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Synthesis and Characterization of the Heterometallic Phosphinidene Clusters $(C_5Me_5)WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$, $(C_5H_5)WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$, and $(C_5Me_5)WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$

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Reaction of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with an excess of tungsten hydrides $LW(CO)_3H$, L = Cp* and Cp, in refluxing toluene produced heterometallic phosphinidene cluster complexes $Cp^*WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ (**1**) and $CpWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (**2**), respectively. Tetranuclear complex **1** has been identified as an intermediate to the trinuclear complex, because heating of **1** under carbon monoxide in refluxing toluene induced a cluster fragmentation, giving an analogous phosphinidene derivative $Cp^*WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (**3**) in 72% yield. The structures of all three complexes were determined by X-ray diffraction. Complex **1** adopts a tetrahedral framework with a phosphinidene capping a WRu_2 face and a hydride associated with the adjacent WRu_2 face, whereas complexes **2** and **3** possess a triply bridging phosphinidene ligand and differ from each other by the location of the edge-bridging hydride ligand. In accordance with structural diversity in the solid state, complex **3** is present as two isomers in solution via rapid hydride migration. Crystal data for **1**: space group $P2_1/c$, $a = 9.813$ (3) Å, $b = 18.253$ (4) Å, $c = 18.463$ (3) Å, $\beta = 93.730$ (18)°, $Z = 4$, final $R = 0.026$, $R_w = 0.025$ for 3750 reflections with $I > 2\sigma(I)$. Crystal data for **2**: space group $P\bar{1}$, $a = 9.3411$ (23) Å, $b = 10.2931$ (14) Å, $c = 12.635$ (3) Å, $\alpha = 85.716$ (15)°, $\beta = 73.743$ (20)°, $\gamma = 73.013$ (14)°, $Z = 2$, final $R = 0.030$, $R_w = 0.035$ for 3659 reflections with $I > 2\sigma(I)$. Crystal data for **3**: space group Cc, $a = 9.711$ (2) Å, $b = 17.800$ (3) Å, $c = 32.398$ (3) Å, $\beta = 90.697$ (22)°, $Z = 8$, final $R = 0.034$, $R_w = 0.035$ for 4487 reflections with $I > 2\sigma(I)$.

Introduction

The reactivity of heterometallic clusters has been of interest for many years.[1] Research in this area is stimulated by a belief that the structures, bonding, and basic reactivity patterns of heterometallic clusters may differ greatly from those of the homometallic clusters. In seeking to exploit the systematic examination of polynuclear heterometallic cluster complexes we have reacted the phenylimido complexes $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ with tungsten hydrides $LW(CO)_3H$, L = C_5H_5 and C_5Me_5,[2] and with acetylide complexes $LW(CO)_3C{\equiv}CPh$[3] in attempts to prepare the heterometallic phenylimido clusters. Our interest in the reactivity of imido clusters prompted us to prepare the phosphinidene clusters of this type. Although there are many reports on the chemistry of homometallic clusters containing the phosphinidene ligand,[4] little work has been directed to the preparation and reactivity study of their heterometallic analogues.[5] In one paper, Carty and co-workers describe a new synthetic route to the open square-pyramidal cluster $Cp_2Ni_2Ru_3(CO)_9(\mu_5\text{-}PPh)$[6] via condensation of the unsaturated trinuclear cluster $Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}PPh_2)$ with $[CpNi(CO)]_2$. Such a condensation reaction involving transition-metal reagents appears to have been incompletely exploited for the synthesis of large-nuclearity heterometallic species, although reactions with unsaturated organic molecules were summarized recently.[7] Thus we started examining the reaction of the related ruthenium complex $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with tungsten hydride complexes $LW(CO)_3H$ because the former is known to undergo CO elimination to afford unsaturated $Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}PPh_2)$. In this report, we describe the preparation and structural studies of three novel phosphinidene complexes prepared from the specified reactions. Our study indicates that the ancillary ligand is notably capable of influencing both the cluster-assembling reaction and the structure of the final products.

Experimental Procedure

General Information and Materials. Infrared spectra were recorded on a Bomen M-100 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400, a Varian Gemini-300 or a Varian Unity-400 instrument, whereas ^{31}P NMR spectra were recorded on the Varian Unity-400 instrument. Chemical shifts are quoted with respect to internal standard tetramethylsilane (^1H and ^{13}C NMR spectroscopy) and external standard 85% H_3PO_4 (^{31}P NMR spectroscopy). Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of the reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck), and the products were separated on commercially available preparative thin-layer chro-

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matographic plates (Kieselgel 60 F_{254}, E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

The phosphido-bridged triruthenium complex $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ was prepared from the reaction of $Ru_3(CO)_{12}$ with diphenylphosphine in THF with sodium benzophenone ketyl as catalyst followed by thermolysis at 50–55 °C in heptane.[8] The tungsten hydride complex $CpW(CO)_3H$ was prepared by protonation of the sodium salt of the $CpW(CO)_3^-$ anion with acetic acid at ambient temperature, whereas the hydride complex $Cp^*W(CO)_3H$ was prepared by the reaction of pentamethylcyclopentadiene with $W(CO)_3(NCEt)_3$ in toluene at 100 °C.[9]

Reaction of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with $Cp^*W(CO)_3H$. In a 50-mL round-bottom reaction flask, the phosphido complex $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ (108 mg, 0.14 mmol) and tungsten hydride $Cp^*W(CO)_3H$ (170 mg, 0.421 mmol) were dissolved in a toluene solution (25 mL) and the resulting solution was brought to reflux for 20 min. The color changed gradually from orange to dark brown. After the solution was cooled to room temperature, the solvent was evaporated in vacuo and the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:7), giving 8 mg of red $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ (0.010 mmol, 6.5%), 10 mg of $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$ (0.01 mmol, 7%), and 65 mg of dark red cluster compound $Cp^*WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ (**1**, 0.063 mmol, 45%) in the order of their elution. Crystals of **1** suitable for X-ray analysis were obtained by recrystallization from a layered solution of dichloromethane–methanol at room temperature.

Spectral data for **1**: MS (FAB, ^{102}Ru, ^{184}W), m/z 1013.75 (M^+); IR (C_6H_{12}) ν(CO) 2060 (m), 2023 (vs), 1995 (vw), 1990 (w), 1968 (m), 1960 (vw), 1898 (w, br), 1864 (w), 1789 (w) cm^{-1}; ^1H NMR ($CDCl_3$, room temperature) δ 8.15 (q, 2 H, J_{H-H} = 7.2 Hz), 7.64 (m, 3 H), 1.97 (s, 15 H), −19.00 (d, 1 H, J_{W-H} = 44.1 Hz and J_{P-H} = 8.5 Hz); ^{13}C NMR ($CDCl_3$, room temperature) (CO) δ 247.1 (J_{P-C} = 5 Hz), 246.5 (J_{P-C} = 32 Hz), 209.3 (J_{W-C} = 157 Hz and J_{P-C} = 10 Hz), 199.4 (J_{P-C} = 4 Hz and J_{C-H} = 9 Hz), 198.2 (3 C, J_{P-C} = 7 Hz), 194.7 (J_{P-C} = 4 Hz and J_{C-H} = 8 Hz), 193.2, 193.0 (J_{P-C} = 4 Hz); ^{31}P NMR ($CDCl_3$, room temperature) δ 373.4 (s, J_{W-P} = 208 Hz). Anal. Calcd for $C_{26}H_{21}O_{10}PRu_3W$: C, 30.87; H, 2.09. Found: C, 30.67; H, 2.16.

Reaction of 1 with Carbon Monoxide. The toluene solution (30 mL) of **1** (100 mg, 0.099 mmol) was refluxed under 1 atm of carbon monoxide for 15 min, during which the color changed from deep red to orange. After the solution was cooled to room temperature, the solvent was evaporated and the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:1), giving 8 mg of orange $Ru_3(CO)_{12}$ (0.012 mmol) and 61 mg of orange $Cp^*WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (**3**, 0.071 mmol, 72%). Crystals of **3** suitable for X-ray analysis were obtained by recrystallization from a layered solution of dichloromethane–methanol at room temperature.

Spectral data for **3**: MS (FAB, ^{102}Ru, ^{184}W), m/z 855.85 (M^+); IR (C_6H_{12}) ν(CO) 2079 (s), 2065 (s), 2059 (vs), 2030 (s), 2019 (vs), 2005 (s), 1992 (m), 1984 (m), 1964 (w), 1928 (vw), 1906 (vw), 1865 (w), 1814 (w) cm^{-1}; ^1H NMR ($CDCl_3$, room temperature) δ 8.18–8.13 (m, 2 H), 7.68–7.61 (m, 3 H), 1.98 (s, 15 H), −19.00 (d, 1 H, J_{W-H} = 44.1 Hz and J_{P-H} = 8.5 Hz); ^{31}P NMR ($CDCl_3$, 233 K) δ 287.0 (s, 0.3P, J_{W-P} = 195 Hz), 257.6 (s, 0.7P, J_{W-P} = 183 Hz). Anal. Calcd for $C_{24}H_{21}O_8PRu_2W$: C, 33.74; H, 2.48. Found: C, 33.35; H, 2.43.

Reaction of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with $CpW(CO)_3H$. The toluene solution (30 mL) of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ (100 mg, 0.125 mmol) and tungsten hydride $CpW(CO)_3H$ (126 mg, 0.375 mmol) was heated at reflux for 30 min. After the solution was cooled to room temperature, the solvent was evaporated in vacuo and the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:7), giving 8 mg of red $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ (0.009 mmol, 7%), 35 mg of orange heterometallic cluster $CpWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (**2**, 0.045 mmol, 36%) and 13 mg of $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$ (0.013 mmol, 10%) in the order of their elution. Crystals of **2** suitable for X-ray analysis were obtained by recrystallization from a layered solution of dichloromethane–methanol at room temperature.

Spectral data for **2**: MS (FAB, ^{102}Ru, ^{184}W), m/z 785.78 (M^+); IR (C_6H_{12}) ν(CO) 2082 (s), 2054 (vs), 2022 (vs), 2008 (vs), 1999 (m), 1979 (m), 1935 (w), 1886 (vw) cm^{-1}; ^1H NMR ($CDCl_3$, room temperature) δ 7.82 (q, 2 H), 7.47 (m, 3 H), 5.15 (s, 5 H), −17.96 (d, 1 H, J_{P-H} = 15.6 Hz); ^{13}C NMR ($CDCl_3$, 273 K) (CO) δ 213.1 (2 C, J_{W-C} = 164 Hz), 197.0 (2 C, J_{P-C} = 43 Hz), 194.6 (2 C, br), 188.2 (2 C, br); ^{13}C NMR ($CDCl_3$, 273 K) δ 138.2 ($i\text{-}C_6H_5$, J_{P-C} = 18 Hz), 134.0 ($o\text{-}C_6H_5$, J_{P-C} = 13 Hz), 130.9 ($p\text{-}C_6H_5$), 129.4 ($m\text{-}C_6H_5$, J_{P-C} = 12 Hz), 85.0 (C_5H_5); ^{31}P NMR ($CDCl_3$, room temperature) δ 376.8 (s, J_{W-P} = 281 Hz). Anal. Calcd for $C_{19}H_{11}O_8PRu_2W$: C, 29.10; H, 1.41. Found: C, 28.83; H, 1.50.

Table I. Experimental Data for the X-ray Diffraction Studies[a]

compd	**1**	**2**	**3**
formula	$C_{26}H_{21}O_{10}PRu_3W\cdot{}^1/_2CH_2Cl_2$	$C_{19}H_{11}O_8\text{-}PRu_2W$	$C_{24}H_{21}O_8\text{-}PRu_2W$
crys syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	Cc (No. 9)
a (Å)	9.813 (3)	9.3411 (23)	9.711 (2)
b (Å)	18.253 (4)	10.2931 (14)	17.800 (3)
c (Å)	18.463 (3)	12.635 (3)	32.398 (8)
α(deg)		85.716 (15)	
β(deg)	93.730 (18)	73.743 (20)	90.697 (22)
γ(deg)		73.013 (14)	
V (Å^3)	3300 (1)	1115.4 (4)	5600 (2)
mol wt	1053.94	784.25	854.39
Z	4	2	8
D_c (g/cm^3)	2.121	2.335	2.027
μ(Mo Kα) (mm^{-1})	44.9	6.68	5.33
transm factors	1.00–0.73	1.00–0.75	1.00–0.78
R; R_w[b]	0.026; 0.025	0.030; 0.035	0.034; 0.035

[a] Features common to all determinations: λ(Mo Kα) = 0.709 30 Å; Nonius CAD-4 diffractometer; temperature, 297 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

Reaction of $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ with $CpW(CO)_3H$. The toluene solution (15 mL) of $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ (20 mg, 0.023 mmol) and tungsten hydride $CpW(CO)_3H$ (15 mg, 0.045 mmol) was heated at reflux for 30 min. After the solution was cooled to room temperature, the solvent was evaporated in vacuo and the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:7), giving 2.4 mg of starting material (0.003 mmol, 12%), 1.2 mg of orange complex **2** (0.002 mmol, 5%), and 6 mg of $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$ (0.006 mmol, 23%).

X-ray Crystallography. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters of **1** were determined from 25 randomly selected high-angle reflections with 2θ angles in the range 21.08–30.28°, whereas the corresponding cell dimensions of complexes **2** and **3** were determined from 25 reflections, with 2θ angles in the range 20.88–31.74 and 18.48–25.48°, respectively. All reflections were corrected for Lorentz, polarization, and absorption effects. All data reduction and refinement were performed using the NRCC-SDP-VAX packages. The structures were solved by direct methods and refined by full-matrix least squares; all non-hydrogen atoms were refined with anisotropic thermal parameters. For complex **1** the space group $P2_1/c$ was identified on the basis of systematic absences. The position of the bridging hydride ligand was obtained from a difference Fourier synthesis and included in the structure factor calculation without refinement. In the final stage of refinement, a molecule of CH_2Cl_2 that came from the recrystallization solvents was located in the lattice; it was included in the analysis and satisfactorily refined with 50% occupancy. Complex **2** crystallized in the triclinic system; the hydride ligand was located and refined successfully. Complex **3** crystallized in the monoclinic system. The space group Cc was assumed and confirmed by the successful solution and refinement of the structure. Due to poor quality of the data, the hydrides were not located, but the hydrogen atoms on the organic ligands were calculated in idealized positions and were included in the structure factor calculation. The combined data collection and refinement parameters are given in Table I. Atomic positional parameters for complex **1** are found in Table II, whereas some selected bond angles and lengths are given in Table III. The corresponding parameters for complexes **2** and **3** are given in Tables IV and V and Tables VI and VII, respectively.

Results and Discussion

Synthesis of Heterometallic Phosphinidene Complexes. Treatment of the triruthenium phosphido complex $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with an excess of tungsten hydride $Cp^*W(CO)_3H$ in refluxing toluene (20 min) produced two homometallic phosphinidene complexes $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ and $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$ and a tetranuclear heterometallic phosphinidene complex $Cp^*WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ (**1**) as a condensation product

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Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for **1**

	x	y	z	B_{iso}, Å^2
W	0.29829 (3)	0.347902 (17)	0.168636 (17)	2.686 (14)
Ru(1)	0.36892 (7)	0.23848 (3)	0.27879 (3)	2.99 (3)
Ru(2)	0.09498 (6)	0.24481 (3)	0.24639 (3)	2.94 (3)
Ru(3)	0.26317 (7)	0.19363 (3)	0.13466 (3)	2.89 (3)
P	0.09463 (21)	0.28405 (11)	0.13120 (11)	2.92 (10)
C(1)	0.4886 (8)	0.3055 (4)	0.2033 (4)	3.5 (4)
C(2)	0.3567 (7)	0.3269 (4)	0.0708 (4)	3.4 (4)
C(3)	0.4383 (8)	0.2832 (4)	0.3647 (4)	3.7 (4)
C(4)	0.5038 (8)	0.1658 (4)	0.2896 (4)	3.8 (4)
C(5)	0.2172 (8)	0.1766 (4)	0.3218 (4)	3.9 (4)
C(6)	−0.0171 (8)	0.3032 (5)	0.3015 (4)	4.7 (5)
C(7)	−0.0457 (8)	0.1760 (4)	0.2363 (4)	3.9 (4)
C(8)	0.4514 (8)	0.1631 (4)	0.1303 (4)	4.3 (5)
C(9)	0.1984 (8)	0.1012 (4)	0.1675 (4)	4.2 (4)
C(10)	0.2149 (8)	0.1766 (4)	0.0350 (4)	4.1 (4)
C(11)	−0.0352 (7)	0.2962 (4)	0.0597 (4)	3.1 (4)
C(12)	−0.0068 (8)	0.3199 (4)	−0.0087 (4)	4.1 (4)
C(13)	−0.1099 (10)	0.3271 (5)	−0.0623 (4)	5.3 (5)
C(14)	−0.2384 (9)	0.3101 (5)	−0.0498 (5)	6.6 (5)
C(15)	−0.2690 (9)	0.2868 (6)	0.0173 (6)	7.8 (6)
C(16)	−0.1674 (9)	0.2791 (5)	0.0725 (4)	5.4 (5)
C(17)	0.4035 (8)	0.4581 (4)	0.1468 (4)	4.0 (4)
C(18)	0.3934 (8)	0.4527 (4)	0.2240 (4)	4.1 (4)
C(19)	0.2565 (9)	0.4535 (4)	0.2392 (4)	3.9 (4)
C(20)	0.1754 (8)	0.4573 (4)	0.1722 (4)	3.8 (4)
C(21)	0.2642 (8)	0.4615 (4)	0.1146 (4)	3.7 (4)
C(22)	0.5294 (9)	0.4689 (5)	0.1088 (5)	6.0 (5)
C(23)	0.5130 (10)	0.4581 (4)	0.2792 (5)	6.0 (5)
C(24)	0.2041 (10)	0.4566 (4)	0.3142 (4)	5.2 (5)
C(25)	0.0242 (9)	0.4681 (4)	0.1644 (5)	5.0 (5)
C(26)	0.2249 (9)	0.4787 (4)	0.0368 (4)	5.1 (5)
O(1)	0.6080 (5)	0.3054 (3)	0.2000 (3)	4.9 (3)
O(2)	0.3930 (5)	0.3229 (3)	0.0127 (3)	4.5 (3)
O(3)	0.4790 (6)	0.3113 (3)	0.4164 (3)	5.7 (3)
O(4)	0.5878 (6)	0.1222 (3)	0.2972 (3)	5.8 (3)
O(5)	0.2044 (6)	0.1275 (3)	0.3611 (3)	5.0 (3)
O(6)	−0.0897 (7)	0.3393 (4)	0.3311 (4)	7.8 (4)
O(7)	−0.1305 (6)	0.1336 (3)	0.2311 (3)	6.4 (3)
O(8)	0.5596 (6)	0.1452 (3)	0.1218 (3)	6.4 (3)
O(9)	0.1627 (7)	0.0462 (3)	0.1857 (4)	6.8 (4)
O(10)	0.1864 (7)	0.1658 (3)	−0.0250 (3)	6.8 (4)
C(27)	0.186 (5)	0.912 (3)	−0.003 (3)	28.1 (21)
Cl(1)	0.0798 (18)	0.9666 (10)	−0.0050 (11)	36.4 (9)
Cl(2)	0.3547 (20)	0.9781 (13)	0.0190 (12)	44.7 (11)
H	0.238	0.312	0.267	4.0

Table III. Selected Bond Distances (Å) and Bond Angles (deg) of **1** (Esd in Parentheses)

(A) Selected Bond Distances

W–Ru(1)	2.9021 (8)	W–Ru(2)	3.1551 (9)
W–Ru(3)	2.9006 (9)	Ru(1)–Ru(2)	2.718 (1)
Ru(1)–Ru(3)	2.910 (1)	Ru(2)–Ru(3)	2.880 (1)
W–P	2.377 (2)	Ru(2)–P	2.244 (2)
Ru(3)–P	2.334 (2)	W–H	2.06
Ru(1)–H	1.86	Ru(2)–H	1.88
W–C(1)	2.083 (8)	W–C(2)	1.969 (8)
Ru(1)–C(1)	2.243 (7)	Ru(1)–C(3)	1.872 (7)
Ru(1)–C(4)	1.875 (8)	Ru(1)–C(5)	2.068 (8)
Ru(2)–C(5)	2.170 (8)	Ru(2)–C(6)	1.878 (8)
Ru(2)–C(7)	1.866 (8)	Ru(3)–C(8)	1.935 (8)
Ru(3)–C(9)	1.916 (8)	Ru(3)–C(10)	1.896 (8)

(B) Selected Bond Angles

Ru(1)–Ru(2)–C(6)	120.7 (3)	Ru(1)–Ru(3)–C(8)	80.5 (2)
Ru(2)–Ru(1)–C(3)	117.9 (2)	Ru(2)–Ru(3)–C(9)	80.9 (2)
Ru(3)–Ru(1)–C(4)	96.1 (2)	Ru(3)–Ru(2)–C(7)	99.5 (2)
Ru(3)–W–C(2)	69.5 (2)	Ru(2)–W–C(6)	122.2 (2)
W–Ru(2)–C(6)	111.6 (3)	W–Ru(1)–C(3)	110.5 (2)

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for **2**

	x	y	z	B_{iso}, Å^2
W	0.21925 (3)	0.28217 (3)	0.113069 (24)	2.768 (12)
Ru(1)	0.00099 (7)	0.12475 (6)	0.23793 (5)	2.85 (3)
Ru(2)	0.16418 (7)	0.24128 (6)	0.35344 (5)	2.92 (3)
P	−0.01357 (21)	0.34661 (17)	0.25914 (15)	2.60 (8)
C(1)	0.3576 (11)	0.0987 (8)	0.1258 (7)	4.6 (4)
C(2)	0.1423 (13)	0.2023 (9)	0.0121 (7)	4.8 (5)
C(3)	0.1157 (11)	−0.0657 (8)	0.1901 (7)	4.0 (4)
C(4)	−0.1406 (11)	0.1580 (10)	0.1486 (8)	4.8 (5)
O(5)	−0.1493 (10)	0.0956 (8)	0.3653 (7)	4.1 (4)
O(6)	0.0430 (11)	0.2258 (8)	0.5003 (7)	4.2 (4)
C(7)	0.2026 (11)	0.4033 (9)	0.3834 (8)	4.7 (5)
C(8)	0.3681 (11)	0.1255 (9)	0.3569 (8)	4.7 (4)
C(9)	−0.1802 (8)	0.4925 (7)	0.2954 (6)	2.9 (3)
C(10)	−0.1622 (10)	0.6221 (8)	0.2916 (8)	4.7 (4)
C(11)	−0.2860 (12)	0.7338 (9)	0.3223 (10)	6.1 (5)
C(12)	−0.4300 (12)	0.7193 (11)	0.3580 (9)	6.1 (5)
C(13)	−0.4521 (12)	0.5936 (12)	0.3614 (12)	7.5 (7)
C(14)	−0.3279 (11)	0.4813 (9)	0.3314 (10)	5.4 (5)
C(15)	0.3712 (19)	0.4256 (16)	0.1146 (9)	9.4 (11)
C(16)	0.4489 (11)	0.3296 (11)	0.0223 (11)	6.7 (6)
C(17)	0.3599 (13)	0.3518 (12)	−0.0491 (8)	5.7 (5)
C(18)	0.2321 (13)	0.4532 (11)	−0.0129 (10)	6.3 (6)
C(19)	0.2291 (15)	0.5041 (10)	0.0829 (12)	8.3 (7)
O(1)	0.4475 (9)	−0.0045 (7)	0.1267 (6)	6.8 (4)
O(2)	0.1097 (12)	0.1641 (10)	−0.0601 (6)	8.3 (6)
O(3)	0.1808 (10)	−0.1713 (6)	0.1649 (6)	6.8 (5)
O(4)	−0.2286 (10)	0.1781 (10)	0.1007 (8)	7.9 (5)
O(5)	−0.2364 (8)	0.0813 (8)	0.4443 (6)	6.2 (4)
O(6)	−0.0316 (10)	0.2127 (8)	0.5848 (6)	7.2 (5)
O(7)	0.2225 (11)	0.5012 (8)	0.4039 (8)	8.0 (5)
O(8)	0.4883 (9)	0.0647 (9)	0.3613 (9)	8.5 (5)
H	0.148 (7)	0.075 (6)	0.322 (5)	2.1 (13)

Table V. Selected Bond Distances (Å) and Bond Angles (deg) of **2** (Esd in Parentheses)

(A) Selected Bond Distances

W–Ru(1)	3.0031 (9)	W–Ru(2)	2.9542 (9)
Ru(1)–Ru(2)	2.910 (1)	W–P	2.381 (2)
Ru(1)–P	2.279 (2)	Ru(2)–P	2.284 (2)
mean W–CO	1.968 (8)	mean Ru–CO	1.920 (9)

(B) Selected Bond Angles

W–C(1)–O(1)	174.3 (8)	W–C(2)–O(2)	169.9 (8)
W–Ru(1)–C(3)	103.2 (2)	W–Ru(1)–C(4)	100.2 (3)
Ru(1)–W–C(1)	76.3 (3)	Ru(1)–W–C(2)	69.3 (3)
Ru(2)–W(1)–C(1)	76.3 (3)	W–Ru(2)–C(7)	96.0 (3)
W–Ru(2)–C(8)	99.4 (2)	Ru(1)–Ru(2)–C(6)	98.3 (3)
Ru(1)–Ru(2)–C(8)	114.5 (3)	Ru(2)–Ru(1)–C(3)	112.2 (3)
Ru(2)–Ru(1)–C(5)	95.8 (3)		

(45%). Extending the reaction time to 30 min reduced the yield of complex **1**. The tetraruthenium complex $\mathrm{Ru_4(CO)_{13}}(\mu_3\text{-PPh})$ was first prepared by Carty and co-workers via the thermal pyrolysis of $\mathrm{Ru_3(CO)_9}(\mu\text{-H})(\mu\text{-PPh_2})$ in heptane solution,[10] whereas the pentanuclear complex $\mathrm{Ru_5(CO)_{15}}(\mu_4\text{-PPh})$ was obtained from the reactions of $\mathrm{Ru_3(CO)_{12}}$ with $\mathrm{CpMn(CO)_2(PCl_2Ph)}$[11] and with an equimolar amount of $\mathrm{PPhH_2}$ in toluene.[12] The formation of **1** is best interpreted as a cluster condensation reaction, in which the reaction proceeded via the formation of unsaturated $\mathrm{Ru_3(CO)_9}(\mu\text{-H})(\mu\text{-PPh_2})$, followed by addition of one molecule of $\mathrm{Cp^*W(CO)_3H}$, reductive elimination of benzene and removal of two CO molecules. Other possibilities, such as prior formation of $\mathrm{Ru_4(CO)_{13}}(\mu_3\text{-PPh})$, followed by reaction with $\mathrm{Cp^*W(CO)_3H}$ via metal-exchange reactions[13] can be completely eliminated because the direct reaction between $\mathrm{Ru_4(CO)_{13}}(\mu_3\text{-PPh})$ and $\mathrm{Cp^*W(CO)_3H}$ produces no complex **1** but a small quantity of $\mathrm{Ru_5(CO)_{15}}(\mu_4\text{-PPh})$ under similar conditions.

On the other hand, the reaction between $\mathrm{Ru_3(CO)_{10}}(\mu\text{-H})(\mu\text{-PPh_2})$ and $\mathrm{CpW(CO)_3H}$ in refluxing toluene failed to give the expected tetranuclear derivative $\mathrm{CpWRu_3(CO)_{10}}(\mu_3\text{-H})(\mu_3\text{-PPh})$

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(13) (a) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (b) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743.

Table VI. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for **3**

	x	y	z	B_{iso}, Å^2
W(1A)	0.57613	0.15984 (3)	0.73451	2.978 (19)
Ru(1A)	0.41827 (11)	0.01446 (6)	0.75154 (4)	3.53 (5)
Ru(2A)	0.60327 (12)	0.06953 (7)	0.81185 (4)	4.04 (5)
P(1A)	0.4114 (3)	0.12678 (19)	0.78525 (11)	3.30 (14)
C(1A)	0.6506 (13)	0.2282 (8)	0.7782 (4)	4.2 (6)
C(2A)	0.7669 (14)	0.1135 (9)	0.7327 (5)	5.6 (8)
C(3A)	0.2766 (16)	0.0095 (8)	0.7100 (5)	5.0 (7)
C(4A)	0.5355 (15)	–0.0702 (8)	0.7377 (5)	5.0 (7)
C(5A)	0.3044 (19)	–0.0339 (9)	0.7907 (5)	6.1 (8)
C(6A)	0.7620 (17)	0.0069 (9)	0.8016 (5)	6.1 (8)
C(7A)	0.5363 (20)	0.0020 (8)	0.8508 (5)	6.2 (9)
C(8A)	0.6813 (17)	0.1344 (10)	0.8534 (5)	6.5 (9)
C(9A)	0.2726 (12)	0.1831 (7)	0.8048 (4)	3.3 (5)
C(10A)	0.1381 (14)	0.1707 (9)	0.7922 (4)	5.2 (8)
C(11A)	0.0316 (14)	0.2161 (9)	0.8069 (5)	5.2 (7)
C(12A)	0.0566 (17)	0.2709 (9)	0.8329 (6)	6.8 (9)
C(13A)	0.1907 (17)	0.2829 (9)	0.8469 (6)	6.3 (9)
C(14A)	0.2972 (15)	0.2413 (9)	0.8332 (5)	5.4 (7)
C(15A)	0.4174 (13)	0.2186 (7)	0.6915 (4)	3.5 (6)
C(16A)	0.5081 (15)	0.2735 (8)	0.7093 (4)	4.4 (7)
C(17A)	0.6415 (16)	0.2582 (8)	0.6938 (5)	5.2 (7)
C(18A)	0.6333 (14)	0.1926 (7)	0.6660 (4)	4.2 (6)
C(19A)	0.4957 (14)	0.1704 (7)	0.6667 (4)	3.7 (6)
C(20A)	0.2663 (15)	0.2199 (9)	0.6942 (5)	5.3 (7)
C(21A)	0.4653 (17)	0.3418 (8)	0.7327 (5)	5.3 (8)
C(22A)	0.7710 (19)	0.3059 (10)	0.6985 (6)	7.1 (10)
C(23A)	0.7519 (18)	0.1636 (11)	0.6410 (5)	7.7 (10)
C(24A)	0.4450 (17)	0.1109 (8)	0.6372 (5)	5.6 (8)
O(1A)	0.6929 (11)	0.2720 (6)	0.8011 (4)	7.1 (6)
O(2A)	0.8782 (10)	0.0961 (7)	0.7288 (4)	7.3 (7)
O(3A)	0.1831 (13)	0.0048 (7)	0.6887 (4)	8.4 (7)
O(4A)	0.6011 (12)	–0.1187 (7)	0.7293 (5)	9.1 (8)
O(5A)	0.2378 (16)	–0.0614 (8)	0.8144 (4)	10.1 (9)
O(6A)	0.8556 (14)	–0.0294 (8)	0.7952 (4)	9.5 (8)
O(7A)	0.4941 (17)	–0.0397 (7)	0.8736 (4)	9.6 (9)
O(8A)	0.7249 (15)	0.1711 (8)	0.8795 (4)	9.8 (8)
W(1B)	0.09508 (6)	0.01781 (3)	0.483536 (20)	3.511 (22)
Ru(1B)	–0.04228 (12)	–0.13129 (7)	0.50537 (4)	4.13 (5)
Ru(2B)	–0.03714 (12)	–0.01278 (7)	0.56346 (4)	4.11 (5)
P(1B)	0.1461 (4)	–0.07549 (20)	0.53561 (11)	3.69 (15)
C(1B)	0.1823 (17)	0.0902 (9)	0.5244 (5)	6.1 (8)
C(2B)	–0.0634 (18)	0.0760 (12)	0.4862 (5)	7.3 (11)
C(3B)	0.0261 (15)	–0.2041 (9)	0.4670 (5)	5.5 (8)
C(4B)	–0.2424 (16)	–0.1218 (12)	0.4889 (5)	7.0 (10)
C(5B)	–0.0574 (18)	–0.2013 (10)	0.5479 (6)	7.4 (10)
C(6B)	–0.2233 (16)	0.0247 (9)	0.5539 (5)	5.3 (8)
C(7B)	–0.0781 (18)	–0.0760 (12)	0.6089 (6)	7.5 (11)
C(8B)	0.0295 (15)	0.0650 (10)	0.5981 (5)	5.5 (8)
C(9B)	0.3012 (13)	–0.1161 (8)	0.5573 (4)	3.8 (6)
C(10B)	0.3422 (17)	–0.1866 (9)	0.5462 (5)	6.2 (8)
C(11B)	0.4663 (17)	–0.2139 (10)	0.5632 (6)	7.3 (9)
C(12B)	0.5443 (19)	–0.1764 (13)	0.5898 (7)	9.2 (12)
C(13B)	0.4983 (18)	–0.1050 (12)	0.6014 (7)	8.6 (12)
C(14B)	0.3792 (16)	–0.0788 (9)	0.5857 (5)	6.0 (8)
C(15B)	0.2604 (14)	–0.0315 (8)	0.4359 (5)	4.3 (6)
C(16B)	0.3087 (14)	0.0370 (9)	0.4517 (4)	4.9 (7)
C(17B)	0.2155 (17)	0.0955 (8)	0.4393 (5)	5.2 (8)
C(18B)	0.1089 (14)	0.0617 (8)	0.4149 (4)	4.4 (7)
C(19B)	0.1376 (14)	–0.0150 (8)	0.4128 (4)	4.1 (6)
C(20B)	0.3373 (15)	–0.1026 (10)	0.4372 (5)	5.6 (8)
C(21B)	0.4462 (17)	0.0506 (11)	0.4725 (5)	7.0 (9)
C(22B)	0.2343 (20)	0.1821 (10)	0.4442 (6)	7.4 (10)
C(23B)	–0.0039 (19)	0.1017 (11)	0.3903 (6)	7.0 (10)
C(24B)	0.0655 (17)	–0.0690 (9)	0.3856 (5)	6.1 (8)
O(1B)	0.2379 (14)	0.1332 (7)	0.5449 (4)	9.2 (8)
O(2B)	–0.1536 (15)	0.1278 (9)	0.4863 (5)	10.7 (9)
O(3B)	0.0705 (14)	–0.2480 (7)	0.4460 (4)	9.0 (8)
O(4B)	–0.3498 (12)	–0.1217 (12)	0.4816 (5)	13.1 (13)
O(5B)	–0.0635 (19)	–0.2478 (8)	0.5727 (5)	11.8 (10)
O(6B)	–0.3334 (11)	0.0415 (9)	0.5504 (4)	9.1 (9)
O(7B)	–0.1026 (18)	–0.1141 (10)	0.6351 (4)	12.6 (11)
O(8B)	0.0695 (12)	0.1119 (8)	0.6205 (4)	8.1 (7)

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) of **3** (Esd in Parentheses)

(A) Selected Bond Distances

W(1A)–Ru(1A)	3.0613 (12)	W(1A)–Ru(2A)	2.9861 (14)
Ru(1A)–Ru(2A)	2.8145 (17)	W(1A)–P(1A)	2.382 (3)
Ru(1A)–P(1A)	2.280 (3)	Ru(2A)–P(1A)	2.283 (4)
mean W–CO	2.02 (1)	mean Ru–CO	1.91 (2)

(B) Selected Bond Angles

W(1A)–C(1A)–O(1A)	174.5 (13)	W(1A)–C(2A)–O(2A)	170.7 (15)
W(1A)–Ru(1A)–C(3A)	105.6 (4)	W(1A)–Ru(1A)–C(4A)	108.5 (4)
Ru(1A)–W(1A)–C(2A)	97.0 (5)	Ru(2A)–W(1A)–C(2A)	74.6 (5)
Ru(2A)–W(1A)–C(1A)	72.8 (4)	W(1A)–Ru(2A)–C(6A)	103.2 (6)
W(1A)–Ru(2A)–C(8A)	107.1 (6)	Ru(1A)–Ru(2A)–C(6A)	100.6 (5)
Ru(1A)–Ru(2A)–C(7A)	91.1 (5)	Ru(2A)–Ru(1A)–C(4A)	93.4 (5)
Ru(2A)–Ru(1A)–C(5A)	93.8 (5)		

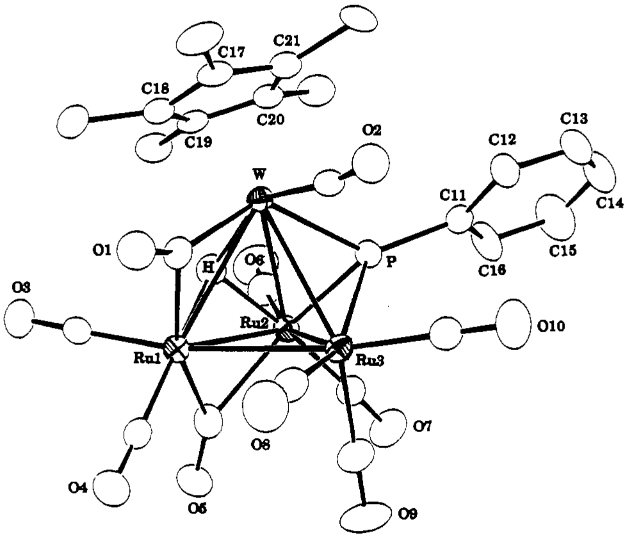

Figure 1. Molecular structure of **1**, showing the atomic numbering scheme.

but produced a trinuclear cluster $CpWRu_2(CO)_8(\mu\text{-H})(\mu_3\text{-PPh})$ in addition to the coproducts $Ru_4(CO)_{13}(\mu_3\text{-PPh})$ and $Ru_5(CO)_{15}(\mu_4\text{-PPh})$. Attempts to prepare the unobserved tetranuclear heterometallic derivative via treatment of $Ru_4(CO)_{13}(\mu_3\text{-PPh})$ with $CpW(CO)_3H$ were unsuccessful, we isolated only the trinuclear derivative **2** (trace, less than 5%) as the only isolable heterometallic complex. These experimental results suggest that the related, unobserved Cp derivative $CpWRu_3(CO)_{10}(\mu_3\text{-H})(\mu_3\text{-PPh})$ may possess a limited lifetime under the reaction conditions examined. Furthermore, because we have observed that the tetranuclear acetylide clusters $LWOs_3(CO)_{11}(C{\equiv}CR)$ undergo CO-induced cluster fragmentation to afford trinuclear derivatives,[14] we decided to carry out the reaction of **1** with carbon monoxide. As expected, we obtained a trinuclear complex, $Cp^*WRu_2(CO)_8(\mu\text{-H})(\mu_3\text{-PPh})$ (**3**), with a molecular formula similar to that of complex **2**, confirming that complex **1** indeed reacted with CO by eliminating a "$Ru(CO)_2$" fragment to afford the trinuclear phosphinidene derivative. However, to our surprise, the IR and ^1H NMR data suggest that complex **3** is present as two isomers in solution (Scheme I). The isomerization reaction is discussed later in detail.

Characterization of 1. This complex shows a molecular ion peak in its FAB mass spectra and fragmentation ions corresponding to successive loss of CO ligands. The solution IR spectrum exhibits seven terminal CO stretching absorption bands and two additional weak absorptions at 1864 and 1785 cm^{-1}, indicating the presence of bridging CO ligands. As these spectroscopic data did not uniquely define its molecular structure, a single-crystal X-ray analysis was carried out.

The structure is shown in Figure 1, and selected bond parameters are presented in Table III. The metal framework may be described as a WRu_3P trigonal-bipyramidal arrangement or a distorted WRu_3 tetrahedron capped by a phospinidene ligand.

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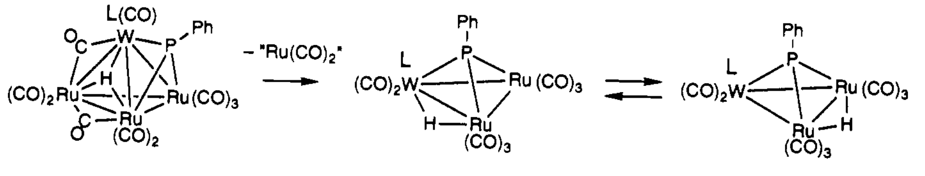
Scheme I



L = Cp*, **1**   L = Cp*, **3b**   L = Cp*, **3a**; L = Cp, **2**

The core arrangement of this molecule is similar to that of the alkylidyne complex $Cp^*WRu_3(CO)_{11}(\mu_3\text{-COMe})$ prepared from the reaction of $Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-COMe})$ with $Cp^*W(CO)_3H$.[15] The metal–metal bond distances are somewhat irregular, with distances in the range 2.718 (1)–3.1551 (9) Å. The W–Ru(2) edge (3.1551 (9) Å), which is part of the metal triangle capped by the phosphinidene ligand, is substantially longer than the W–Ru(1) (2.9021 (8) Å) and W–Ru(3) (2.9006 (9) Å) edges. In addition, there are eight terminal and two bridging CO ligands in the molecule. The three Ru atoms are each coordinated by three, two, and two terminal CO ligands, respectively; the W atom is bonded to a Cp* ligand and carries only one terminal CO ligand. The bridging CO ligands are associated with the adjacent edges that share the common metal atom Ru(1). One edge, Ru(1)–Ru(2), is the shortest metal–metal bond of the entire molecule (2.718 (1) Å). For the sake of comparison, the average Ru–Ru distance in the triruthenium carbonyl complex $Ru_3(CO)_{12}$ is 2.854 Å.[16]

The molecule also contains a bridging hydride, as indicated by its ^1H NMR spectrum, in which a high-field signal at δ −19.00 with coupling constants $J_{W-H} = 69.2$ Hz and $J_{P-H} = 8.5$ Hz were observed. The value of the chemical shift is in the range expected for the hydride that usually occupies a position bridging two or three metal atoms,[17] although the J_{W-H} coupling constant favors the mode of edge-bridging because the observed coupling constant slightly exceeds those of the edge-bridging hydrides in the complexes $Cp^*WRu_3(CO)_{10}(\mu\text{-H})_3$ and $Cp^*WRu_3(CO)_{11}(\mu\text{-H})$[18] and the related phosphinidene derivative **3b** (vide infra). However, the hydride ligand, as determined by the difference Fourier method, is not associated with the W–Ru(2) edge but with the nearby triangular face defined by atoms W, Ru(1), and Ru(2). The respective bond distances are W–H = 2.06, Ru(1)–H = 1.86, and Ru(2)–H = 1.88 Å. A survey of interatomic angles within the molecule shows that the deposition of the CO ligands on this WRu_2 face is distorted away from the hydride ligand, consistent with the distinction of a face-bridging hydride. For example, the two bridging CO ligands are almost parallel to the WRu_2 base (the dihedral angles to the plane W–Ru(1)–C(1) and to the plane Ru(1)–Ru(2)–C(5) are 168.6 (3) and 179.6 (3)°, respectively); the terminal CO ligands attached to Ru(1) (Ru(2)–Ru(1)–C(3) = 117.9 (2) and W–Ru(1)–C(3) = 110.5 (2)°) and Ru(2) (Ru(1)–Ru(2)–C(6) = 120.7 (3) and W–Ru(2)–C(6) = 111.6 (3)°) show clearly that they are not perpendicular to the WRu_2 basal plane. Similar distortion of the CO ligands surrounding the face-bridging hydride was reported in the tetranuclear clusters $Fe_3Pt(CO)_{10}(\mu_3\text{-H})(\mu_3\text{-COMe})(PPh_3)$[19] and $Co_3Fe(CO)_9(\mu_3\text{-H})[P(OMe)_3]_3$.[20] Finally, despite this strong evidence in favor of the face-bridging hydride, that the hydride bridges the W–Ru(2) edge must be considered as an alternative because of its enlarged length, the expanded W–Ru(2)–C(6) angle (111.6 (3)°) and the strong coupling to ^{183}W isotope in its ^1H NMR spectrum.

Interpretation of the ^{13}C NMR data was possible after we understood the molecular structure. The ^{13}C NMR spectrum shows two bridging CO resonances at δ 247.1 ($J_{P-C} = 5$ Hz) and 246.5 ($J_{P-C} = 32$ Hz), one terminal W–CO signal at δ 209.3 ($J_{W-C} = 157$ Hz and $J_{P-C} = 10$ Hz), and five Ru–CO resonances at δ 199.4 ($J_{P-C} = 4$ Hz and $J_{C-H} = 9$ Hz), 198.2 ($J_{P-C} = 7$ Hz), 194.7 ($J_{P-C} = 4$ Hz and $J_{C-H} = 8$ Hz), 193.2, and 193.0 ($J_{P-C} = 4$ Hz) with intensity ratio 1:3:1:1:1. The doublet at δ 198.2 with intensity three is due to the unique $Ru(CO)_3$ unit that undergoes rapid 3-fold rotation and couples to the phosphorus atom. The multiplets at δ 199.4 and 194.7 are due to the CO ligands being transoid to the hydride because of the observation of small $^2J_{C-H}$ coupling, whereas the sharp singlet at δ 193.2 is assigned to the C(3)O(3) ligand because this signal has no detectable J_{P-C} coupling and C(3) is located far from the phosphorus atom.

Characterization of 2. Orange, air-stable, crystals of **2** suitable for structural determination were obtained from a layered solution of CH_2Cl_2–methanol, and a single-crystal diffraction study was performed. The ORTEP diagram is shown in Figure 2, and selected bond parameters are presented in Table V. Complex **2** is isostructural with the related phenylimido cluster $CpWRu_2(CO)_8(\mu\text{-H})(\mu_3\text{-NPh})$[2a] and isoelectronic to the triruthenium complex $Ru_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-PPh})$.[21] The molecule consists of a slightly distorted isosceles WRu_2 geometry with bond distances W–Ru(1) = 3.0042 (9), W–Ru(2) 2.9538 (9), and Ru(1)–Ru(2) = 2.9101 (9) Å. Each ruthenium atom is associated with three terminal CO ligands, while the tungsten atom is capped by a Cp ligand and linked to two semibridging CO ligands. The phosphinidene ligand of this molecule resides on the WRu_2 triangular face opposite the semibridging W–CO ligands, and its phenyl substituent is parallel to the W–Ru(1) bond. The W–P distance (2.380 (2) Å) and the Ru–P distances (2.279 (2) and 2.284 (2) Å) are consistent with those of the metal–phosphorus single bond. The bridging hydride ligand, as determined by the difference Fourier method and refined successfully, is associated with the unique Ru–Ru bond with Ru(1)–H = 1.90 (6) and Ru(2)–H = 1.84 (6) Å. The angle involving the axial CO ligands on Ru atoms (Ru(1)–Ru(2)–C(8) = 114.7 (2) and Ru(2)–Ru(1)–C(3) = 112.0 (2)°) is enlarged with respect to the equatorial CO ligands (Ru(1)–Ru(2)–C(6) = 98.4 (3) and Ru(2)–Ru(1)–C(5) = 96.2 (2)°).

Information about the location of hydride in solution is provided by the ^1H and ^{13}C NMR spectroscopies. The ^1H NMR spectrum exhibits a doublet at δ −17.96, showing only the phosphorus–hydrogen coupling ($J_{P-H} = 15.6$ Hz). In the ^{13}C NMR spectrum measured at 273 K, there are four resonances at δ 213.1 ($J_{W-C} = 164$ Hz), 197.0 ($J_{P-C} = 43$ Hz), 194.6, and 188.2 in an intensity ratio 2:2:2:2 for the CO ligands, implying that the hydride is also located on the same Ru–Ru edge in solution.

Crystal Structure of 3. The two crystallographically independent molecules in the asymmetric unit are structurally

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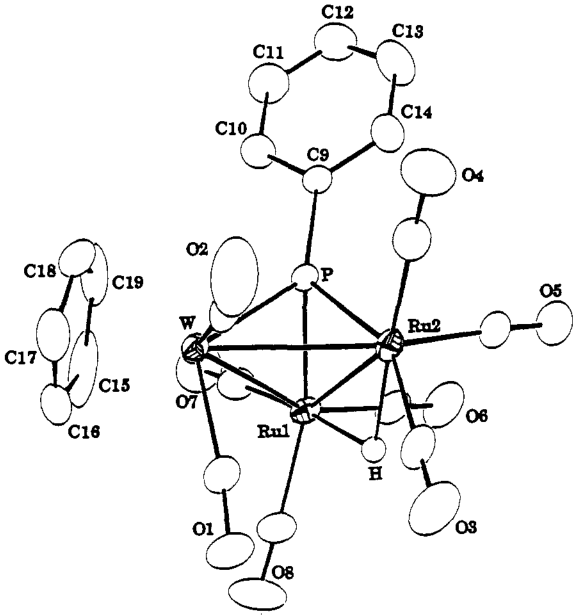

Figure 2. Molecular structure of **2**, showing the atomic numbering scheme.

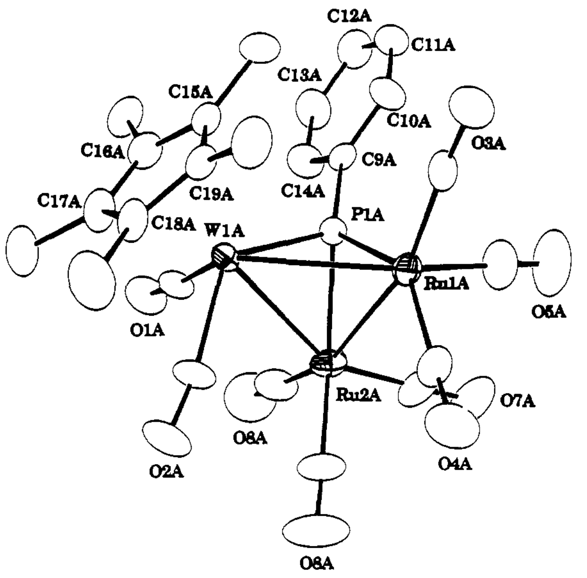

Figure 3. Molecular structure of **3**, showing the atomic numbering scheme.

equivalent with the molecular structure, and the selected parameters of one of these is illustrated in Figure 3 and Table VII, respectively. Three metal atoms are capped by a phosphorus atom to give a distorted-tetrahedral core arrangement. The W–P distance (2.382 (3) Å) is substantially longer than the other two essentially equal Ru–P distances (average 2.281 Å) in the molecule. The Cp* ligand is coordinated to the tungsten atom and bends toward the face defined by the atoms W(1A), Ru(1A), and P(1A). Six of the CO ligands bond terminally to the ruthenium atoms, while the two remaining CO ligands on the tungsten are slightly nonlinear, indicating some semibridging character. The W(1A)–Ru(1A) bond (3.0613 (12) Å) is significantly longer than W(1A)–Ru(2A) (2.9861 (14) Å) and Ru(1A)–Ru(2A) (2.8145 (17) Å). The hydride was not located directly, but the long W(1A)–Ru(1A) distance and the fact that equatorial CO ligands on atom Ru(1A) bend away from the metal–metal vector W(1A)–Ru(1A)–C(3A) = 105.6 (4) and W(1A)–Ru(1A)–C(4A) = 108.5 (4)°) suggest that the hydride bridges this edge. The possibility that the hydride bridges the second longest W(1A)–Ru(2A) edge is eliminated because the Ru–W–C(carbonyl) angles are acute (Ru(2A)–W(1A)–C(2A) = 74.6 (5) and Ru(2A)–W(1A)–C(1A) = 72.8 (4)°). For the same reason, the hydride ligand is not associated with the unique Ru–Ru bond because the equatorial Ru–Ru–C(carbonyl) angles are in the range 100.6 (5)–91.1 (5)°, the mean value being 94.7° (Table VII). Thus, the structure established in the solid state represents that of the isomer **3b** in solution.

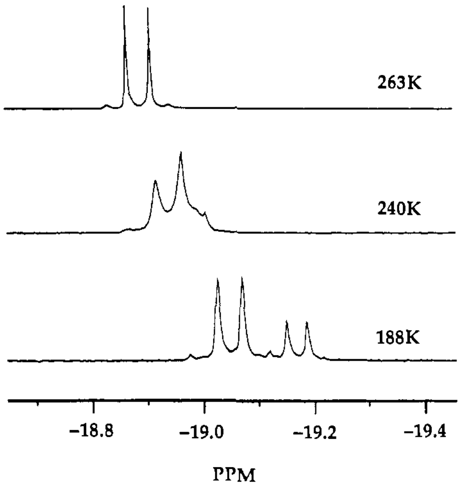

Figure 4. Variable-temperature ^1H NMR spectra of **3** in the bridging hydride region.

Solution Isomerization of 3. The ^1H NMR spectrum of **3** at 263 K exhibits a hydride resonance with coupling to both tungsten and phosphorus atoms (J_{P-H} = 17.2 Hz and J_{W-H} = 44.0 Hz) (Figure 4). The total intensity of the tungsten satellites (10%) is substantially smaller than the natural abundance of the ^{183}W isotope (14.3%), indicating the existence of two rapidly interconvertible isomers in which one isomer possesses tungsten–hydride coupling but the second exhibits no coupling to the tungsten atom. Therefore, under the condition of rapid exchange, the integration of the satellites will be smaller than the ratio of the ^{183}W isotope. When the temperature was lowered to 240 K, the doublet resonances broadened and coalesced to the baseline as expected. At 188 K, two sets of signals at δ −19.05 (J_{P-H} = 17.6 Hz and J_{W-H} = 57.6 Hz) and −19.17 (J_{P-H} = 14.4 Hz) were observed in an intensity ratio 2.3:1. Since the first hydride doublet was flanked by characteristic tungsten satellites, this signal is assigned to the isomer **3b** which possesses a structure similar to that in the solid state. The latter is assigned to the isomer **3a**; the hydride is associated with the Ru–Ru edge because this signal is not coupled to the tungsten atom. In accordance with the presence of two isomers in solution, the ^{31}P NMR spectrum at 233 K shows two signals at δ 287.0 (J_{W-P} = 195 Hz) and 257.6 (J_{W-P} = 183 Hz) in an intensity ratio 1:2.3.

The novel dynamic behavior is due to rapid hydride migration between the adjacent W–Ru and Ru–Ru bonds. Such hydride migration is not a remarkable process in the chemistry of transition-metal cluster complexes; there are many precedents in the literature.[22] However, the most unusual feature of our work is the observation of shifting of the bridging hydride from the Ru–Ru to the W–Ru edge by variation of the auxiliary ligand on the tungsten atom. We speculate that the enhanced electron-donating capability of the Cp* ligand may cause a buildup of charge on the tungsten atom; this charge can in turn be relieved by transferring the excess electron density to the bridging hydride ligand. Thus the hydride is attracted to the W–Ru edge for the respective Cp* derivative. A similar explanation has been used to account for the conformational preference of the $LM(CO)_2$ center, M = W and Mo, and the formation of semibridging CO ligands in the MCo_2 alkylidyne clusters.[23] In this vein, we also note that in the tetrahedral complexes $Cp^*WOs_3(CO)_{12}H$, the

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dominant isomer possesses a bridging hydride linked to the electron-rich Cp*W(CO)$_2$ center.[24] In contrast, the major isomer of the respective Cp derivative CpWOs$_3$(CO)$_{12}$H in solution carries a bridging hydride associated with an Os–Os bond.[25]

Summary. A summary of the reactions performed in this work appears in Scheme I. Condensation of Ru$_3$(CO)$_{10}$(μ-PPh$_2$) and Cp*W(CO)$_3$H proved to be a convenient method to generate the tetranuclear phosphinidene cluster **1**. This complex seems to be the first tetrahedral cluster complex containing a μ_3-PR ligand to have been characterized by X-ray crystallography. Mays and co-workers have reported the preparation of several tetrahedral μ_3-PR cluster complexes via reaction of the anion [Ru$_3$(CO)$_9$(μ-H)(μ_3-PPh)]$^-$ with cationic complexes of Re, Rh, and Ir,[26] but their structures were proposed on the basis of the spectroscopic data. Butterfly clusters containing a triply bridging phosphinidene ligand located on an open triangle have been reported for tetranuclear complexes Ru$_4$(CO)$_{13}$(μ_3-PPh)[10] and Os$_4$(CO)$_{13}$(μ-H)$_2$(μ_3-PC$_6$H$_{11}$).[27] Interestingly, complex **1** does not react with CO to afford a butterfly cluster via cleavage of a single metal–metal bond but produces a degradation product **3** through elimination of a Ru(CO)$_2$ fragment. In the reaction with CpW(CO)$_3$H, we obtained the trinuclear complex **2** without prior formation of the tetranuclear phosphinidene cluster. Finally, the ^{1}H NMR spectra demonstrate that complex **3** exists as two isomers undergoing rapid hydride migration in solution. The dominant isomer possesses a hydride bridging the W–Ru edge. For the related complex **2** and the phenylimido complexes LWRu$_2$(CO)$_8$(μ-H)(μ_3-NPh), L = Cp and Cp*,[2a] there is only one isomer in solution and the hydride bridges the unique Ru–Ru edge.

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Supplementary Material Available: Tables of crystal data, nonessential bond distances and angles, calculated positions of atoms, and anisotropic thermal parameters for complexes **1–3** (21 pages). Ordering information is given on any current masthead page.

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