Platinum–Osmium Cluster Complexes from the Addition of Pt(PBu$^t_3$) Groups to Os$_3$(CO)$_{12}$

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Three new compounds, PtOs$_3$(CO)$_{12}$(PBu$^t_3$) (**10**), Pt$_2$Os$_3$(CO)$_{12}$(PBu$^t_3$)$_2$ (**11**), and Pt$_3$Os$_3$(CO)$_{12}$(PBu$^t_3$)$_3$ (**12**), have been obtained from the reaction of Pt(PBu$^t_3$)$_2$ with Os$_3$(CO)$_{12}$ (**9**). The products were formed by the sequential addition of 1–3 Pt(PBu$^t_3$) groups to the three Os–Os bonds of the metal cluster of Os$_3$(CO)$_{12}$. In solution, compounds **10**–**12** interconvert among themselves by intermolecular exchange of the Pt(PBu$^t_3$) groups. When **11** is treated with PPh$_3$, the mono- and bis(PPh$_3$) derivatives of **9**, Os$_3$(CO)$_{11}$(PPh$_3$) and Os$_3$(CO)$_{10}$(PPh$_3$)$_2$, were obtained by elimination of the Pt(PBu$^t_3$) groups together with one and two CO ligands, respectively. When heated, compound **11** was transformed into the new compound Pt$_2$Os$_3$(CO)$_{10}$(PBu$^t_3$)(PBu$^t_2$CMe$_2$CH$_2$)(μ-H) (**13**) by the loss of two CO ligands and a metalation of one of the methyl groups of one of the PBu$^t_3$ ligands. Compounds **10**–**13** have been characterized by single-crystal X-ray diffraction analyses.

Introduction

We have recently shown that the compound M(PBu$^t_3$)$_2$, M = Pd and Pt, can readily eliminate one PBu$^t_3$ ligand, and the resulting M(PBu$^t_3$) group can then be readily added to metal−metal bonds in certain polynuclear metal−carbonyl cluster complexes by forming electron-deficient adducts having bridging M(PBu$^t_3$) groups. For example, the reactions of M(PBu$^t_3$)$_2$, M = Pd and Pt, with Ru$_3$(CO)$_{12}$ and Ru$_6$(CO)$_{17}$-(μ_6-C) yield the tri- and di-M(PBu$^t_3$) adducts Ru$_3$(CO)$_{12}$[Pd-(PBu$^t_3$)]$_3$ (**1**) and Ru$_6$(CO)$_{17}$(μ_6-C)[M(PBu$^t_3$)]$_2$, M = Pd (**2**) and M = Pt (**3**), respectively.[1]

1

2 M = Pd
3 M = Pt
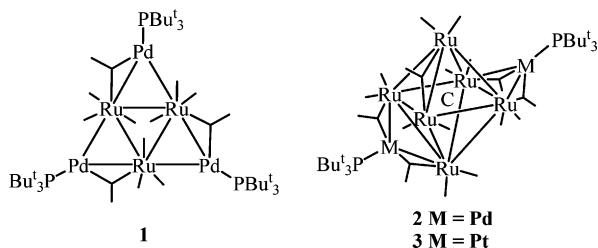
We have also shown that Pd(PBu$^t_3$)$_2$ and Pt(PBu$^t_3$)$_2$ add to Ru$_5$(CO)$_{15}$(μ_5-C), affording the adducts Ru$_5$(CO)$_{15}$(C)-

[M(PBu$^t_3$)], M = Pd (**4**) and M = Pt (**5**). Compounds **4** and **5** both exist in solution as mixtures of open and closed isomers (e.g., **5a** and **5b**) that interconvert rapidly on the NMR time scale at room temperature.[2]

5a   **5b**
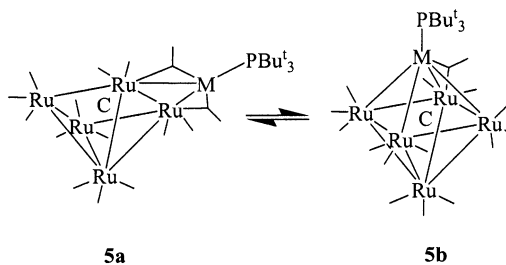
Pt(PBu$^t_3$)$_2$ reacts with Ir$_4$(CO)$_{12}$ to yield a di-adduct, Pt$_2$Ir$_4$(CO)$_{12}$(PBu$^t_3$)$_2$ (**6**), having two Pt(PBu$^t_3$) groups bridging oppositely positioned edges of the Ir$_4$ tetrahedron.[3]


6
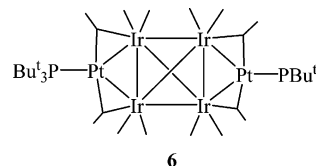
Some compounds are able to add and activate selected small molecules. For example, compound **5** is able to add

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(1) (a) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Manson, J.; Smith, M. D.; Webster, C. E. *J. Am. Chem. Soc.* **2004**, *126*, 5253. (b) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 5628.

hydrogen[4] and alkynes[5] under mild conditions. The reaction of $Pt(PBu^t_3)_2$ with $Re_2(CO)_{10}$ yielded the new highly unsaturated platinum−rhenium complex $Pt_3Re_2(CO)_6(PBu^t_3)_2$ (**7**) that readily adds 3 equiv of hydrogen at room temperature to yield the hexahydrido complex $Pt_3Re_2(CO)_6(PBu^t_3)_3$-$(\mu\text{-H})_6$ (**8**).[6]
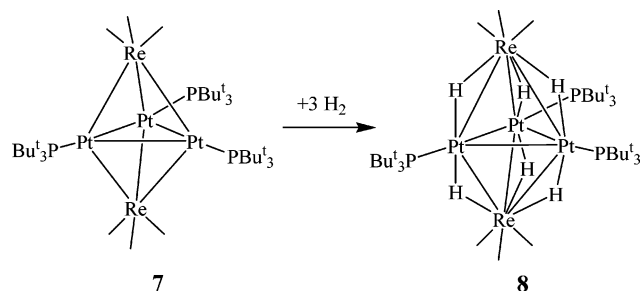
We have now investigated the reaction of $Pt(PBu^t_3)_2$ with $Os_3(CO)_{12}$ (**9**), and have obtained three new compounds, $PtOs_3(CO)_{12}(PBu^t_3)$ (**10**), $Pt_2Os_3(CO)_{12}(PBu^t_3)_2$ (**11**), and $Pt_3Os_3(CO)_{12}(PBu^t_3)_3$ (**12**), formed by the sequential addition of 1−3 $Pt(PBu^t_3)$ groups to the three Os−Os bonds of $Os_3(CO)_{12}$. When **11** was treated with PPh_3, the mono- and bis(PPh_3) derivatives of $Os_3(CO)_{12}$ were formed. When heated to reflux in hexane solvent, compound **11** was transformed into the new compound $Pt_2Os_3(CO)_{10}(PBu^t_3)$-$(PBu^t_2CMe_2CH_2)(\mu\text{-H})$ (**13**) by the loss of two CO ligands and a metalation of one of the methyl groups of one of the PBu^t_3 ligands. The synthesis and structural characterizations of compounds **10** and **13** are included in this report.

Experimental Section

General Data. All the reactions were performed under a nitrogen atmosphere using Schlenk techniques. Reagent-grade solvents were dried by the standard procedures, and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FT-IR spectrophotometer. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400 and 162 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were externally referenced against 85% o-H_3PO_4. ^1H NMR spectra at various temperatures were recorded on a Varian Innova 500 spectrometer operating at 500 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). PPh_3 was purchased from Aldrich, and $Pt(PBu^t_3)_2$ was purchased from Strem. $Os_3(CO)_{12}$ was prepared according to the previously reported procedure.[7] Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel on 60 Å F_{254} glass plates.

Synthesis of $PtOs_3(CO)_{12}(PBu^t_3)$, (10), $Pt_2Os_3(CO)_{12}(PBu^t_3)_2$, (11), and $Pt_3Os_3(CO)_{12}(PBu^t_3)_3$ (12). A 25.0 mg amount of Os_3-$(CO)_{12}$ (0.028 mmol) was dissolved in 20 mL of CH_2Cl_2 in a 50 mL three-neck flask. To this solution was added a 50.0 mg amount

of $Pt(PBu^t_3)_2$ (0.084 mmol), and the reaction solution was allowed to stir at room temperature for 3 h. The solvent was then removed in vacuo, and the product was separated by TLC using a 5:1 hexane−methylene chloride solvent mixture to yield (in the order of elution) 8.0 mg (22%) of orange **10**, 22.8 mg (48%) of red **11**, and 7.5 mg (13%) of purple **12**. Spectral data for **10**: IR ν_{CO} (cm^{-1}, CH_2Cl_2) 2112 (m), 2068 (m), 2060 (m), 2046 (m), 2027 (vs), 1972 (w), 1783 (vw, br); ^1H NMR (toluene-d_8) δ 1.25 (d, 27H, CH_3, $^3J_{P-H}$ = 13 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 130.7 (s, 1P, $^1J_{Pt-P}$ = 6010 Hz). Anal. Calcd: C, 22.10; H, 2.07. Found: C, 21.95; H, 1.87. Spectral data for **11**: IR ν_{CO} (cm^{-1}, CH_2Cl_2) 2094 (w), 2036 (m), 2016 (s), 1959 (w), 1773 (w, br); ^1H NMR (toluene-d_8) δ 1.30 (d, 54H, CH_3, $^3J_{P-H}$ = 13 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 124.6 (s, 1P, $^1J_{Pt-P}$ = 6006 Hz). Anal. Calcd: C, 25.41; H, 3.18. Found: C, 24.74; H, 3.21. Spectral data for **12**: IR ν_{CO} (cm^{-1}, CH_2Cl_2) 2075 (vw), 2026 (m), 2002 (s), 1938 (w, br), 1777 (w, br); ^1H NMR (toluene-d_8) δ 1.35 (d, 81H, CH_3, $^3J_{P-H}$ = 13 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 122.0 (s, 1P, $^1J_{Pt-P}$ = 5987 Hz). Anal. Calcd: C, 27.47; H, 3.86. Found: C, 27.65; H, 3.72.

Improved Yield of 12. A 17.0 mg amount of $Os_3(CO)_{12}$ (0.019 mmol) was dissolved in 20 mL of CH_2Cl_2 in a 50 mL three-neck flask. A 40.0 mg amount of $Pt(PBu^t_3)_2$ (0.067 mmol) was added, and the solution was heated to reflux for 2 h. The solvent was removed in vacuo, and the products were isolated by TLC using a 5:1 hexane−methylene chloride solvent mixture to yield 9.4 mg (24%) of **12**.

Synthesis of $Pt_2Os_3(CO)_{10}(PBu^t_3)(PBu^t_2CMe_2CH_2)(\mu\text{-H})$ (13). A 9.9 mg amount of **9** (0.011 mmol) was dissolved in 20 mL of hexane in a 50 mL three-neck flask. A 28.7 mg amount of Pt-$(PBu^t_3)_2$ (0.048 mmol) was added, and the reaction mixture was heated to reflux for 50 min. The solvent was then removed in vacuo, and the product was separated by TLC using a 6:1 hexane−methylene chloride solvent mixture to yield 4.0 mg (22%) of gray **13**. Trace amounts of **10**, **11**, and **12** were also present on the TLC plate. Spectral data for **13**: IR ν_{CO} (cm^{-1}, CH_2Cl_2) 2053 (s), 2042 (s), 2002 (vs), 1976 (s), 1957(w, sh), 1941(w, br), 1847 (w, br), 1712 (m); ^1H NMR (toluene-d_8, 35 °C) δ 2.54 (d, 2H, CH_2, $^3J_{P-H}$ = 9 Hz, $^2J_{Pt-H}$ = 79 Hz), 1.47 (d, 18H, $^3J_{P-H}$ = 13 Hz), 1.38 (d, 6H, $^3J_{P-H}$ = 13 Hz), 1.02 (d, 27H, $^3J_{P-H}$ = 13 Hz), −7.06 (d, 1H, $^2J_{P-H}$ = 11 Hz, $^1J_{Pt-H}$ = 556 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 114.4 (s, 1P, $^1J_{Pt-P}$ = 2617 Hz), 24.0 (s, 1P, $^1J_{Pt-P}$ = 2538 Hz). Anal. Calcd: C, 24.82; H, 3.28. Found: C, 24.97; H, 3.02.

Transformation of 11 to $Pt_2Os_3(CO)_{10}(PBu^t_3)(PBu^t_2CMe_2CH_2)$-$(\mu\text{-H})$ (13). An 11.5 mg amount of **11** (0.0068 mmol) was dissolved in 20 mL of hexane solvent in a 50 mL three-neck flask, and the solution was heated to reflux for 30 min. The solvent was removed in vacuo, and the products were isolated by TLC using a 6:1 hexane−methylene chloride solvent mixture to yield 3.3 mg (30%) of **13**.

Reaction of 11 with PPh_3. A 12.8 mg amount of **11** (0.0075 mmol) was dissolved in 15 mL of CH_2Cl_2 in a 50 mL three-neck flask. A 19.7 mg amount of PPh_3 (0.075 mmol) was added, and the reaction continued at room temperature for 1 h. The solvent was removed in vacuo, and the products were isolated by TLC using a 7:1 hexane−methylene chloride solvent mixture to yield (in the order of elution) 3.0 mg (35%) of orange $Os_3(CO)_{11}(PPh_3)$, 1.4 mg (13%) of yellow $Os_3(CO)_{10}(PPh_3)_2$, and 1.7 mg (18%) of yellow $Pt_3(PBu^t_3)_3(CO)_3$.

Reaction of 11 with CO. A 10.5 mg amount of **11** (0.0062 mmol) was dissolved in 15 mL of CH_2Cl_2 in a 50 mL three-neck flask. CO gas was purged through the solution at room temperature for 10 min. The solvent was removed in vacuo, and the products were isolated by TLC using a 6:1 hexane−methylene chloride

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(3) Adams, R. D.; Captain, B.; Hall, M. B.; Smith, J. L., Jr.; Webster, C. E. *J. Am. Chem. Soc.* **2005**, *127*, 1007.
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(5) Adams, R. D.; Captain, B.; Zhu, L. *Organometallics* **2005**, *24*, 2419.
(6) Adams, R. D.; Captain, B. *Angew. Chem., Int. Ed.* **2005**, *44*, 2531.
(7) Johnson, B. F. G.; Lewis, J. *Inorg. Synth.* **1972**, *13*, 93.

Table 1. Crystallographic Data for Compounds **10**–**13**

	10	11	12	13
empirical formula	$PtOs_3PO_{12}C_{24}H_{27}$	$Pt_2Os_3P_2O_{12}C_{36}H_{54}$	$Pt_3Os_3P_3O_{12}C_{48}H_{81}$	$Pt_2Os_3P_2O_{10}C_{34}H_{54}$
fw	1304.12	1701.51	2098.91	1645.49
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
a (Å)	15.0192(12)	8.8946(5)	15.4925(7)	9.0638(3)
b (Å)	14.9866(12)	15.0086(8)	23.1548(10)	19.2055(7)
c (Å)	15.1717(12)	17.9146(10)	18.1868(8)	25.2024(9)
α (deg)	90	74.321(1)	90	90
β (deg)	112.716(2)	89.139(1)	103.424(1)	90
γ (deg)	90	83.406(1)	90	90
V (Å^3)	3150.1(4)	2287.0(2)	6345.8(5)	4387.1(3)
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
Z value	4	2	4	4
ρ_{calc} (g cm^{-3})	2.750	2.471	2.197	2.491
μ (Mo Kα; mm^{-1})	16.596	14.522	12.696	15.133
T (K)	294(2)	294(2)	296(2)	296(2)
$2\Theta_{max}$ (deg)	50.0	52.0	56.6	56.6
no. of obs. ($I > 2\sigma(I)$)	4789	7232	11893	9546
no. of params	380	514	648	464
GOF[a]	1.035	1.041	1.089	1.139
max. shift in cycle	0.001	0.000	0.002	0.018
residuals[a] (R1; wR2)	0.0477; 0.1171	0.0460; 0.0981	0.0440; 0.1207	0.0559; 0.1124
abs corr[b] (max/min)	1.000/0.271	1.000/0.506	1.000/0.383	1.000/0.183
largest peak in final diff. map (e Å^3)	2.093	2.072	2.777	3.307

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$. [b] Correction was applied using the program SADABS.

solvent mixture to yield 4.1 mg (77%) of **9** and 3.1 mg (39%) of yellow Pt$_3$(PBu^t$_3$)$_3$(CO)$_3$.

Crystallographic Analyses. Orange single crystals of **10** and red single crystals of **11** suitable for diffraction analysis were grown by evaporation of the solvent from a hexane–methylene chloride solution at room temperature. Red single crystals of **12** suitable for diffraction analysis were grown by slow evaporation of the solvent from a hexane–methylene chloride solution at 8 °C. Dark red single crystals of **13** suitable for diffraction analysis were grown by slow evaporation of the solvent from a benzene solution at 8 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[8] Corrections for Lorentz and polarization effects were also applied by SAINT. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and were refined by full-matrix least-squares on F^2, using the SHELXTL software package.[9] Crystal data, data collection parameters, and results of the analyses for compounds are listed in Table 1.

Compounds **10** and **12** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was confirmed for both structures on the basis of the systematic absences observed in the data. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the *tert*-butyl groups were placed in geometrically idealized positions and included as standard riding atoms. For **12**, a chemically reasonable starting solution provided good positions for all Pt, Os, P, O, and C atoms, but yielded negative thermal parameters for some of the C atoms, high R factors (R1 ∼ 12%), some large electron density peaks, which are chemically unreasonable, and a systematic pattern of F$_{obs}$ ≫ F$_{calc}$, indicative

of some form of crystal twinning. By trial and error, the twin element was determined to be a 2-fold rotation about the [101] direction. The corresponding twin law is, by rows, {0 0 1/0 $\bar{1}$ 0/1 0 0}. This twin law was implemented in the final refinement stages to give low R factors (R1 = 4.77%) and good displacement parameters. The highest peak in the final difference Fourier map was 2.09 e A^{-3}, located near the Pt(1) atom. The final refined batch scale factor indicated the crystal to be composed of 89% major twin component and 11% minor twin component.

Compound **11** 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. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and refined as standard riding atoms. Compound **13** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was identified on the basis of the systematic absences in the data. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions, and were refined as standard riding atoms. The hydride ligand was located and refined with an isotropic thermal parameter. The refined Flack parameter was 0.025, indicating that the correct enantiomorph was selected.

Results and Discussion

Three new compounds, PtOs$_3$(CO)$_{12}$(PBu^t$_3$) (**10**), Pt$_2$Os$_3$-(CO)$_{12}$(PBu^t$_3$)$_2$ (**11**), and Pt$_3$Os$_3$(CO)$_{12}$(PBu^t$_3$)$_3$ (**12**), have been obtained from the reaction of Pt(PBu^t$_3$)$_2$ with Os$_3$(CO)$_{12}$ in the yields of 22, 48, and 13%, respectively. Each product was analyzed by IR, ^{1}H and ^{31}P NMR, C and H elemental analysis, and a single-crystal X-ray diffraction analysis. ORTEP diagrams of the molecular structure of compounds **10**–**12** are shown in Figures 1–3, respectively. Each compound consists of a triangular cluster of three osmium atoms with a Pt(PBu^t$_3$) group bridging 1–3 of the Os–Os bonds, respectively. For each addition of a Pt(PBu^t$_3$) group, two Pt–Os bonds are formed. In each case, one of the two

(8) *SAINT+*, version 6.2a; Bruker Analytical X-ray System, Inc.: Madison, WI, 2001.
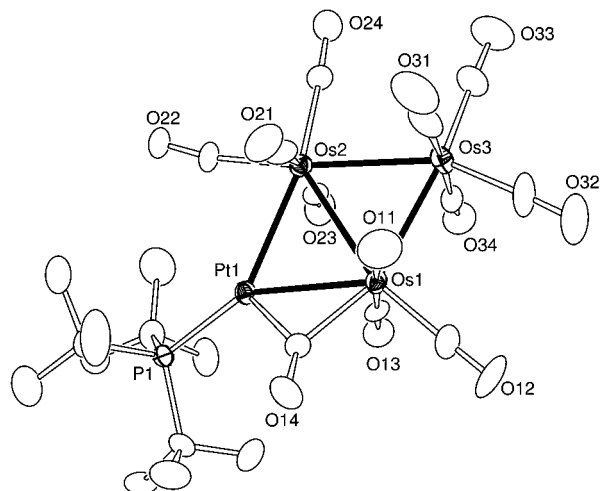(9) Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.
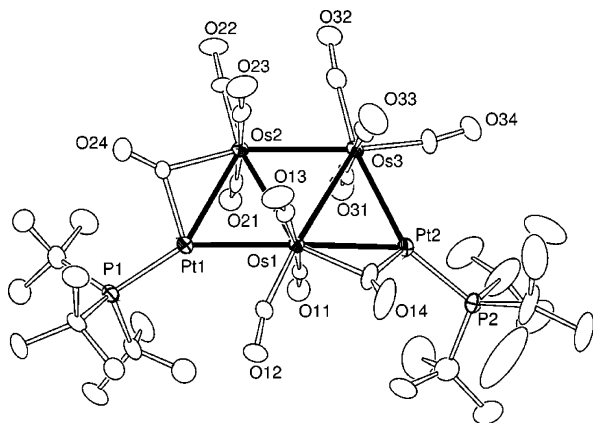
Figure 1. ORTEP diagram of **10** showing thermal ellipsoids at the 30% probability level. Selected interatomic distances (Å) are Pt(1)−P(1) = 2.293(4), Pt(1)−Os(1) = 2.7929(9), Pt(1)−Os(2) = 2.8602(9), Os(1)−Os(2) = 2.9588(9), Os(1)−Os(3) = 2.8633(10), and Os(2)−Os(3) = 2.9108(10).

Figure 2. ORTEP diagram of **11** showing thermal ellipsoids at the 30% probability level. Selected interatomic distances (Å) are Pt(1)−P(1) = 2.292(3), Pt(1)−Os(1) = 2.8480(6), Pt(1)−Os(2) = 2.8042(6), Pt(2)−P(2) = 2.296(3), Pt(2)−Os(1) = 2.8527(6), Pt(2)−Os(3) = 2.7954(6), Os(1)−Os(2) = 2.9388(6), Os(1)−Os(3) = 3.0031(6), and Os(2)−Os(3) = 2.9103(6).

Pt−Os bonds contains a bridging carbonyl ligand that was derived from the original $Os_3(CO)_{12}$ compound. In compound **10**, the CO-bridged Pt−Os bond is significantly shorter than the unbridged Pt−Os bond, Pt(1)−Os(1) = 2.7929(9) Å vs Pt(1)−Os(2) = 2.8602(9) Å, and the Pt−bridged Os−Os bond, Os(1)−Os(2) = 2.9588(9) Å, is significantly longer than the two unbridged Os−Os bonds, Os(1)−Os(3) = 2.8633(10) Å and Os(2)−Os(3) = 2.9108(10) Å. The four metal atoms are not coplanar. The platinum atom lies 0.464(1) Å out of the plane defined by the three osmium atoms.

For **11**, the CO-bridged Pt−Os bond to Pt(1), Pt(1)−Os(2) = 2.8042(6) Å, is shorter than the nonbridged bond, Pt(1)−Os(1) = 2.8480(6) Å, as in **10**; however, for Pt(2), the opposite is observed. The nonbridged bond, Pt(2)−Os(3) = 2.7954(6) Å, is shorter than the CO bridged bond, Pt(2)−Os(1) = 2.8527(6) Å. This could be explained by crowding effects; in particular, Os(1) has four metal atoms bonded to it, whereas Os(2) and Os(3) have only three metal
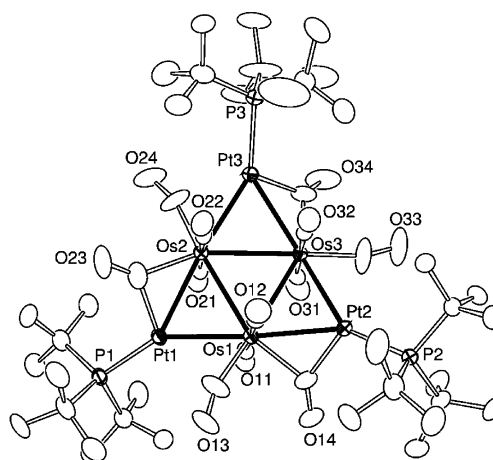

Figure 3. ORTEP diagram of **12** showing thermal ellipsoids at the 30% probability level. Selected interatomic distances (Å) are Pt(1)−P(1) = 2.301(3), Pt(1)−Os(1) = 2.7880(5), Pt(1)−Os(2) = 2.8175(6), Pt(2)−P(2) = 2.296(2), Pt(2)−Os(1) = 2.7986(5), Pt(2)−Os(3) = 2.8027(5), Pt(3)−P(3) = 2.300(3), Pt(3)−Os(2) = 2.7792(6), Pt(3)−Os(3) = 2.8178(5), Os(1)−Os(2) = 2.9536(5), Os(1)−Os(3) = 2.9519(6), and Os(2)−Os(3) = 2.9718(5).

atoms bonded to them. Therefore, the Pt(2)−Os(1) bond might be expected to be longer than a metal−metal bond to Os(3), Pt(2)−Os(3), as is observed. In **11**, the Pt-bridged Os−Os bonds, Os(1)−Os(2) = 2.9388(6) Å and Os(1)−Os(3) = 3.0031(6) Å, are significantly longer than the non-Pt-bridged Os − Os bond, Os(2)−Os(3) = 2.9103(6) Å, but the two Pt-bridged Os−Os bonds are also very different in length. The reason for this is not clear, and may be related to more-subtle electronic bonding factors. The five metal atoms are not coplanar. Pt(1) and Pt(2) are 0.566(1) and 0.640(1) Å out of the plane, respectively, that is defined by the three osmium atoms on the same side.

For **12**, the CO-bridged bonds to Pt(1) and Pt(3), Pt(1)−Os(2) = 2.8175(6) Å and Pt(3)−Os(3) = 2.8178(5) Å, are both longer than the non-CO-bridged Pt−Os bonds, Pt(1)−Os(1) = 2.7880(5) Å and Pt(3)−Os(2) = 2.7792(6) Å. For Pt(2), the CO-bridged bond Pt(2)−Os(1) = 2.7986(5) Å is slightly shorter than the non-CO bridged bond Pt(2)−Os(3) = 2.8027(5) Å. All three Os−Os bonds, Os(1)−Os(2) = 2.9536(5) Å, Os(1)−Os(3) = 2.9519(6) Å, and Os(2)−Os(3) = 2.9718(5) Å, are significantly longer than those in **9**, 2.877(3) Å,[10] and those in the nonbridged Os−Os bonds in **10** and **11**. The six metal atoms are not coplanar. Pt(1) lies on one side of the Os₃ plane, −0.652(1) Å out of the plane, whereas Pt(2) and Pt(3) lie on the other side, 0.662-(1) and 0.543(1) Å out of the plane, respectively. This differs from compound **1**, in which all three palladium atoms lie on the same side of the Ru₃ plane.[1] The yield of **12** can be increased to 24% by increasing the molar ratio of Pt(PBuᵗ₃)₂: $Os_3(CO)_{12}$ in the original reaction.

In solution, compounds **10**−**12** interconvert by intermolecular exchange of the Pt(PBuᵗ₃) groups (see Scheme 1). For example, a toluene-d_8 solution of pure **10** is transformed into a mixture of **10**, **11**, and **12** in a ratio of 21:56:23 in 24 h at room temperature, as determined by ¹H NMR spectros-

(10) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Scheme 1

9   **10**   **11**   **12**
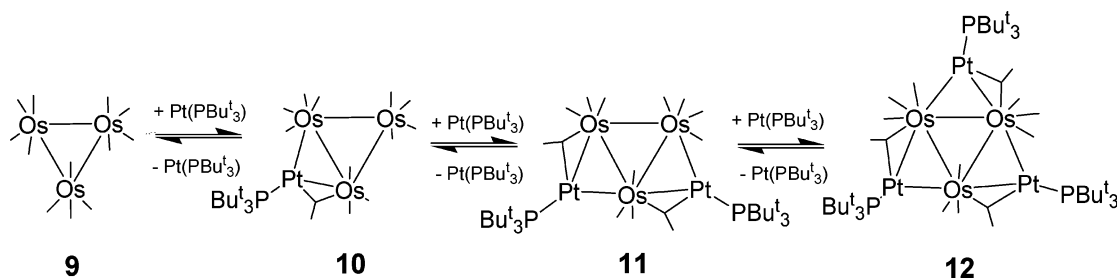
copy. This ratio is very similar to that of the isolated yields in the original synthesis of the compounds. Compound **9** is also formed during this period, and precipitates from the solution. Similarly, a solution of pure **11** is transformed into a mixture of **10**, **11**, and **12** in a ratio similar to that derived from **10**, 29:56:15 in 24 h at room temperature, as determined by ^{1}H NMR spectroscopy. Despite this ongoing exchange process, each of the compounds can be separated in pure form by TLC on silica gel, and crystals of the pure compounds can be obtained if they are crystallized in a timely way (e.g., in less than 1 h). As there was no loss of CO from **9**, each of the products **10**−**12** could be viewed as a Pt(PBu$^t_3$) adduct of **9** formed by the sequential addition of one, two, and three Pt(PBu$^t_3$) groups to the Os−Os bonds, respectively.

Overall, compound **10** has only 60 cluster valence electrons, which is two less than the amount usually found for butterfly tetrahedral cluster complexes, 62. Compound **11** has 72 cluster valence electrons and compound **12** has 84 cluster valence electrons, four and six electrons less, respectively, than the number required for each of the metal atoms to achieve 18-electron configurations. The electron deficiencies for each compound can be explained by the presence of 16-electron configurations on each of the added platinum atoms.

When **11** is treated with PPh$_3$ at room temperature, the mono- and bis(PPh$_3$) derivatives of Os$_3$(CO)$_{12}$, Os$_3$(CO)$_{11}$-(PPh$_3$) and Os$_3$(CO)$_{10}$(PPh$_3$)$_2$, were obtained in 35 and 13% yields, respectively, by elimination of the Pt(PBu$^t_3$) groups together with one and two CO ligands, accordingly. Pt$_3$-(PBu$^t_3$)$_3$(CO)$_3$ was obtained in 18% yield from this reaction, which accounts for the bulk of the Pt(PBu$^t_3$) groups and the CO ligands that were eliminated. Although Os$_3$(CO)$_{11}$(PPh$_3$) and Os$_3$(CO)$_{10}$(PPh$_3$)$_2$ can be obtained directly from the reaction of **9** with PPh$_3$, this reaction requires heating to 140 °C, and a number of side products are obtained by *ortho*-metalation of the phenyl rings and also by the cleavage of P−C bonds.[11] The formation of Os$_3$(CO)$_{11}$(PPh$_3$) and Os$_3$-(CO)$_{10}$(PPh$_3$)$_2$ from **11** shows that the Pt(PBu$^t_3$) groups facilitate the removal of the CO ligands from the triosmium cluster. When compound **11** was treated with CO, Os$_3$(CO)$_{12}$ (77% isolated yield) and Pt$_3$(PBu$^t_3$)$_3$(CO)$_3$ (39% isolated yield) were obtained.

When heated to reflux in a hexane solvent for 30 min, compound **11** was transformed into the new compound Pt$_2$-Os$_3$(CO)$_{10}$(PBu$^t_3$)(PBu$^t_2$CMe$_2$CH$_2$)(μ-H) (**13**) in 30% yield. Compound **13** can be obtained in 22% yield in one step directly from the reaction of **9** with Pt(PBu$^t_3$)$_2$ in a refluxing hexane solvent for a period of 1 h. Compound **13** was analyzed by IR, variable temperature ^{1}H NMR, ^{31}P NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **13** is shown in Figure 4. The metal cluster of **13** consists of a tetrahedral-shaped
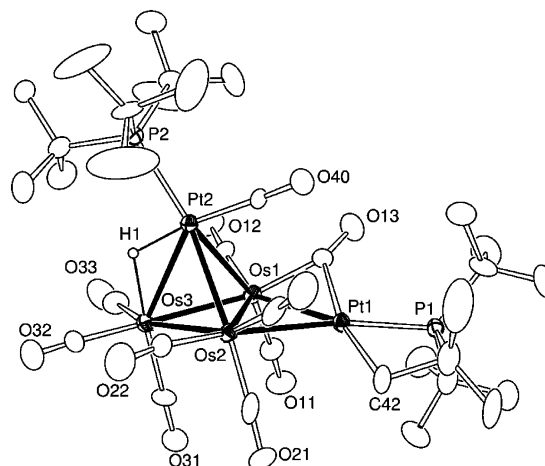

Figure 4. ORTEP diagram of **13** showing thermal ellipsoids at the 30% probability level. Selected interatomic distances (Å) are Pt(1)−P(1) = 2.276(3), Pt(1)−Os(1) = 2.6903(7), Pt(1)−Os(2) = 2.8068(7), Pt(1)−C(42) = 2.078(16), Pt(2)−P(2) = 2.423(4), Pt(2)−Os(1) = 2.8448(8), Pt(2)−Os(2) = 2.8150(8), Pt(2)−Os(3) = 2.8620(8), Pt(2)−H(1) = 1.59(10), Os(1)−Os(2) = 2.6601(8), Os(1)−Os(3) = 2.7315(8), Os(2)−Os(3) = 2.7708(8), and Os(3)−H(1) = 1.82(10).

group of four metal atoms, one platinum and three osmium atoms. A second platinum atom Pt(1) bridges one of the Os−Os bonds, Os(1)−Os(2). The platinum atom, Pt(1), contains a PBu$^t_3$ ligand that is metalated on one of its methyl groups to form a four-membered ring, Pt(1)−P(1)−C(41)−C(42), with Pt(1)−C(42) = 2.078(16) Å. There are other examples of PBu$^t_3$ ligands metalated by platinum at the methyl group, including [Pt(PBu$^t_2$CMe$_2$CH$_2$)Cl]$_2$,[12] [Pt(PBu$^t_2$-CMe$_2$CH$_2$){N$_2$CMeC(H)CMe}]$_2$,[13] Pt(PBu$^t_2$CMe$_2$CH$_2$)P-(C$_6$H$_{11}$)$_3$,[14] and Pt(PBu$^t_2$CMe$_2$CH$_2$)(η^1-C$_5$H$_5$).[15] The carbonyl-

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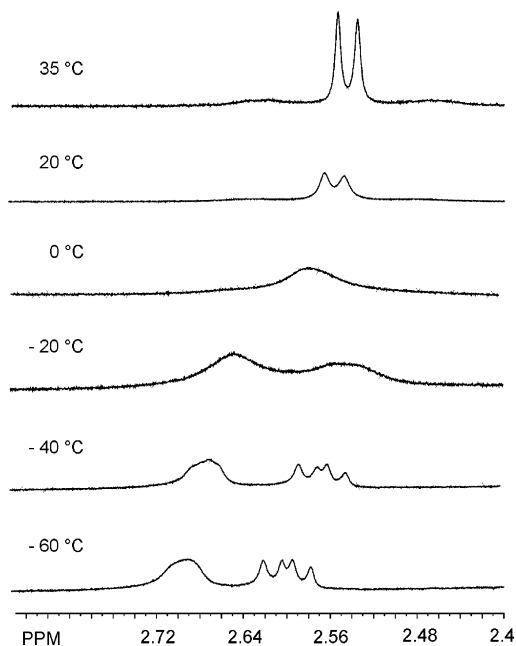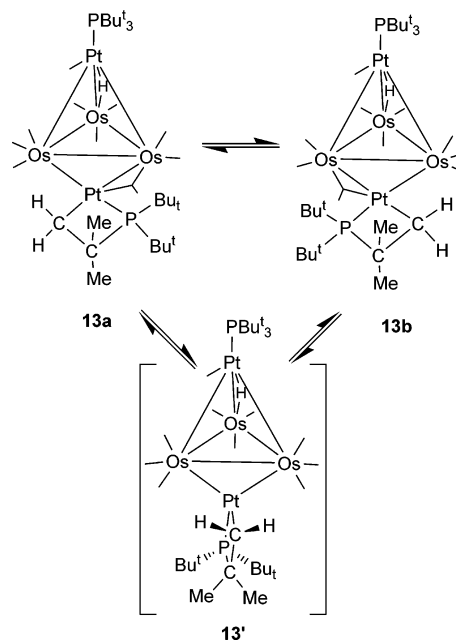
Figure 5. ^{1}H NMR spectra of **13** at various temperatures in the region of 2.40−2.95 ppm.

ligand-bridged Pt(1)−Os(1) bond is significantly shorter than the other Pt−Os bonds, Pt(1)−Os(1) = 2.6903(7) Å and Pt(1)−Os(2) = 2.8068(7) Å. The compound contains one hydrido ligand H(1) that was located and refined crystallographically. It was found as a bridge across the Pt(2)−Os(3) bond, Pt(2)−H(1) = 1.59(10) Å and Os(3)−H(1) = 1.82(10) Å. Accordingly, the Pt(2)−Os(3) bond, 2.8620(8) Å, was the longest metal−metal bond in the molecule.[16] The resonance of the hydrido ligand was observed in the ^{1}H NMR spectrum at −7.06 ppm, with appropriate one- and two-bond couplings to [195]Pt, at 556 Hz , and ^{31}P, at 11 Hz. Compound **13** contains a total of 70 cluster valence electrons, which is four less than the number expected for an edge-bridged tetrahedron. This could be explained by assuming that the two platinum atoms have 16-electron configurations, but there could be some intrinsic electronic unsaturation within the metal−metal bond framework in this compound, because all three osmium−osmium bonds, Os(1)−Os(2) = 2.6601(8) Å, Os(1)−Os(3) = 2.7315(8) Å, and Os(2)−Os(3) = 2.7708(8) Å, are shorter than all the Os−Os bonds in compounds **10**−**12**, and more than 0.20 Å shorter than those in **9**.[10]

Variable temperature ^{1}H NMR studies of **13** show that the metalated PBu$^t_3$ ligand is dynamically averaging its resonances rapidly on the NMR time scale at room temperature and above. For example, the metalated methylene group, C(42) in Figure 4, appears as a doublet, δ = 2.54, $^3J_{P-H}$ = 9 Hz, at 35 °C (see Figure 5). Very broad satellites due to coupling to [195]Pt, $^2J_{Pt-H}$ = 79 Hz, are also detectable. As the temperature is lowered, the doublet collapses and reforms as two broad resonances at −60 °C: one at ap-

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Scheme 2

proximately 2.70 ppm and another at 2.60 ppm. This is consistent with the inequivalence of the CH$_2$ protons as shown in the solid state structure, but only the resonance at 2.60 ppm shows the expected fine structure at this temperature. The methyl groups on the carbon atom adjacent to the methylene group and the two Bu^t groups on P(1) also appear as averaged doublets at 35 °C. The resonances of both sets of groups broaden when the temperature is lowered; however, only the resonance of the averaged methyl groups is resolved into two new doublets at 1.02 ppm, $^3J_{P-H}$ = 13 Hz, and 1.57 ppm, $^3J_{P-H}$ = 13 Hz, at −60 °C. The resonances of the Bu^t groups are complicated at low temperatures by a slowing of the rotation about their P−C bonds, a phenomenon which is well-established for these ligands.[17] The simplest way that the resonances of the metalated ligand could be averaged would be for the molecule to convert to its enantiomer, e.g., **13a** goes to **13b**, as shown in Scheme 2. It seems unlikely that a fully dissociative process is involved because of the apparent Pt−H coupling observed in the fast-exchange limit. A nondissociative process involving a dihedral-twist mechanism of the entire metalated ligand, as illustrated by the intermediate **13′**, could achieve this result intramolecularly. A similar process involving a rotation of the metalated ligand accompanied by cleavage and reformation of the Pt−P bond without cleavage of the Pt−C bond could achieve the same result. Note the CO ligand bridging the Os−Pt bond in **13a** must move to a terminal position, and one of the terminal CO ligands on the neighboring osmium atom must move into a bridging position in **13b** to complete the process. Bridge−terminal CO ligand exchanges are well-known to be facile.[18]

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Summary

In previous studies, we showed that three Pd(PBu$^t_3$) groups could be added to Ru$_3$(CO)$_{12}$ to form a tris adduct of Ru$_3$-(CO)$_{12}$.[1] By using Os$_3$(CO)$_{12}$ and Pt(PBu$^t_3$)$_2$, we have now shown that Pt(PBu$^t_3$) groups can be sequentially added to each of the Os$-$Os bonds in this triangular Os$_3$ cluster complex. We have shown previously that Pd(PBu$^t_3$) and Pt(PBu$^t_3$) groups can move from one metal$-$metal bond to another intramolecularly about the surface of a metal cluster complex with relative ease.[2,19] In this work, we have now shown that Pt(PBu$^t_3$) groups can also exchange between molecules intermolecularly from **10** to **11** to **12**, but the rate is relatively slow. Each of compounds **10**$-$**12** can be isolated by chromatography, and can be obtained in a pure form by crystallization. We have also demonstrated that the Pt(PBu$^t_3$) groups can facilitate the removal of CO ligands from Os$_3$-(CO)$_{12}$ that can lead to the formation of phosphine-substituted derivatives under very mild conditions. In addition, we have observed the first example of a metalation of one of the methyl groups on the PBu$^t_3$ ligand in a bimetallic cluster complex containing a Pt(PBu$^t_3$) group.

Supporting Information Available: CIF tables for the structural analyses of compounds **10**$-$**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0515507

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