(3)	101.15(2)	Pt(1)-Ru(1)-Pt(2)	51.99(2)
Pt(2)-Pt(1)-Ru(4)	63.27(2)	Pt(1)-Ru(1)-Ru(3)	58.38(2)
Ru(1)-Pt(1)-Ru(2)	80.70(3)	Pt(2)-Ru(1)-Ru(3)	92.86(3)
Ru(1)-Pt(1)-Ru(3)	59.12(3)	Pt(1)-Ru(2)-Pt(2)	52.62(2)
Ru(1)-Pt(1)-Ru(4)	93.27(3)	Pt(1)-Ru(2)-Ru(3)	59.07(2)
Ru(2)-Pt(1)-Ru(3)	59.03(2)	Pt(2)-Ru(2)-Ru(3)	93.94(3)
Ru(2)-Pt(1)-Ru(4)	122.21(3)	Pt(1)-Ru(3)-Ru(1)	62.50(3)
Ru(3)-Pt(1)-Ru(4)	152.35(3)	Pt(1)-Ru(3)-Ru(2)	61.90(2)
Pt(1)-Pt(2)-Ru(1)	64.88(2)	Ru(1)-Ru(3)-Ru(2)	83.77(3)
Pt(1)-Pt(2)-Ru(2)	64.35(2)	Pt(1)-Ru(4)-Pt(2)	55.65(2)
Pt(1)-Pt(2)-Ru(4)	61.08(2)	Ru(2)-C(21)-O(21)	167(1)
Ru(1)-Pt(2)-Ru(2)	81.99(3)	M-C(av)-O	175(1)

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

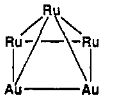
(3) (27%), were obtained from the reaction of 1 with diphenylacetylene in refluxing heptane (97 °C). Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of molecular structure of 2 is shown in Figure 1. Selected final atomic positional parameters are listed in Table II. Selected interatomic bond distances and angles are listed in Tables III and IV. The molecule contains a cluster of two platinum and three ruthenium atoms in the form of a distorted square pyramid. Similar structures were observed for the complexes $Ni_2Ru_3(CO)_8Cp_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (8)[9] and $Au_2Ru_3(CO)_9(COMe)(PPh_3)_2H$ (9).[10] The platinum atoms in 2 are located in the apical position, Pt(1), and one of the basal positions, Pt(2). In compounds 8 and 9, the heteronuclear pair of metal atoms are both located in basal positions. A similar pattern was also observed in the heteronuclear carbido cluster complexes $M_2Fe_3(CO)_{14}(C)$ (M = Co or Rh)[11] 10.



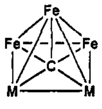
(2)



(8)



(9)



(10)

The metal–metal bond distances in 2 range from 2.666(1) Å for Pt(2)–Ru(3) to 2.9369(9) Å for Pt(1)–Pt(2). These distances are not unusual.[12] Each ruthenium atom contains two carbonyl ligands while each platinum atom only has one. One of the eight carbonyl ligands, C(32)–O(32) is a slight asymmetrical bridge, Ru(2)···C(32) = 2.58(1) Å, Ru(3)–C(32)–(32) = 162.4(9)°. There are three PhC_2Ph ligands in this complex. Two of these are triply bridging and adopt the usual μ_3-∥ mode: one is on the Pt_2Ru triangle Pt(1), Pt(2), Ru(3) and one is on the $PtRu_2$ triangle Pt(1), Ru(1), Ru(2). The third PhC_2Ph ligand is a quadruple bridge spanning the base of the square pyramid. Compound 8 contains a similar quadruply bridging alkyne ligand.[9] The four basal metal atoms of 2 do not lie in a perfect plane. Their deviation from the mean plane is Pt(2) −0.05, Ru(1) +0.19, Ru(2) −0.18, and Pt(3) +0.19 Å. The similar pattern was also observed in the structure of the complex $Os_6(CO)_{17}(\mu_4\text{-}\eta^2\text{-}HC_2Et)$.[13] Compound 2 contains total of 72 electrons which is two less than the 74 expected for a square-pyramidal cluster.[14] Previous studies have shown that clusters containing diplatinum groups often contain two fewer electrons than predicted by the conventional electron counting theories.[15]

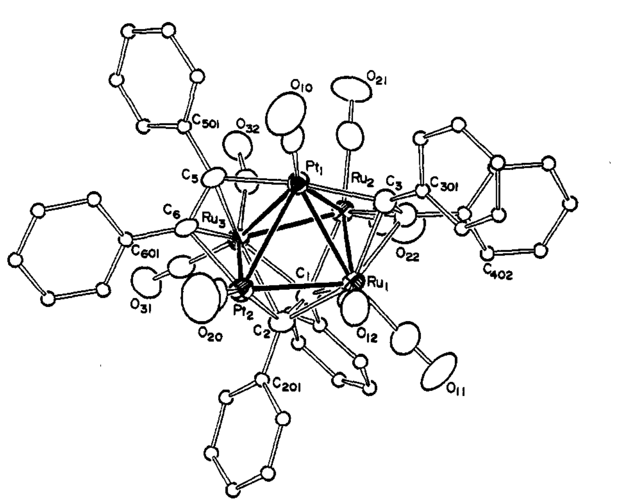


Figure 1. An ORTEP drawing of $Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (2) showing 50% probability thermal ellipsoids.

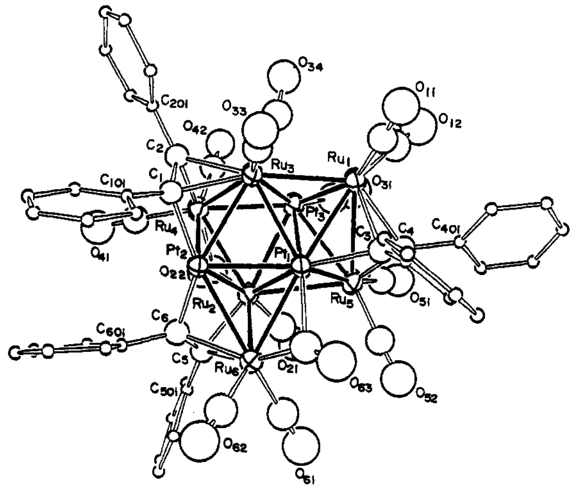


Figure 2. An ORTEP diagram of $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (3) showing 50% probability thermal ellipsoids.

An ORTEP drawing of molecular structure of 3 is shown in Figure 2. Selected final atomic positional parameters are listed in Table V. Selected interatomic bond distances

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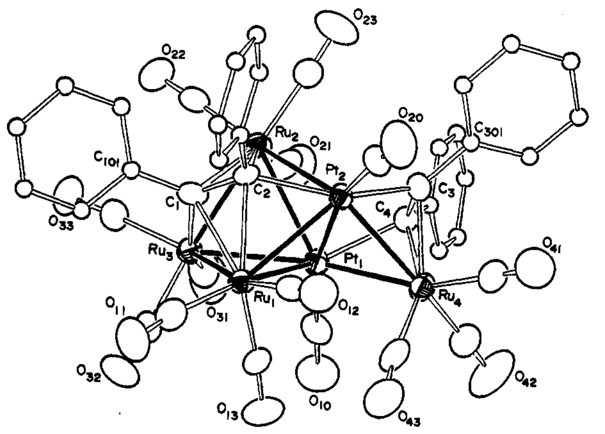

Figure 3. An ORTEP drawing of $Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (4) showing 50% probability thermal ellipsoids.

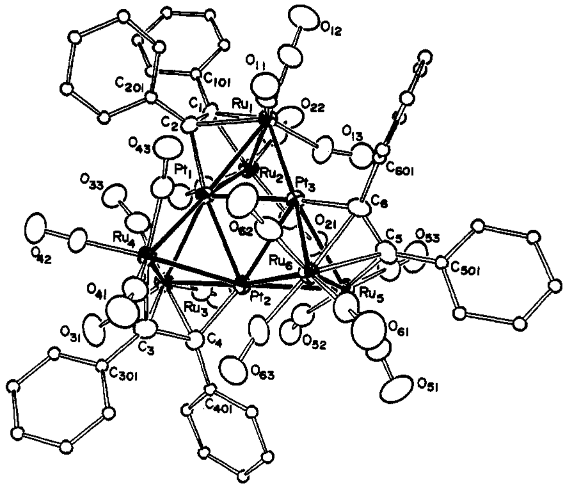

Figure 4. An ORTEP diagram of $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (5) showing 50% probability thermal ellipsoids.

Table XI. Positional Parameters and B(eq) Values for $Pt_3Ru_6(CO)_{18}(C_2Ph_2)_3$, 5

atom	x	y	z	B(eq), Å^2
Pt(1)	0.35182(06)	0.20276(05)	0.87949(06)	2.55(4)
Pt(2)	0.21483(06)	0.24105(05)	0.99981(06)	2.57(4)
Pt(3)	0.19885(06)	0.24509(05)	0.80339(06)	2.66(4)
Ru(1)	0.33828(12)	0.23147(11)	0.68993(12)	2.80(7)
Ru(2)	0.46113(13)	0.33317(10)	0.83303(12)	3.05(8)
Ru(3)	0.38522(12)	0.23328(11)	1.09103(12)	2.85(7)
Ru(4)	0.26241(12)	0.09735(10)	0.99361(12)	2.68(7)
Ru(5)	0.13138(12)	0.35700(11)	0.94099(12)	2.93(7)
Ru(6)	0.03992(12)	0.20037(11)	0.88561(12)	2.93(7)
O(11)	0.1810(12)	0.0860(10)	0.5984(11)	4.4(8)
O(12)	0.3756(13)	0.2309(11)	0.4743(13)	6(1)
O(13)	0.2832(11)	0.3908(11)	0.7044(11)	5.3(8)
O(21)	0.3827(12)	0.4737(10)	0.9464(12)	5.1(8)
O(22)	0.5719(14)	0.4436(11)	0.7223(13)	6(1)
O(23)	0.6284(12)	0.3520(10)	0.9806(13)	5.6(9)
O(31)	0.5062(13)	0.2379(10)	1.2756(14)	6(1)
O(32)	0.4740(12)	0.4118(10)	1.1387(12)	4.9(8)
O(33)	0.5413(11)	0.1760(10)	0.9807(11)	4.9(8)
O(41)	0.0940(13)	−0.0125(11)	1.0350(13)	6.1(9)
O(42)	0.3753(14)	−0.0237(11)	1.0196(12)	7(1)
O(43)	0.2217(11)	0.0160(09)	0.7645(11)	4.5(7)
O(51)	0.0070(13)	0.4326(12)	1.0776(14)	7(1)
O(52)	0.2838(12)	0.4321(09)	1.1160(12)	4.4(7)
O(53)	0.1808(14)	0.5039(12)	0.8638(15)	7(1)
O(61)	−0.1631(14)	0.1615(12)	0.8903(14)	7(1)
O(62)	0.0254(11)	0.0272(11)	0.7738(13)	5.6(8)
O(63)	0.0381(11)	0.1590(10)	1.0927(12)	5.0(8)
C(1)	0.4849(14)	0.2303(12)	0.7395(14)	2.5(9)
C(2)	0.4268(14)	0.1670(13)	0.7619(13)	3(1)
C(3)	0.2676(14)	0.1590(13)	1.1432(14)	3(1)
C(4)	0.2471(14)	0.2357(11)	1.1446(14)	2.6(9)
C(5)	0.0341(14)	0.3075(13)	0.8171(15)	2.9(9)
C(6)	0.0702(14)	0.2521(13)	0.7546(14)	3(1)
C(11)	0.2359(17)	0.1385(16)	0.6338(15)	3(1)
C(12)	0.3602(17)	0.2302(14)	0.5564(18)	4(1)
C(13)	0.3033(19)	0.3302(15)	0.7161(19)	5(1)
C(21)	0.4091(16)	0.4203(14)	0.9078(17)	4(1)
C(22)	0.5290(18)	0.4017(14)	0.7640(17)	4(1)
C(23)	0.5627(18)	0.3442(13)	0.9261(17)	4(1)
C(31)	0.4566(17)	0.2345(14)	1.2055(17)	4(1)
C(32)	0.4361(17)	0.3467(16)	1.1178(16)	4(1)
C(33)	0.4734(18)	0.1955(15)	1.0060(16)	5(1)
C(41)	0.1566(19)	0.0320(15)	1.0170(17)	4(1)
C(42)	0.3326(17)	0.0227(15)	1.0123(16)	4(1)
C(43)	0.2444(16)	0.0536(14)	0.8478(18)	4(1)
C(51)	0.0538(16)	0.4053(15)	1.0221(17)	4(1)
C(52)	0.2317(16)	0.3936(14)	1.0518(18)	3(1)
C(53)	0.1645(17)	0.4483(15)	0.8924(18)	4(1)
C(61)	−0.0860(17)	0.1781(15)	0.8875(17)	4(1)
C(62)	0.0322(16)	0.0937(16)	0.8163(15)	4(1)
C(63)	0.0547(16)	0.1801(13)	1.0170(18)	4(1)

and angles are listed in Tables VI and VII. The cluster contains three platinum and six ruthenium atoms and can be described as a tricapped octahedron Ru(2), Ru(3), Ru(4), Pt(1), Pt(2), Pt(3) containing a bond between the capping atoms Ru(1) and Ru(5). This appears to be a new structural type for nine metal cluster complexes.[14] With 22 metal–metal bonds, 18-electron configurations can be assigned to each metal atom although two of the metal–metal bonds must be viewed formally as donor/acceptor bonds, Pt(1) → Ru(5) and Ru(3) → Pt(2). Two of the metal–metal bonds in 3 are unusually long, Ru(1)–Ru(5) = 3.125(2) Å and Pt(1)–Pt(3) = 3.124(1) Å, but bonds of similar lengths have been observed in other platinum,[16] ruthenium,[17] and platinum–ruthenium[18] cluster complexes. Compound 3 contains three μ_3-|| PhC_2Ph ligands that occupy $PtRu_2$ triangular groupings. It is worth pointing out that for two of the three PhC_2Ph ligands, the acetylenic C–C bond is not completely parallel to one of the three metal–metal bonds of the $PtRu_2$ triangle as usually observed for μ_3-|| ligands. The angles between these acetylenic C–C vectors and the closest metal–metal vectors are 12.8° for C(3)–C(4) vs Pt(1)–Ru(5) and 9.0° for C(1)–C(2) vs Pt(2)–Ru(4), respectively. This distortion is probably due to steric effects. There are 14 carbonyl ligands, and two of them are bridges across the Ru(2)–Ru(4) and Pt(1)–Ru(6) bonds.

When compound 3 was treated with carbon monoxide (1 atm) at 25 °C, three products, $Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (4, 16%), $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (5, 20%), and a partially characterized compound **X**, were isolated. Compounds 4 and 5 were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of molecular structure of 4 is shown in Figure 3. Selected final atomic positional parameters are listed in Table VIII. Selected interatomic bond distances and angles are listed in Tables IX and X. Compound 4 contains six metal atoms. Five, the two platinum and three ruthenium atoms, are arranged in the form of a square pyramid as found in 2. The fourth ruthenium atom bridges the Pt–Pt edge of the square pyramid. The Pt–Pt bond distance in 4 is significantly

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Table XII. Intramolecular Distances[a] for 5

Pt(1)–Pt(2)	2.774(1)	Pt(3)–Ru(6)	2.726(2)
Pt(1)–Pt(3)	2.736(1)	Pt(3)–C(6)	2.02(2)
Pt(1)–Ru(1)	2.734(2)	Pt(3)–C(13)	2.48(3)
Pt(1)–Ru(2)	2.756(2)	Ru(1)–Ru(2)	2.675(3)
Pt(1)–Ru(3)	2.806(2)	Ru(1)–C(1)	2.25(2)
Pt(1)–Ru(4)	2.852(2)	Ru(1)–C(2)	2.20(2)
Pt(1)–C(2)	2.06(2)	Ru(2)–C(1)	2.07(2)
Pt(1)–C(33)	2.46(2)	Ru(3)–Ru(4)	2.733(3)
Pt(1)–C(43)	2.72(2)	Ru(3)–C(3)	2.22(2)
Pt(2)–Pt(3)	2.685(1)	Ru(3)–C(4)	2.22(2)
Pt(2)–C(52)	2.57(2)	Ru(4)–C(3)	2.08(2)
Pt(2)–Ru(3)	2.795(2)	Ru(5)–Ru(6)	2.742(3)
Pt(2)–Ru(4)	2.724(2)	Ru(5)–C(5)	2.07(2)
Pt(2)–Ru(5)	2.799(2)	Ru(6)–C(5)	2.28(2)
Pt(2)–Ru(6)	2.835(2)	Ru(6)–C(6)	2.20(2)
Pt(2)–C(4)	2.03(2)	C(1)–C(2)	1.37(3)
Pt(2)–C(63)	2.47(2)	C(3)–C(4)	1.43(3)
Pt(3)–Ru(1)	2.670(2)	C(5)–C(6)	1.36(3)
Pt(3)–Ru(2)	3.877(2)	Ru–C(av)	1.89(3)
Pt(3)–Ru(5)	2.778(2)	O–C(av)	1.15(3)

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

Table XIII. Intramolecular Bond Angles[a] for 5

Pt(2)–Pt(1)–Pt(3)	58.31(3)	Ru(3)–Pt(2)–Ru(6)	163.13(6)
Pt(2)–Pt(1)–Ru(1)	116.12(5)	Ru(4)–Pt(2)–Ru(5)	159.58(6)
Pt(2)–Pt(1)–Ru(2)	113.80(5)	Ru(4)–Pt(2)–Ru(6)	103.95(6)
Pt(2)–Pt(1)–Ru(3)	60.11(4)	Ru(5)–Pt(2)–Ru(6)	58.24(6)
Pt(2)–Pt(1)–Ru(4)	57.90(4)	Pt(1)–Pt(3)–Pt(2)	61.56(3)
Pt(3)–Pt(1)–Ru(1)	58.43(4)	Pt(1)–Pt(3)–Ru(1)	60.75(4)
Pt(3)–Pt(1)–Ru(2)	89.79(5)	Pt(1)–Pt(3)–Ru(5)	114.08(5)
Pt(3)–Pt(1)–Ru(3)	116.99(5)	Pt(1)–Pt(3)–Ru(6)	116.10(5)
Pt(3)–Pt(1)–Ru(4)	98.05(5)	Pt(2)–Pt(3)–Ru(1)	121.61(5)
Ru(1)–Pt(1)–Ru(2)	58.31(6)	Pt(2)–Pt(3)–Ru(5)	61.63(5)
Ru(1)–Pt(1)–Ru(3)	159.34(6)	Pt(2)–Pt(3)–Ru(6)	63.19(5)
Ru(1)–Pt(1)–Ru(4)	140.10(6)	Ru(1)–Pt(3)–Ru(5)	141.51(7)
Ru(2)–Pt(1)–Ru(3)	103.21(6)	Ru(1)–Pt(3)–Ru(6)	158.74(6)
Ru(2)–Pt(1)–Ru(4)	160.94(6)	Ru(5)–Pt(3)–Ru(6)	59.75(6)
Ru(3)–Pt(1)–Ru(4)	57.76(5)	Pt(1)–Ru(1)–Pt(3)	60.82(4)
Pt(1)–Pt(2)–Pt(3)	60.13(3)	Pt(1)–Ru(1)–Ru(2)	61.26(6)
Pt(1)–Pt(2)–Ru(3)	60.51(4)	Pt(3)–Ru(1)–Ru(2)	92.98(7)
Pt(1)–Pt(2)–Ru(4)	62.48(4)	Pt(1)–Ru(3)–Pt(2)	59.38(4)
Pt(1)–Pt(2)–Ru(5)	112.20(5)	Pt(1)–Ru(3)–Ru(4)	61.96(5)
Pt(1)–Pt(2)–Ru(6)	111.43(5)	Pt(2)–Ru(3)–Ru(4)	59.03(6)
Pt(3)–Pt(2)–Ru(3)	119.13(5)	Pt(2)–Ru(5)–Pt(3)	57.56(4)
Pt(3)–Pt(2)–Ru(4)	102.54(5)	Pt(2)–Ru(5)–Ru(6)	61.53(6)
Pt(3)–Pt(2)–Ru(5)	60.81(4)	Pt(3)–Ru(5)–Ru(6)	59.19(6)
Pt(3)–Pt(2)–Ru(6)	59.12(4)	Pt(2)–Ru(6)–Pt(3)	57.70(4)
Ru(3)–Pt(2)–Ru(4)	59.35(6)	Pt(2)–Ru(6)–Ru(5)	60.23(6)
Ru(3)–Pt(2)–Ru(5)	137.55(6)	Pt(3)–Ru(6)–Ru(5)	61.05(6)
Ru(1)–C(13)–O(13)	162(2)		
Ru(3)–C(33)–O(33)	161(2)		
Ru(4)–C(43)–O(43)	167(2)		
Ru(5)–C(52)–O(52)	163(2)		
Ru(6)–C(63)–O(63)	161(2)		
Ru–C(av)–O	177(2)		

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

shorter than that in 2, 2.5325(6) vs 2.9396(9) Å. This may be due to the presence of the bridging ruthenium atom. All other metal–metal bond distances in 4 are similar to those in 2. There are total 14 terminal carbonyl ligands. Each ruthenium atom has three, and each platinum atom has one. In addition to the quadruply bridging PhC_2Ph ligand, there is one triply bridging PhC_2Ph ligand on the Pt_2Ru triangle Pt(1), Pt(2), Ru(4). Compound 4 contains 88 valence electrons which is exactly the number predicted for an edge-bridged square-pyramidal structure.[14]

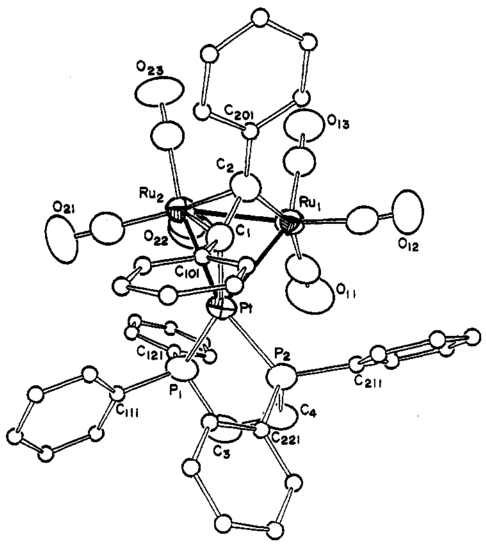


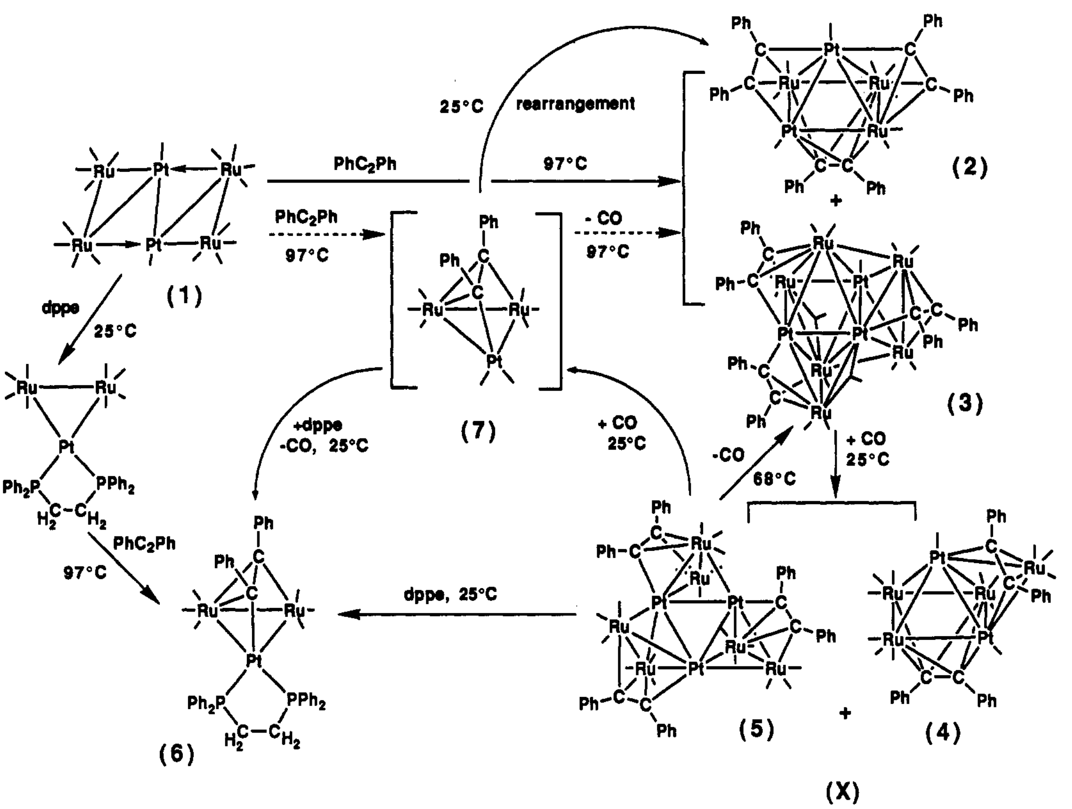
Figure 5. An ORTEP diagram of $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(dppe)$ (6) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) for 6 are: Pt–Ru(1) = 2.766(1), Pt–Ru(2) = 2.684(1), Ru(1)–Ru(2) = 2.725(1), Pt–P(1) = 2.308(4), Pt–P(2) = 2.277(4), Pt–C(1) = 2.09(1), Ru(1)–C(1) = 2.56(1), Ru(2)–C(1) = 2.03(1), Ru(2)–C(1) = 2.19(1), Ru(2)–C(2) = 2.23(1), C(1)–C(2) = 1.38(2); Pt–Ru(1)–Ru(2) = 58.52(4), Pt–Ru(2)–Ru(1) = 61.50(4), Ru(1)–Pt–Ru(2) = 59.99(4).

Table XIV. Positional Parameters and *B*(eq) Values for $PtRu_2(CO)_6(PhC_2Ph)(dppe)$, 6

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt	0.72367(03)	0.06257(03)	0.02464(03)	3.22(3)
Ru(1)	0.72061(06)	−0.03831(05)	−0.05560(06)	3.76(6)
Ru(2)	0.75204(06)	−0.04772(05)	0.07111(06)	3.53(6)
P(1)	0.79490(18)	0.13244(19)	0.0497(02)	4.1(2)
P(2)	0.68823(18)	0.13804(17)	−0.03980(20)	3.7(2)
O(11)	0.8169(07)	0.0346(07)	−0.1252(08)	10(1)
O(12)	0.6341(06)	−0.0460(06)	−0.1654(07)	7.9(9)
O(13)	0.7654(06)	−0.1622(05)	−0.0884(06)	7.3(8)
O(21)	0.7698(06)	−0.0067(07)	0.2104(06)	8.0(9)
O(22)	0.8765(06)	−0.0416(06)	0.0210(08)	8.0(9)
O(23)	0.7629(06)	−0.1841(06)	0.1006(07)	8.2(9)
C(1)	0.6673(06)	−0.0083(06)	0.0482(07)	3.2(8)
C(2)	0.6693(06)	−0.0651(07)	0.0191(07)	3.4(7)
C(3)	0.7845(07)	0.2007(07)	−0.0018(08)	5(1)
C(4)	0.7513(07)	0.1835(06)	−0.0642(08)	4.4(8)
C(11)	0.7825(09)	0.0073(08)	−0.0997(09)	6(1)
C(12)	0.6663(09)	−0.0383(07)	−0.1243(09)	5(1)
C(13)	0.7477(07)	−0.1146(08)	−0.0766(08)	5(1)
C(21)	0.7625(08)	−0.0216(07)	0.1578(10)	6(1)
C(22)	0.8296(09)	−0.0417(07)	0.0406(09)	6(1)
C(23)	0.7589(07)	−0.1329(08)	0.0896(08)	5(1)

An ORTEP of diagram of molecular structure of 5 is shown in Figure 4. Selected final atomic positional parameters are listed in Table XI. Selected interatomic bond distances and angles are listed in Tables XII and XIII. To a first approximation the structure of 5 can be viewed as a combination of three M_4 tetrahedra. Two of these are closed tetrahedra: Pt(1), Pt(2), Ru(3), Ru(4) and Pt(2), Pt(3), Ru(5), Ru(6). The third, Pt(1), Pt(3), Ru(1), Ru(2), is a "butterfly" tetrahedron. The three tetrahedra are joined via the platinum atoms which form a triangle in the center of the cluster. This is another new structural type for nine-metal clusters.[14] All metal–metal bond distances in 5 are similar to those found in 1–4. The long distance between Pt(3) and Ru(2), 3.877(2) Å, indicates that there is no bonding interaction between these two metal atoms. In compound 5 there are 18 carbonyl ligands: two are semibridging ligands, Pt(3)···C(13) = 2.48(3) Å and Pt(1)···C(33) = 2.46(2) Å. The three PhC_2Ph ligands bridge the three $PtRu_2$ triangles: Pt(1), Ru(1), Ru(2); Pt(2); Ru(3), Ru(4); and Pt(3), Ru(5), Ru(6). In this way, the molecule of 5 appears to have an approximate C_3 axis that is perpendicular to the Pt_3

Scheme I



triangle and passes through its center. It is apparent that compound 5 is an assembly of three $PtRu_2(\mu_3\text{-}\eta^4\text{-}PhC_2Ph)$ groupings that are linked through the platinum atoms. Compound 5 contains total 126 valence electrons, which is two less than that expected for a condensed polyhedron of this type. This could be remedied by the formation of a metal–metal bond between Pt(3) and Ru(2), but this has not happened. Thus, platinum atom, Pt(3), is left with a 16-electron configuration.

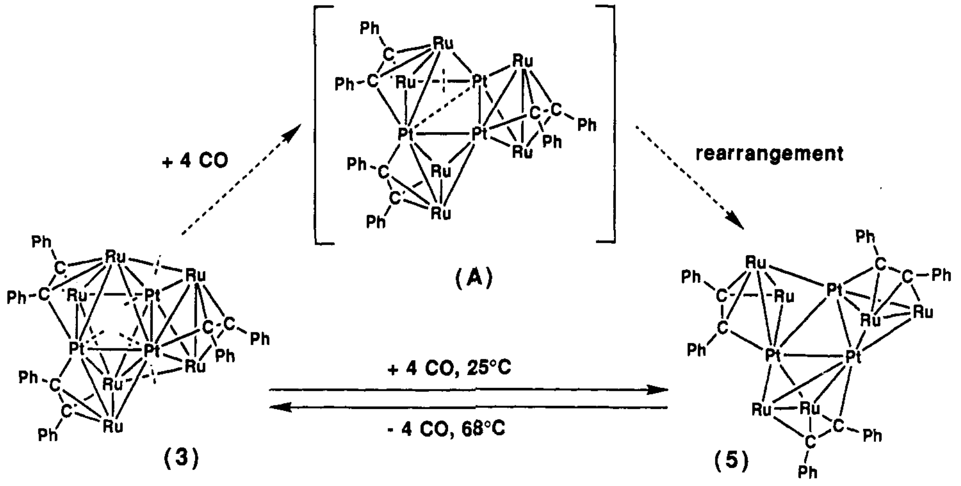
We suspected that 5 could be split into three trinuclear $PtRu_2(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ cluster complexes by ligand addition, and this was achieved by treatment of 5 with dppe in a hexane solution at 25 °C. The new compound 6, $PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$(dppe), was obtained in a 10% yield. When 5 was treated with CO followed by an addition of dppe, compound 6 was obtained in much better yield (46%). When treated with CO (1 atm) in the absence of dppe, there was evidence of the formation of a new compound detected by IR spectroscopy that was only stable under a CO atmosphere. When the CO atmosphere was removed, it decomposed and compounds 2 (40%) and 4 (10%) were formed. We suspect that this species is the complex $PtRu_2(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ (7) formed by the fragmentation of 5. When the reaction was performed in the presence of dppe, the complex 6 was formed which we feel is simply a more stable derivative of 7. We found that the complex 6 could also be obtained in 36% yield from the reaction of $PtRu_2(CO)_8$(dppe) with PhC_2Ph in refluxing heptane solvent.

Compound 6 was characterized by single-crystal X-ray diffraction analysis, and an ORTEP of diagram of its molecular structure is shown in Figure 5. Selected final atomic positional parameters are listed in Table XIV. Compound 6 consists of a triangular cluster with one platinum atom and two ruthenium atoms. The metal–metal bond distances in 6 are similar to those in $PtRu_2(CO)_8$(dppe). The dppe ligand is chelated to the platinum atom. The two Pt–P bond distances in 6, Pt–P(1) = 2.308(4) Å and Pt–P(2) = 2.277(4) Å, are slightly different, but are similar to those found in $PtRu_2(CO)_8$(dppe) and $PtRu_2(CO)_6(dppe)_2$.[3b] The triply bridging PhC_2Ph ligand does not adopt a perfect $\mu_3\text{-}\|$ bond mode. The angle between the acetylenic C–C and the Pt–Ru(1) vectors is 10.7°. Compound 6 contains six linear terminal carbonyl ligands on the ruthenium atoms which are arranged to minimize their steric repulsions. There is a total 46 valence electrons in the cluster; thus the platinum atom is believed to have only a 16-electron configuration. As found in $PtRu_2(CO)_8$(dppe), the platinum atom in 6 has a nonplanar coordination geometry. The dihedral angle between the $PtRu_2$ and PtP_2 planes is 58.2°.

Although the structure of compound X was not established, some of its chemical properties were investigated. When treated with CO, X yielded 4 and 5, and when treated with CO followed by an addition of dppe, compound 6 was obtained. Thus, it is believed that compound X is either an isomer of 3 or some species whose number of CO ligands lies between the number in 3 and the number in 5.

The results of this study are summarized in Scheme I. The principal product from the reaction of 1 with PhC_2Ph was the nine-metal cluster complex 3. Its formula suggests that it is a combination of three $PtRu_2(PhC_2Ph)$ groupings. We have shown previously that complex 1 can be split into two $PtRu_2$ fragments by reaction with dppe. Thus, we believe that 3 was formed by a splitting of 1 into $PtRu_2(PhC_2Ph)$ fragments upon reaction with PhC_2Ph that followed by a reassembly into 3. The mode of formation of the minor product 2 is not clear at this time. Compound 3 adds 4 equiv of CO under very mild conditions, 1 atm/25 °C, to yield 5, which contains a more opened cluster as a result of the metal–metal bond cleavages that accompany the CO addition. Also formed

Scheme II



was compound 4 whose formula suggests that one of the PtRu$_2$ fragments was eliminated and a product **X** whose formula has not been unambigously established, but which appears to be a nine-metal cluster similar to 3 and 5 with a different number of CO ligands.

It is relatively easy to visualize the formation of compound 5 from 3, see Scheme II. The addition four carbonyl ligands to 3 induces the cleavage of several metal–metal bonds (dashed lines in Scheme II). Although several intermediates may be traversed, one could imagine one intermediate **A**, formed without the cleavage of any metal–metal bonds in the alkyne-bridged PtRu$_2$ triangles. Through cleavage of one Pt–Ru bond and the formation of one Pt–Pt bond, compound 5 would be obtained directly from **A**. When heated to 68 °C, compound 5 eliminates four CO ligands to reform 3 in an almost quantitative yield. The structure of 5 also suggests a straightforward pathway for cluster assembly from three PtRu$_2$(CO)$_6$(PhC$_2$Ph) groupings.

Compound 5 reacted with CO to form a species that was stable only under a CO atmosphere and that we have formulated as the trinuclear PtRu$_2$ species 7, Scheme I. When 7 was allowed to decompose in the absence of dppe, significant amounts of 2, 4, and **X** were formed. When the reaction of 5 with CO was performed in the presence of dppe, the compound 6 was obtained. We feel that compound 6 is simply a stabilized form of 7 that was unambiguously characterized through a crystal-structure analysis. The most efficient route to 6 was the reaction of PtRu$_2$(CO)$_8$(dppe) with PhC$_2$Ph in refluxing heptane solvent (97 °C).

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Supplementary Material Available: Tables of phenyl ring and hydrogen atom positional parameters and anisotropic thermal parameters (35 pages). Ordering information is given on any current masthead page.

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