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Cluster Synthesis. 35. On the Way to High-Nuclearity Platinum–Osmium Cluster Complexes. Synthesis and Structural Characterizations of $Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$ and $Pt_4Os_6(CO)_{21}(COD)(\mu\text{-}H)_2$ (COD = Cycloocta-1,5-diene)

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The new platinum–osmium carbonyl cluster complex $Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$ (3) was obtained in 31% yield from the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ (1) with two equiv of $Pt(COD)_2$ at 25 °C. When a solution of compound 3 in hexane solvent was heated to reflux, it was transformed into the new decanuclear complex $Pt_4Os_6(CO)_{21}(COD)(\mu\text{-}H)_2$ (4) in 16% yield by the condensation of two molecules of 3. The yield of 4 can be increased to 30% by the addition of small amounts of CO. Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound 3 contains a triangular Os_3 cluster that is capped on one face by a triply bridging Pt(COD) group and bridged on one edge by a second Pt(COD) grouping. Compound 3 is formally electron deficient. This can be attributed to the 16-electron configuration of the edge-bridging Pt(COD) grouping. The structure of compound 4 was found to consist of triangulated alternating layers of osmium and platinum atoms with a capping Pt(COD) grouping on one of the triosmium faces. Crystal data: for 3, space group, $P\bar{1}$, $a = 10.368$ (1) Å, $b = 14.358$ (3) Å, $c = 9.861$ (2) Å, $\alpha = 102.80$ (2)°, $\beta = 91.61$ (2)°, $\gamma = 96.39$ (1)°, $R = 0.036$ for 2484 reflections; for 4, space group, $P2_1/c$, $a = 14.708$ (3) Å, $b = 15.484$ (3) Å, $c = 19.313$ (2) Å, $\beta = 90.85$ (1)°, $R = 0.034$ for 2485 reflections.

Introduction

The chemistry of bimetallic cluster complexes containing platinum has attracted considerable attention[1] because of the importance of platinum alloy catalysts to the process of petroleum reforming.[2] An understanding of the structure and reactivity of these complexes may contribute to our understanding of the structure and function of the catalysts.

We have recently discovered that the reactions of the pentacarbonyl complexes of iron,[3] ruthenium,[4] and osmium[5] with $Pt(COD)_2$,[6] COD = cycloocta-1,5-diene, will produce a variety of new heteronuclear carbonyl cluster complexes containing platinum, and we have shown that some of these can be condensed thermally into unusually high nuclearity heteronuclear metal cluster complexes.[7] We have now investigated the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ (1) with $Pt(COD)_2$. In a preliminary report on this reaction, Ewing et al.[8] described the formation of the complex $PtOs_3(CO)_{10}(COD)(\mu\text{-}H)_2$ (2), which was reported to be difficult to purify. Our studies have confirmed this, but we have also found that when 1 is allowed to react with 2 equiv of $Pt(COD)_2$, a new and more stable complex, $Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$ (3), is formed. When 3 is heated to reflux in hexane solvent, it undergoes a self condensation to yield the decanuclear complex $Pt_4Os_6(CO)_{21}(COD)(\mu\text{-}H)_2$ (4). The results of this study are described in this report.

Experimental Section

General Information. All the reactions were performed under an atmosphere of nitrogen, unless otherwise indicated. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. $Os_3(CO)_{10}(\mu\text{-}H)_2$[9] and $Pt(COD)_2$[10] were prepared by the reported procedures. TLC separations were performed in air on plates (0.25 mm silica gel 60 F_{254}). IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotmeter. ^1H NMR spectra were recorded on a Brüker AM-300 spectrometer. Elemental analyses were performed at Desert Analytics, Tucson, AZ.

Reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ (1) with $Pt(COD)_2$. A 40.0-mg (0.047-mmol) sample of 1 and 50.0 mg (0.122 mmol) of $Pt(COD)_2$ were dissolved in 1.0 mL CH_2Cl_2 in a 15-mL three-necked flask. The solution was stirred at 25 °C under nitrogen for 15 min. The solution was then concentrated and separated by TLC with a solvent mixture of hexane and CH_2Cl_2 (3/1). An orange band yielded 20.5 mg of $Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$ (3) (31%). When the reaction is performed in more dilute solutions, the yield is lower. Solutions of compound 3 are slightly unstable in air and undergo significant decomposition in a few hours. IR ν(CO) (cm^{-1}) in hexane: 2071 (m), 2033 (m), 2013 (vs), 1992 (m), 1971 (m), 1953 (w), 1933 (w). ^1H NMR (δ in $CDCl_3$): 5.45 (t, 8 H, CH, $^2J_{Pt-H} = 59$ Hz), 1.8–2.4 (m, 16 H, CH_2), −18.30 (t, 2 H, OsH, $^2J_{Pt-H} = 28$ Hz). Anal. Calcd (found): C, 20.98 (19.54); H, 1.83 (1.83). A small green band was also eluted. IR ν(CO) (cm^{-1}) in hexane: 2083 (m), 2058 (vs), 2033 (vs), 2011 (s), 2000 (m), 1988 (s), 1976 (m), 1933 (w, br); ^1H NMR (δ in $CDCl_3$): 4.92 (t, 4 H, $^2J_{Pt-H} = 52$ Hz), 1.3–1.8 (m, 8 H), −12.39 (t, 2 H, $^2J_{Pt-H} = 25$ Hz). This compound is unstable and could not be characterized further.

Pyrolysis of 3. A 22.0-mg sample of 3 was dissolved in 30 mL of hexane in a 100-mL three-necked flask. The solution was refluxed under nitrogen for 3 h. The solvent was removed under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2 and separated by TLC with a solvent mixture of hexane and CH_2Cl_2 (3/2). A green band yielded 3.2 mg of $Pt_4Os_6(CO)_{21}(COD)(\mu\text{-}H)_2$ (4) (16%). IR ν(CO) (cm^{-1}) in CH_2Cl_2: 2098 (m), 2069 (m), 2051 (vs), 2044 (s), 2030 (m), 1970 (w, br). ^1H NMR (δ in $CDCl_3$): 6.11 (t, 4 H, CH, $^2J_{Pt-H} = 60$ Hz), 2.2–2.7 (m, 8 H, CH_2), −16.44 (s, 2 H, OsH). Anal. Calcd (found): C, 13.32 (13.43); H, 0.60 (0.42).

Reaction of 3 with CO. A 6.5-mg sample of 3 was dissolved in $CDCl_3$ and placed in an NMR tube at 25 °C. The tube was then evacuated and filled with CO. The solution immediately changed color from orange to a dark brown. An NMR spectrum of this sample showed that no 3 remained in the solution but did show the presence of free H_2. The solution was then separated by TLC to yield 0.5 mg of $PtOs_2(CO)_{10}$,[11] a trace of $Pt_2Os_3(CO)_{14}$,[12] a trace of $Pt_2Os_4(CO)_{18}$,[11] and 0.4 mg of 4.

Pyrolysis of 3 with the Addition of CO. Under nitrogen, 9.9 mg of 3 was dissolved in 20 mL of hexane in a 50-mL three-necked flask equipped with a reflux condenser. A disposable pipet connected to a CO tank was inserted into the solution through a rubber septum in one of the necks. The solution was brought to reflux, and a few bubbles of CO were admitted through the pipet. The color of the solution turned dark in a few seconds. The solution was then refluxed for an additional 40 min. IR spectra showed that no starting material remained. The mixture was

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Table I. Crystal Data for Compounds **3** and **4**

	3	**4**
empirical formula	$Pt_2Os_3O_9C_{22}H_{26}$	$Pt_4Os_6O_{21}C_{29}H_{14}\cdot CH_2Cl_2$
fw	1431.26	2704.70
crystal system	triclinic	monoclinic
lattice params		
a, Å	10.368 (1)	14.708 (3)
b, Å	14.358 (3)	15.484 (3)
c, Å	9.861 (2)	19.313 (2)
α, deg	102.80 (2)	90.00
β, deg	91.61 (2)	90.85 (1)
γ, deg	96.39 (1)	90.00
V, Å^3	1420.3 (4)	4398 (2)
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z value	2	4
D_{calcd}, g/cm^3	3.35	4.09
μ(Mo Kα), cm^{-1}	233.5	301.8
temp, °C	20	20
$2\theta_{max}$, deg	42.0	40.0
no. of observns ($I > 3\sigma(I)$)	2484	2485
no. of variables	227	418
residuals: R; R_w	0.036; 0.042	0.034; 0.034
goodness of fit indicator	2.05	1.26
max shift in, final cycle	0.03	0.02
largest peak in final diff map, e$^-$/Å^3	1.64	1.19
abs cor	analytical	empirical

separated as described above to yield 2.7 mg of **4**, 30%.

Crystallographic Analyses. Orange crystals of **3** were grown by evaporation of solvent from a hexane solution at 25 °C. Dark green crystals of **4** were grown by evaporation of solvent from a solution in 1/4 hexane/CH_2Cl_2 at 25 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. The data were processed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving library, version 5.0, obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[13a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[13b] Both structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net}^2)^2]^{1/2}/Lp$.

Compound **3** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All atoms larger than carbon were refined anisotropically. The carbon atoms were refined with isotropic thermal parameters. The hydride ligands were not located and were ignored, but the hydrogen atoms on the COD ligands were calculated in idealized positions and were included in the structure factor calculations without refinement.

Compound **4** crystallized in a monoclinic crystal system. The space group $P2_1/c$ was identified on the basis of the systematic absences observed during the collection of the data. All atoms larger than carbon were refined anisotropically. The carbon atoms were refined with isotropic thermal parameters. The hydride ligands were not located and were ignored, but the hydrogen atoms on the COD ligands were calculated in idealized positions and were included in the structure factor calculations without refinement. In the final stages of refinement a molecule of CH_2Cl_2 that had cocrystallized from the crystallization solvent was located in the lattice. It was included in the analysis and satisfactorily refined with a 100% occupancy.

Table II. Positional Parameters and *B*(eq) for **3**

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.81852 (8)	0.22076 (6)	0.50530 (8)	2.56 (4)
Pt(2)	0.49646 (8)	0.29330 (6)	0.21421 (8)	2.46 (4)
Os(1)	0.74898 (9)	0.11753 (6)	0.24302 (9)	2.51 (4)
Os(2)	0.56062 (8)	0.21136 (6)	0.42471 (8)	2.42 (4)
Os(3)	0.74661 (9)	0.32697 (6)	0.30696 (8)	2.50 (4)
O(17)	0.7305 (19)	−0.0618 (13)	0.3570 (15)	5.4 (9)
O(18)	1.0269 (18)	0.1031 (15)	0.1623 (20)	7 (1)
O(19)	0.6430 (19)	0.0212 (13)	−0.0532 (16)	6 (1)
O(21)	0.5868 (16)	0.0786 (12)	0.6272 (17)	4.7 (8)
O(22)	0.2799 (15)	0.1196 (13)	0.3735 (16)	4.9 (8)
O(23)	0.499 (2)	0.3797 (13)	0.6493 (18)	7 (1)
O(31)	1.0352 (17)	0.3802 (13)	0.3960 (19)	5.6 (9)
O(32)	0.8243 (19)	0.4226 (12)	0.0712 (17)	5.4 (9)
O(33)	0.6696 (17)	0.5120 (12)	0.4771 (19)	5.6 (9)
C(1)	0.514 (2)	0.3151 (18)	0.003 (2)	4.2 (5)
C(2)	0.487 (3)	0.3995 (19)	0.089 (3)	4.9 (6)
C(3)	0.349 (3)	0.434 (2)	0.092 (3)	5.7 (6)
C(4)	0.253 (3)	0.393 (2)	0.176 (3)	5.7 (7)
C(5)	0.281 (2)	0.2988 (17)	0.214 (2)	3.9 (5)
C(6)	0.302 (2)	0.2197 (16)	0.119 (2)	3.6 (5)
C(7)	0.291 (3)	0.2089 (18)	−0.040 (3)	4.6 (6)
C(8)	0.416 (3)	0.239 (2)	−0.096 (3)	6.0 (7)
C(9)	0.809 (3)	0.2774 (19)	0.743 (3)	5.1 (6)
C(10)	0.885 (3)	0.3461 (18)	0.692 (2)	4.5 (6)
C(11)	1.025 (3)	0.357 (2)	0.708 (3)	7.0 (8)
C(12)	1.098 (3)	0.279 (2)	0.643 (3)	5.8 (7)
C(13)	1.016 (3)	0.1948 (19)	0.546 (3)	4.7 (6)
C(14)	0.934 (3)	0.1254 (18)	0.585 (3)	4.5 (6)
C(15)	0.912 (3)	0.122 (2)	0.735 (3)	6.2 (7)
C(16)	0.869 (3)	0.211 (2)	0.820 (3)	6.0 (7)
C(17)	0.739 (2)	0.0079 (17)	0.312 (2)	3.1 (5)
C(18)	0.924 (3)	0.1070 (18)	0.191 (3)	4.4 (6)
C(19)	0.678 (2)	0.0573 (18)	0.057 (3)	4.0 (5)
C(21)	0.590 (2)	0.1288 (18)	0.551 (2)	3.8 (5)
C(22)	0.384 (2)	0.1558 (16)	0.390 (2)	3.2 (5)
C(23)	0.520 (2)	0.3164 (18)	0.561 (2)	3.7 (5)
C(31)	0.926 (3)	0.3501 (17)	0.373 (2)	3.5 (5)
C(32)	0.794 (2)	0.3846 (17)	0.162 (2)	3.7 (5)
C(33)	0.692 (2)	0.4407 (19)	0.415 (2)	4.0 (5)

Table III. Intramolecular Distances for **3**[a]

Pt(1)–Os(1)	2.713 (1)	Os(2)–Os(3)	2.844 (1)
Pt(1)–Os(2)	2.748 (1)	Os(2)–C(21)	1.94 (3)
Pt(1)–Os(3)	2.863 (1)	Os(2)–C(22)	1.90 (3)
Pt(1)–C(21)	2.68 (2)	Os(2)–C(23)	1.88 (2)
Pt(1)–C(31)	2.67 (2)	Os(3)–C(31)	1.93 (3)
Pt(2)–Os(2)	2.705 (1)	Os(3)–C(32)	1.86 (3)
Pt(2)–Os(3)	2.681 (1)	Os(3)–C(33)	1.89 (3)
Os(1)–Os(2)	2.924 (1)	C(1)–C(2)	1.38 (3)
Os(1)–Os(3)	2.936 (1)	C(5)–C(6)	1.34 (3)
Os(1)–C(17)	1.84 (2)	C(9)–C(10)	1.39 (3)
Os(1)–C(18)	1.91 (3)	C(13)–C(14)	1.36 (3)
Os(1)–C(19)	1.93 (3)	O–C(av)	1.15 (3)

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

Results

From the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ (**1**) with 2 equiv of $Pt(COD)_2$ in CH_2Cl_2 solvent at 25 °C, we have obtained the new mixed-metal cluster complex $Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$ (**3**) in 31% yield. When the reaction of **1** with $Pt(COD)_2$ was followed by ^1H NMR spectroscopy, the intermediate $PtOs_3(CO)_{10}(COD)_2(\mu\text{-}H)_2$ (**2**)[7] was observed as the principle product formed with the addition of up to 1 equiv of $Pt(COD)_2$. A small amount of a compound that exhibits a resonance at −12.39 ppm in addition to resonances of a COD ligand was also observed to form. Efforts to isolate this compound were only partially successful due to its instability (i.e., we were able to obtain its IR spectrum (see Experimental Section), but crystals for a structural analysis could not be obtained). When the amount of $Pt(COD)_2$ exceeded 1 equiv, compound **3** was observed to form and the amount of **2** declined. Compound **3** is also slightly unstable in solutions exposed to air, but crystals suitable for a single-crystal X-ray diffraction were obtained.

An ORTEP diagram of the structure of **3** is shown in Figure 1. Final atom positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The cluster consists of a triangular triosmium cluster that is capped on one face by a triply bridging Pt(COD) group and bridged on one edge by a second Pt(COD) grouping. The Pt-capped tri-

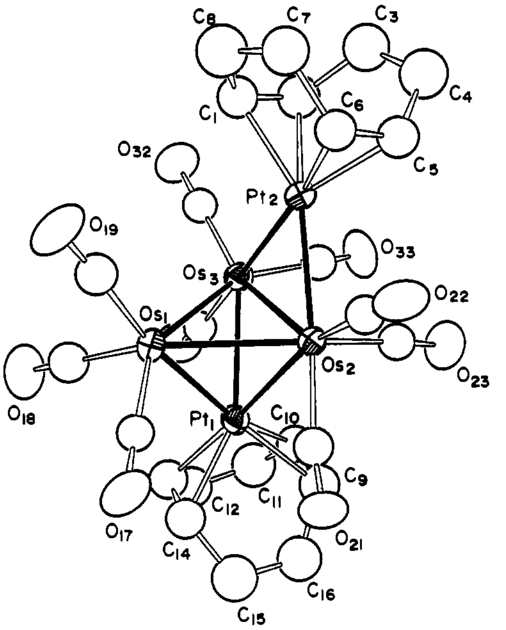

Figure 1. ORTEP drawing of $Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$ (**3**), showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Bond Angles for **3**[a]

Os(1)–Pt(1)–Os(2)	64.74 (4)	Pt(2)–Os(2)–Os(3)	57.72 (3)
Os(1)–Pt(1)–Os(3)	63.45 (3)	Os(1)–Os(2)–Os(3)	61.16 (3)
Os(2)–Pt(1)–Os(3)	60.87 (3)	Pt(1)–Os(3)–Pt(2)	115.65 (4)
Os(2)–Pt(2)–Os(3)	63.75 (3)	Pt(1)–Os(3)–Os(1)	55.78 (3)
Pt(1)–Os(1)–Os(2)	58.20 (3)	Pt(1)–Os(3)–Os(2)	57.56 (3)
Pt(1)–Os(1)–Os(3)	60.76 (3)	Pt(2)–Os(3)–Os(1)	87.25 (4)
Os(2)–Os(1)–Os(3)	58.07 (3)	Pt(2)–Os(3)–Os(2)	58.53 (3)
Pt(1)–Os(2)–Pt(2)	118.83 (4)	Os(1)–Os(3)–Os(2)	60.76 (3)
Pt(1)–Os(2)–Os(1)	57.06 (3)	Os(2)–C(21)–O(21)	170 (2)
Pt(1)–Os(2)–Os(3)	61.57 (3)	Os(3)–C(31)–O(31)	165 (2)
Pt(2)–Os(2)–Os(1)	87.05 (4)	Os–C(av)–O	177 (2)

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

osmium grouping is very similar to that of the complex $PtOs_3(CO)_{10}(COD)(\mu\text{-}H)_2$ (**2**) that was structurally characterized by Ewing et al.[7] The Pt–Os bonding to this capping group is somewhat irregular. The Pt–Os distances range from 2.713 (1) to 2.863 (1) Å, but a similar pattern was also observed in **2**, 2.714 (1)–2.811 (1) Å. A platinum atom bridges the Os(2)–Os(3) edge, and the Pt–Os distances to this group are slightly shorter, 2.681 (1) and 2.705 (1) Å. The molecule contains two equivalent bridging hydride ligands as indicated by ^1H NMR spectroscopy; $\delta = -18.30$ ppm. A small Pt–H coupling of 25 Hz indicates that they are not bonded directly to the platinum atoms. They were not located directly in the structural analysis, but are believed to bridge the long Os–Os bonds, Os(1)–Os(2) = 2.924 (1) Å and Os(1)–Os(3) = 2.936 (1) Å in the Os_3 triangle. The hydride ligands in **2** were proposed to lie in the corresponding positions. Each platinum atom contains one COD ligand, and each osmium atom contains three linear terminal carbonyl ligands. The cluster has a total of 72 valence electrons which is two less than the value expected for an electron-precise edge-bridged tetrahedron.[14] It is believed that the electron deficiency is associated with the edge-bridging Pt(COD) grouping, which probably has only a 16-electron configuration. Similar electron deficiencies in related cluster complexes containing platinum have been rationalized by Mingos.[15]

Table V. Positional Parameters and *B*(eq) for **4**

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.76597 (9)	0.47986 (9)	0.38252 (7)	2.51 (7)
Pt(2)	0.66724 (8)	0.19321 (10)	0.42412 (7)	2.19 (6)
Pt(3)	0.72656 (8)	0.19458 (10)	0.29517 (7)	2.22 (6)
Pt(4)	0.84360 (8)	0.18674 (10)	0.39785 (7)	2.34 (7)
Os(1)	0.63952 (9)	0.33823 (9)	0.34610 (7)	2.22 (7)
Os(2)	0.83636 (9)	0.33792 (9)	0.31948 (7)	2.31 (7)
Os(3)	0.77378 (9)	0.33006 (9)	0.46235 (7)	2.19 (7)
Os(4)	0.76604 (11)	0.03823 (10)	0.45551 (8)	2.83 (8)
Os(5)	0.83235 (10)	0.03432 (10)	0.31250 (8)	2.83 (8)
Os(6)	0.63558 (10)	0.04451 (10)	0.33992 (8)	2.75 (8)
Cl(1)	0.2067 (15)	0.2140 (15)	0.3547 (10)	16 (2)
Cl(2)	0.3018 (12)	0.3701 (11)	0.3455 (10)	12 (1)
O(11)	0.6108 (15)	0.4653 (18)	0.2278 (12)	4 (1)
O(12)	0.5065 (16)	0.4337 (19)	0.4359 (12)	5 (2)
O(13)	0.4781 (17)	0.2391 (18)	0.2832 (14)	5 (2)
O(20)	0.5130 (18)	0.242 (2)	0.5169 (17)	7 (2)
O(21)	0.9560 (17)	0.2207 (16)	0.2313 (15)	5 (2)
O(22)	0.8133 (16)	0.4358 (16)	0.1852 (11)	4 (1)
O(23)	1.0132 (16)	0.4297 (18)	0.3564 (13)	5 (2)
O(30)	0.6557 (19)	0.2309 (18)	0.1539 (14)	5 (2)
O(31)	0.8347 (19)	0.2198 (17)	0.5873 (15)	5 (2)
O(32)	0.9345 (18)	0.438 (2)	0.5075 (15)	7 (2)
O(33)	0.6428 (18)	0.4226 (18)	0.5581 (12)	5 (2)
O(40)	1.0292 (18)	0.191 (2)	0.4671 (14)	7 (2)
O(41)	0.9305 (17)	0.0362 (19)	0.5532 (14)	6 (2)
O(42)	0.6448 (16)	0.0817 (18)	0.5765 (13)	5 (2)
O(43)	0.716 (3)	−0.148 (2)	0.4781 (17)	8 (2)
O(51)	0.884 (2)	−0.1532 (18)	0.2850 (17)	7 (2)
O(52)	1.0333 (18)	0.073 (2)	0.3232 (14)	7 (2)
O(53)	0.8291 (19)	0.0757 (20)	0.1572 (13)	6 (2)
O(61)	0.579 (2)	−0.1431 (19)	0.3539 (17)	7 (2)
O(62)	0.5499 (16)	0.0530 (19)	0.1950 (12)	5 (2)
O(63)	0.4548 (17)	0.0963 (19)	0.4041 (17)	7 (2)
C(1)	0.849 (3)	0.577 (3)	0.3375 (20)	4.6 (8)
C(2)	0.891 (3)	0.642 (3)	0.385 (2)	6.4 (9)
C(3)	0.838 (3)	0.651 (3)	0.450 (2)	5.2 (8)
C(4)	0.768 (3)	0.578 (3)	0.4646 (20)	4.7 (8)
C(5)	0.6817 (19)	0.577 (2)	0.4391 (15)	1.6 (6)
C(6)	0.641 (3)	0.641 (3)	0.391 (2)	5.8 (9)
C(7)	0.695 (3)	0.656 (3)	0.324 (2)	7.1 (9)
C(8)	0.767 (3)	0.590 (3)	0.311 (2)	4.8 (8)
C(11)	0.626 (2)	0.420 (3)	0.2735 (19)	3.3 (8)
C(12)	0.560 (2)	0.400 (2)	0.3981 (16)	2.1 (7)
C(13)	0.542 (3)	0.271 (3)	0.307 (2)	4.4 (8)
C(20)	0.572 (3)	0.223 (2)	0.4824 (19)	3.2 (7)
C(21)	0.907 (3)	0.257 (2)	0.2676 (20)	3.5 (8)
C(22)	0.818 (2)	0.402 (3)	0.2397 (20)	3.6 (8)
C(23)	0.943 (3)	0.400 (3)	0.3449 (18)	3.4 (8)
C(30)	0.685 (3)	0.216 (3)	0.207 (2)	4.6 (8)
C(31)	0.810 (3)	0.256 (3)	0.538 (2)	4.3 (8)
C(32)	0.871 (2)	0.399 (2)	0.4842 (17)	2.6 (7)
C(33)	0.692 (2)	0.388 (2)	0.5242 (18)	2.5 (7)
C(40)	0.962 (3)	0.192 (3)	0.4445 (19)	3.9 (8)
C(41)	0.869 (3)	0.038 (3)	0.516 (2)	4.3 (8)
C(42)	0.692 (2)	0.069 (3)	0.5282 (19)	3.5 (8)
C(43)	0.737 (3)	−0.077 (4)	0.474 (2)	6.5 (9)
C(51)	0.860 (3)	−0.080 (3)	0.2943 (20)	4.4 (8)
C(52)	0.958 (3)	0.059 (3)	0.3222 (19)	3.7 (8)
C(53)	0.830 (3)	0.067 (3)	0.216 (2)	5.4 (9)
C(61)	0.600 (3)	−0.068 (3)	0.354 (2)	5.1 (9)
C(62)	0.583 (2)	0.051 (2)	0.2476 (18)	2.6 (7)
C(63)	0.526 (3)	0.079 (3)	0.3807 (19)	3.9 (8)
C(101)	0.291 (5)	0.272 (5)	0.380 (4)	11.9 (7)

When solutions of **3** in hexane solvent were refluxed under a nitrogen atmosphere for 3 h, the new high nuclearity mixed-metal cluster complex **4** was formed in 16% yield. When this solution was refluxed in the presence of small amounts of added CO, the yield of **4** was increased to 30%. Compound **4** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **4** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. The cluster can be described as two fused Pt_3Os_3 octahedra that share the Pt_3 triangular face. In addition, there is a capping Pt(COD) grouping on the Os(1)–Os(2)–Os(3) tri-

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

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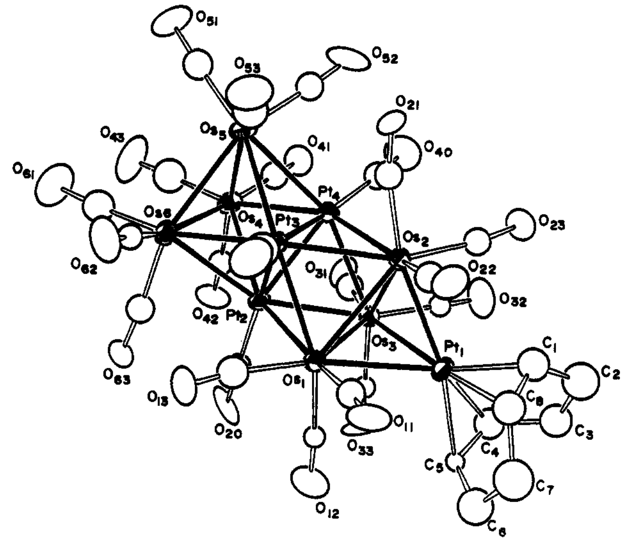

Figure 2. ORTEP diagram of $Pt_4Os_6(CO)_{21}(COD)(\mu\text{-}H)_2$ (**4**), showing 50% probability thermal ellipsoids.

Table VI. Intramolecular Distances for **4**[a]

Pt(1)–Os(1)	2.954 (2)	Os(1)–Os(3)	2.971 (2)
Pt(1)–Os(2)	2.724 (2)	Os(1)–C(11)	1.89 (4)
Pt(1)–Os(3)	2.787 (2)	Os(1)–C(12)	1.83 (3)
Pt(1)–C(1)	2.13 (4)	Os(1)–C(13)	1.92 (4)
Pt(1)–C(4)	2.20 (4)	Os(2)–Os(3)	2.924 (2)
Pt(1)–C(5)	2.24 (3)	Os(2)–C(21)	1.92 (4)
Pt(1)–C(8)	2.20 (4)	Os(2)–C(22)	1.85 (4)
Pt(2)–Pt(3)	2.651 (2)	Os(2)–C(23)	1.90 (4)
Pt(2)–Pt(4)	2.652 (2)	Os(3)–C(31)	1.92 (4)
Pt(2)–Os(1)	2.731 (2)	Os(3)–C(32)	1.83 (4)
Pt(2)–Os(3)	2.731 (2)	Os(3)–C(33)	1.94 (4)
Pt(2)–Os(4)	2.866 (2)	Os(4)–Os(5)	2.943 (2)
Pt(2)–Os(6)	2.853 (2)	Os(4)–Os(6)	2.924 (2)
Pt(2)–C(20)	1.86 (4)	Os(4)–C(41)	1.90 (4)
Pt(3)–Pt(4)	2.609 (2)	Os(4)–C(42)	1.85 (4)
Pt(3)–Os(1)	2.755 (2)	Os(4)–C(43)	1.87 (6)
Pt(3)–Os(2)	2.781 (2)	Os(5)–Os(6)	2.954 (2)
Pt(3)–Os(5)	2.945 (2)	Os(5)–C(51)	1.85 (5)
Pt(3)–Os(6)	2.823 (2)	Os(5)–C(52)	1.89 (4)
Pt(3)–C(30)	1.84 (4)	Os(5)–C(53)	1.93 (5)
Pt(4)–Os(2)	2.789 (2)	Os(6)–C(61)	1.84 (5)
Pt(4)–Os(3)	2.751 (2)	Os(6)–C(62)	1.94 (4)
Pt(4)–Os(4)	2.805 (2)	Os(6)–C(63)	1.89 (4)
Pt(4)–Os(5)	2.882 (2)	C(1)–C(8)	1.31 (5)
Pt(4)–C(40)	1.95 (4)	C(4)–C(5)	1.36 (4)
Os(1)–Os(2)	2.948 (2)	O–C(av)	1.15 (5)

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

angular face. Each osmium atom contains three linear terminal carbonyl ligands. Each platinum atom in the Pt_3 triangle contains one terminal carbonyl ligand. Compound **4** is structurally very similar to the decanuclear cluster complex $Pt_4Os_6(CO)_{22}(COD)$ (**5**) that was prepared by a different method,[8] except that **4** contains two equivalent hydride ligands in place of the bridging CO group. As observed in **5**, the platinum–platinum bonds are much shorter than the osmium–osmium bonds: Pt–Pt = 2.609 (2)–2.652 (2) Å; Os–Os = 2.924 (2)–2.971 (2) Å. The hydride ligands in **4**, $\delta = -16.44$ ppm, that exhibit no detectable coupling to platinum were not observed crystallographically, but their assignment to bridging positions across the Os(4)–Os(5) and Os(5)–Os(6) bonds can be safely inferred by the presence of the large Os–Os–C bond angles to the axial carbonyls at the Os(4)–Os(5) and Os(5)–Os(6) bonds: Os(4)–Os(5)–C(51) = 106 (1)°, Os(6)–Os(5)–C(51) = 108 (1)°, Os(5)–Os(4)–C(43) = 104 (1)°, and Os(5)–Os(6)–C(61) = 105 (1)° compared to the much smaller angles Os(6)–Os(4)–C(43) = 92 (1)° and Os(4)–Os(6)–C(61) = 92 (1)° at the Os(4)–Os(6) bond. The enlargement of M–M–CO angles is a well-established effect of the steric interactions of bridging hydride ligands.[16] Also, the Os(4)–Os(5) and Os(5)–Os(6) distances are slightly longer than the Os(4)–Os(6) distance. Bond lengthening is another consequence of the presence of a bridging hydride ligand although the lengthening observed in **4** is much smaller than that found in small clusters.[16] As in **5**, the spacing between the Pt_3 layer and two Os_3 layers is significantly different. The distance to the Os(1), Os(2), Os(3) layer is 2.23 Å while the distance to the Os(4), Os(5), Os(6) layer is 2.36 Å. The corresponding distances in **5** are nearly the same, 2.22 and 2.39 Å.[7]

Table VII. Intramolecular Bond Angles for **4**[a]

Os(1)–Pt(1)–Os(2)	62.40 (5)	Pt(1)–Os(1)–Pt(2)	113.00 (6)
Os(1)–Pt(1)–Os(3)	62.25 (5)	Pt(1)–Os(1)–Pt(3)	112.96 (6)
Os(2)–Pt(1)–Os(3)	64.09 (5)	Pt(1)–Os(1)–Os(2)	54.99 (5)
Pt(3)–Pt(2)–Pt(4)	58.94 (5)	Pt(1)–Os(1)–Os(3)	56.11 (5)
Pt(3)–Pt(2)–Os(1)	61.55 (5)	Pt(2)–Os(1)–Pt(3)	57.79 (5)
Pt(3)–Pt(2)–Os(3)	92.99 (6)	Pt(2)–Os(1)–Os(2)	87.48 (5)
Pt(3)–Pt(2)–Os(4)	91.86 (6)	Pt(2)–Os(1)–Os(3)	57.04 (5)
Pt(3)–Pt(2)–Os(6)	61.59 (5)	Pt(3)–Os(1)–Os(2)	58.24 (5)
Pt(4)–Pt(2)–Os(1)	93.66 (6)	Pt(3)–Os(1)–Os(3)	85.89 (5)
Pt(4)–Pt(2)–Os(3)	61.45 (5)	Os(2)–Os(1)–Os(3)	59.22 (5)
Pt(4)–Pt(2)–Os(4)	60.96 (6)	Pt(1)–Os(2)–Pt(3)	119.72 (7)
Pt(4)–Pt(2)–Os(6)	90.70 (6)	Pt(1)–Os(2)–Pt(4)	116.50 (7)
Os(1)–Pt(2)–Os(3)	65.90 (5)	Pt(1)–Os(2)–Os(1)	62.61 (5)
Os(1)–Pt(2)–Os(4)	151.19 (6)	Pt(1)–Os(2)–Os(3)	58.99 (5)
Os(1)–Pt(2)–Os(6)	109.10 (6)	Pt(3)–Os(2)–Pt(4)	55.88 (5)
Os(3)–Pt(2)–Os(4)	107.79 (6)	Pt(3)–Os(2)–Os(1)	57.41 (5)
Os(3)–Pt(2)–Os(6)	150.28 (6)	Pt(3)–Os(2)–Os(3)	86.33 (5)
Os(4)–Pt(2)–Os(6)	61.49 (5)	Pt(4)–Os(2)–Os(1)	86.35 (6)
Pt(2)–Pt(3)–Pt(4)	60.55 (5)	Pt(4)–Os(2)–Os(3)	57.52 (5)
Pt(2)–Pt(3)–Os(1)	60.66 (5)	Os(1)–Os(2)–Os(3)	60.78 (5)
Pt(2)–Pt(3)–Os(2)	92.65 (6)	Pt(1)–Os(3)–Pt(2)	118.53 (6)
Pt(2)–Pt(3)–Os(5)	93.85 (6)	Pt(1)–Os(3)–Pt(4)	115.69 (7)
Pt(2)–Pt(3)–Os(6)	62.73 (5)	Pt(1)–Os(3)–Os(1)	61.64 (5)
Pt(4)–Pt(3)–Os(1)	94.07 (6)	Pt(1)–Os(3)–Os(2)	56.92 (5)
Pt(4)–Pt(3)–Os(2)	62.22 (6)	Pt(2)–Os(3)–Pt(4)	57.87 (5)
Pt(4)–Pt(3)–Os(5)	62.16 (6)	Pt(2)–Os(3)–Os(1)	57.07 (5)
Pt(4)–Pt(3)–Os(6)	92.26 (6)	Pt(2)–Os(3)–Os(2)	87.97 (6)
Os(1)–Pt(3)–Os(2)	64.35 (5)	Pt(4)–Os(3)–Os(1)	86.59 (6)
Os(1)–Pt(3)–Os(5)	152.50 (6)	Pt(4)–Os(3)–Os(2)	58.77 (5)
Os(1)–Pt(3)–Os(6)	109.29 (6)	Os(1)–Os(3)–Os(2)	60.00 (5)
Os(2)–Pt(3)–Os(5)	110.41 (6)	Pt(2)–Os(4)–Pt(4)	55.76 (5)
Os(2)–Pt(3)–Os(6)	151.88 (7)	Pt(2)–Os(4)–Os(5)	89.59 (6)
Os(5)–Pt(3)–Os(6)	61.56 (5)	Pt(2)–Os(4)–Os(6)	59.04 (5)
Pt(2)–Pt(4)–Pt(3)	60.51 (5)	Pt(4)–Os(4)–Os(5)	60.12 (5)
Pt(2)–Pt(4)–Os(2)	92.44 (6)	Pt(4)–Os(4)–Os(6)	86.31 (6)
Pt(2)–Pt(4)–Os(3)	60.68 (5)	Os(5)–Os(4)–Os(6)	60.46 (5)
Pt(2)–Pt(4)–Os(4)	63.28 (5)	Pt(3)–Os(5)–Pt(4)	53.19 (5)
Pt(2)–Pt(4)–Os(5)	95.30 (6)	Pt(3)–Os(5)–Os(4)	84.69 (6)
Pt(3)–Pt(4)–Os(2)	61.90 (5)	Pt(3)–Os(5)–Os(6)	57.19 (5)
Pt(3)–Pt(4)–Os(3)	93.45 (6)	Pt(4)–Os(5)–Os(4)	57.55 (5)
Pt(3)–Pt(4)–Os(4)	94.15 (6)	Pt(4)–Os(5)–Os(6)	84.36 (6)
Pt(3)–Pt(4)–Os(5)	64.65 (5)	Os(4)–Os(5)–Os(6)	59.44 (5)
Os(2)–Pt(4)–Os(3)	63.72 (6)	Pt(2)–Os(6)–Pt(3)	55.68 (5)
Os(2)–Pt(4)–Os(4)	153.03 (7)	Pt(2)–Os(6)–Os(4)	59.46 (5)
Os(2)–Pt(4)–Os(5)	112.06 (6)	Pt(2)–Os(6)–Os(5)	89.61 (6)
Os(3)–Pt(4)–Os(4)	108.95 (6)	Pt(3)–Os(6)–Os(4)	87.27 (6)
Os(3)–Pt(4)–Os(5)	154.28 (7)	Pt(3)–Os(6)–Os(5)	61.25 (5)
Os(4)–Pt(4)–Os(5)	62.32 (6)	Os(4)–Os(6)–Os(5)	60.10 (5)
		M–C(av)–O	174.00 (5)

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

Discussion

As reported previously,[7] compound **1** reacts with $Pt(COD)_2$ when added in only 1 equiv to yield complex **2**. Compound **2** is simply a Pt(COD) adduct of **1**. Compound **2** is difficult to purify[7] and is not very stable, but it has been thoroughly characterized including a crystal structure analysis. When **1** is allowed to react with 2 equiv of $Pt(COD)_2$, the new compound **3** is formed. In this reaction, a bridging Pt(COD) grouping is substituted for the bridging CO ligand in **2**. A summary of these results is shown in Scheme I. Compound **3** is electron deficient by two electrons

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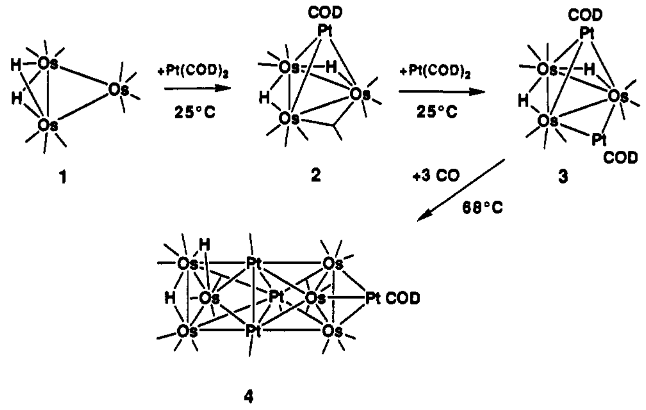
Scheme I



due to the 16-electron configuration of the platinum atom of the bridging Pt(COD) grouping. Compound **3** is also somewhat unstable and its solutions slowly decompose in air in a few hours. Solutions of **3** exposed to CO are rapidly decomposed to yield hydrogen, $PtOs_2(CO)_{10}$,[11] a trace of $Pt_2Os_3(CO)_{14}$,[12] a trace of $Pt_2Os_4(CO)_{18}$,[11] and a small amount of **4**. In the solid state, compound **3** is more stable.

When heated under a nitrogen atmosphere, compound **3** is transformed to the high-nuclearity metal cluster complex **4**, but the yield is relatively low. This can be attributed in part to the fact that the reaction requires the addition of 3 mol of CO. If small amounts of CO are added to the reaction, the yield of **4** is nearly doubled.

Compound **4** exhibits the same selective segregation of the platinum and osmium into triangular groupings of the pure elements as compound **5**. The distance between the Pt_3 and Os_3 layers is significantly smaller in the Pt(COD) capped layer than in the noncapped layer. A similar effect was observed in **5**. An explanation for this is not available at present. It appears that it should be possible to obtain **4** directly from **5** by decarbonylation and addition of hydrogen. Efforts to accomplish this are in progress.

There are relatively few examples of high-nuclearity mixed-metal cluster complexes that contain platinum.[17-19] Several years ago Chini prepared a series of high nuclearity platinum carbonyl cluster complexes $[Pt_3(CO)_6]_n^{2-}$ (n = 2-5) based on triangulated layers of platinum lying in nearly eclipsed conformations.[20] It appears that **4** and **5** may be prototypes for a more extensive series of higher nuclearity metal cluster complexes whose structures are based on alternating triangular layers of platinum and osmium having staggered conformations. Efforts to prepare these are now in progress.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters (5 pages); tables of structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

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Platinum-Assisted Addition of Carbonyl-Stabilized Phosphorus Ylides to Benzonitrile To Give Iminophosphorane Complexes of Platinum(II). Crystal and Molecular Structure of *trans*-$[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}CHCO_2Et\}(NCPh)]\cdot{}^1/_2Me_2CO$

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Ylides $Ph_3P{=}CHCO_2R$ (R = Et, Me) add to *trans*-$[PtCl_2(NCPh)_2]$ to give the first iminophosphorane complexes of platinum $[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}CHCO_2R\}(NCPh)]$. The complex with R = Et crystallizes with a half-molecule of acetone and is triclinic, space group $P\bar{1}$, with a = 10.753 (1) Å, b = 13.264 (2) Å, c = 14.047 (2) Å, α = 92.25 (1)°, β = 110.65 (1)°, γ = 104.26 (1)°, V = 1799.4 (4) Å^3, and Z = 2. The structure was refined to values of R = 0.025 and R_w = 0.026. The complex has a trans geometry. The P-N [1.641 (4) Å] bond distance is longer than that in free iminophosphoranes. A reaction pathway leading to these complexes is proposed. The E configuration adopted by the iminophosphorane ligand seems to be that minimizing repulsions between PPh_3 and substituents attached to the methine carbon atom.

Introduction

Iminophosphoranes ($R_3P{=}NR'$) are interesting compounds because of their widespread utility as key intermediates in the synthesis of natural products[3] and other nitrogen-phosphorus compounds.[4] Some of them have been found to possess semiconductor properties,[5] and some have been used as building blocks of backbone polymers.[6] Surprisingly, their use as ligands is very limited,[7] and therefore, the knowledge of how coordination could

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