

Convenient Room-Temperature Synthesis of the Phosphinidene-Capped Clusters $[(\text{Ph}_3\text{P})_2\text{N}][(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-PR})]$ (R = Ph, *t*-Bu)

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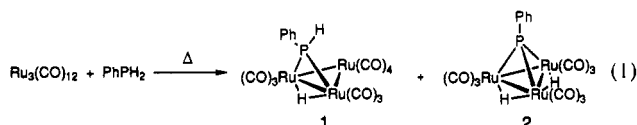
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Received September 26, 1991

Introduction

One common synthetic route to phosphinidene-capped clusters is the thermolytic reaction of a primary phosphine ligand with mononuclear or multinuclear binary metal–carbonyl complexes. The elevated reaction temperatures are usually required to promote dissociation of the carbonyl ligands so coordination and subsequent activation of the primary phosphine ligand is achieved. We are pursuing milder preparations for phosphinidene-capped clusters so primary *silyl*/phosphines, which undergo a number of undesirable reactions in the presence of metal complexes at elevated temperatures, can be employed as reagents.¹

The employment of "activated" complexes which are coordinatively unsaturated or in which the carbon monoxide ligands have been partially replaced by more labile donors² offers one method of achieving more selective cluster chemistry at lower temperatures. In the course of our attempts to prepare ruthenium phosphinidene clusters³ under mild conditions, we have investigated the reactivity of primary phosphines with the activated complexes $\text{Ru}_3(\text{CO})_x(\text{NCMe})_y$ ($x = 10, y = 2; x = 11, y = 1$)⁴ and $[\text{PPN}][\text{Ru}_3(\text{CO})_{11}\text{Cl}]$.⁵ The thermolytic reaction of the parent carbonyl, $\text{Ru}_3(\text{CO})_{12}$, and H_2PPh in refluxing hexane yields a mixture of the phosphido-bridged cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-P}(\text{H})\text{Ph})$ (**1**) and the phosphinidene-capped cluster $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-PPh})$ (**2**) (eq 1); at higher temperatures, other



products derived from either orthometalation of the phenyl ring or further H_2PPh substitution are observed.^{3a} Utilization of activated cluster starting materials enables the phosphido-bridged complex **1** to be selectively synthesized at room temperature by reaction of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ and H_2PPh and enables selective production of the anionic phosphinidene clusters $[\text{PPN}][(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-PR})]$ (**3a**, R = Ph; **3b**, R = *t*-Bu) in a facile

one-pot reaction between $[\text{Ru}_3(\text{CO})_{11}\text{Cl}]^-$ and H_2PR (R = Ph, *t*-Bu). The chemistry observed for these ruthenium complexes will be compared to that of the analogous osmium complexes.

Results and Discussion

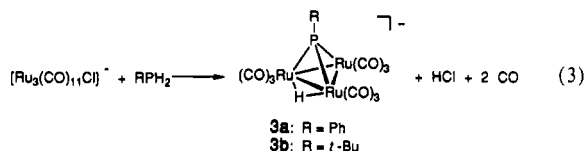
Addition of PhPH_2 to Acetonitrile-Substituted $\text{Ru}_3(\text{CO})_{12}$. The addition of 1 equiv of phenylphosphine to a solution of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ in an acetonitrile/ CH_2Cl_2 mixture results in the formation of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}[\mu\text{-P}(\text{H})\text{Ph}]$ (**1**), which can be isolated in fair yield (eq 2). Crystals of **1** form upon reducing



the solution volume, eliminating the need for the usual chromatography.^{3a} The phosphido cluster, **1**, is still observed as the primary product when 2 equiv of phenylphosphine are added to $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ as well as when $\text{Ru}_3(\text{CO})_{11}(\text{NCCH}_3)$ is employed as the ruthenium starting material; no stable primary phosphine complexes are observed.

The monophosphine-substituted osmium complexes $\text{Os}_3(\text{CO})_{11}(\text{PH}_2\text{R})$ (R = Ph, H) are isolable,^{3a,6} unlike their ruthenium counterparts. Presumably the ruthenium monosubstituted phosphine complexes are not as inert as the osmium complexes, and loss of carbon monoxide or acetonitrile occurs with oxidative addition of a P–H bond to the cluster to yield $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}[\mu\text{-P}(\text{H})\text{R}]$ as the stable product.

Addition of PhPH_2 or *t*-BuPH₂ to $[\text{Ru}_3(\text{CO})_{11}\text{Cl}]^-$. The addition of phenyl- or *t*-butylphosphine to the halide cluster $[\text{Ru}_3(\text{CO})_{11}\text{Cl}]^-$, prepared in situ in tetrahydrofuran solution, produces complexes formulated as anionic phosphinidene clusters on the basis of their infrared and ³¹P NMR spectra. The pattern observed in the infrared spectrum of the P(*t*-Bu) cluster is identical to that observed for the PPh cluster but is shifted by approximately 4 cm^{-1} to lower energy. Since the phosphinidene product was negatively charged, it was initially postulated that the halide ligand remained bound to the cluster as observed by Lavigne and co-workers in the syntheses of acetylene-capped clusters from $[\text{PPN}][\text{Ru}_3(\text{CO})_{11}\text{Cl}]$.⁷ Crystals of the (*t*-Bu)PH₂ reaction product were obtained in an initial preparation, and a single-crystal X-ray diffraction study (see below) showed the correct product formulation to be $[\text{PPN}][(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-PR})]$ (**3a**, R = Ph; **3b**, R = *t*-Bu) (eq 3). Compound **3a** has been previously

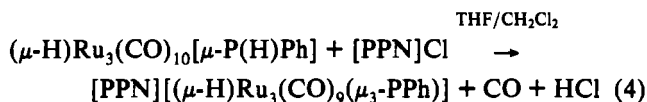


prepared by deprotonation of the neutral phosphinidene cluster **2** with methanolic KOH followed by metathesis with $[\text{PPN}]\text{Cl}$.⁸ The method reported here represents a convenient one-pot room temperature route to these anionic phosphinidene-capped clusters.

Deprotonation of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}[\mu\text{-P}(\text{H})\text{Ph}]$. A tetrahydrofuran solution of the phosphido-bridged cluster **1** can be instantaneously converted to **3a** by addition of a stoichiometric amount of $[\text{PPN}]\text{Cl}$ dissolved in a minimum amount of CH_2Cl_2 (eq 4). As previously observed for reactions of halide salts with clusters,^{2,5} the solvent plays a role in the reaction by controlling the extent of dissociation of the salt, and in neat dichloromethane

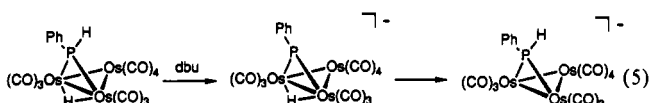
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- (3) See for example: (a) Iwasaki, F.; Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Wheatley, P. J. *J. Organomet. Chem.* **1981**, *213*, 185. (b) Natarajan, K.; Scheidsteger, O.; Hutner, G. *J. Organomet. Chem.* **1981**, *221*, 301. (c) Field, J. S.; Haines, R. J.; Smit, D. N. *J. Organomet. Chem.* **1981**, *224*, C49. (d) MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87.
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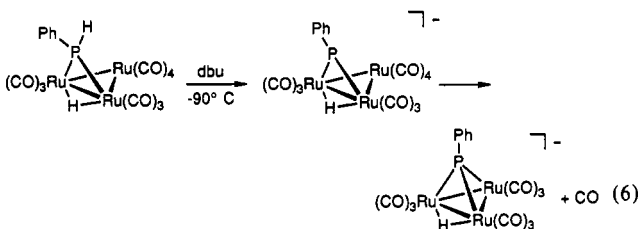


solution, the [PPN]Cl reaction takes several days. The ability of [PPN]Cl to carry out the above reaction suggests that the halide ligand in $[\text{Ru}_3(\text{CO})_{11}\text{Cl}]^-$ both facilitates substitution of the primary phosphine ligand on the cluster as previously observed^{2,5} and acts as a base to generate the phosphinidene cluster anion. [PPN]Cl has been previously employed as a base to convert $\text{Os}_3(\text{CO})_{11}(\text{PH}_3)$ to the anionic phosphido-bridged cluster $[\text{PPN}][\text{Os}_3(\text{CO})_{10}(\mu\text{-PH}_2)]^-$.^{6a}

The reaction of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}[\mu\text{-P}(\text{H})\text{Ph}]$, the osmium analogue of **1**, toward bases has been explored.^{6a,9} The cluster $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}[\mu\text{-P}(\text{H})\text{Ph}]$ does not react with chloride, but the stronger base dbu (dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene) removes the phosphorus-bound hydrogen atoms to convert the kinetic product, $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-PPh})]^-$, which has been spectroscopically characterized.^{6a} The cluster-bound hydride ligand then slowly migrates to the phosphorus atom (eq 5). In the



ruthenium case, where the hydride ligands are more acidic, it is not clear whether reaction with a base would remove the phosphorus-bound hydrogen atom or the hydride ligand. A low-temperature ³¹P NMR study was carried out to attempt to delineate the course of this reaction. At -90 °C, after the addition of 1 equiv of dbu to a solution of **1** in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$, quantitative conversion to a new species is observed in the ³¹P NMR spectrum with a doublet at 76 ppm ($J_{\text{P-H}} = 19.4$ Hz), upfield from the resonance observed for **1** (81 ppm). The loss of the large coupling due to a hydrogen atom directly bound to phosphorus and the retention of coupling to the hydride ligand are consistent with the formulation of the intermediate as $[(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-PPh})]^-$, analogous to the osmium product. Warming of this mixture to room temperature produces **3a** with evolution of carbon monoxide (eq 6). The greater lability of the ruthenium-bound carbon monoxide ligands in comparison to osmium again seems to govern the products produced.



The cleavage of P-H bonds by anionic ruthenium carbonyl clusters as in the formation of **3a** and **3b** is not without precedent. Puddephatt and co-workers observed P-H bond cleavage upon addition of $\text{R}(\text{H})\text{PCH}_2\text{PR}''$ to $\text{Ru}_3(\text{CO})_{12}$ in the presence of catalytic amounts of [PPN]CN to yield $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-P}(\text{R})\text{CH}_2\text{PR}'')$.¹⁰ The addition of the phosphine to the cluster proceeds by reaction of the anionic species $[\text{Ru}_3(\text{CO})_{11}\text{CN}]^-$.

X-ray Structure Determination of $[\text{PPN}][(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-P}(\text{t-Bu}))]^-$ (3b**).** A thermal ellipsoid plot of the cluster anion in **3b** is displayed in Figure 1. Bond lengths and angles relevant to the cluster anion are displayed in Table I. The three ruthenium atoms are arranged as an isosceles triangle. The hydride ligand

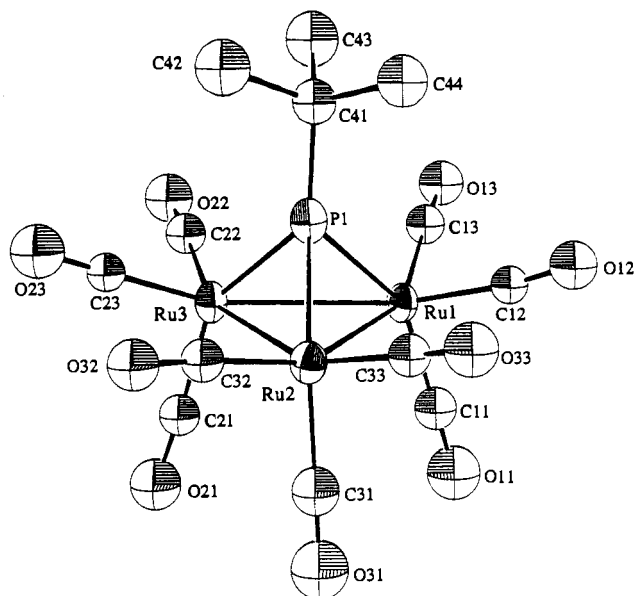


Figure 1. Thermal ellipsoid plot (30%) of the anion of **3b**.

was not located in the experiment; however, the third edge, between Ru(1) and Ru(2) (2.949 (3) Å), is approximately 0.1 Å longer than the other two sides, suggesting that the hydride ligand is bridging that edge. The lengths of the hydride-bridged edge and the unbridged Ru-Ru edges agree very well with the corresponding distances observed in the crystal structure of the dihydride **2**.^{3a} The phosphinidene phosphorus atom sits 1.57 Å above the Ru_3 plane.

Experimental Section

All manipulations were carried out under nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, diisopropyl ether, and hexanes were distilled from sodium benzophenone ketyl, dichloromethane was distilled from P_4O_{10} , and acetonitrile was distilled from CaH_2 . Phenylphosphine (Aldrich) and *t*-butylphosphine (Quantum Design) were degassed and vacuum distilled before use. [PPN]Cl (PPN⁺ = bis(triphenylphosphine)ammonium cation) (Alfa) was dried in a 130 °C oven before use. Triruthenium dodecacarbonyl¹¹ and $\text{Ru}_3(\text{CO})_x(\text{MeCN})_y$ ($x = 10, y = 2$; $x = 11, y = 1$)⁴ were prepared by following published procedures. Proton NMR spectra were recorded on a Bruker AC-200, a Bruker WM-250, or a Varian XL-400 spectrometer and referenced to residual protons in the solvent. Phosphorus spectra were recorded on the same instruments operating at 81, 101, and 162 MHz, respectively, and were referenced to the [PPN]⁺ in solution (25 ppm) or to an external sample of H_3PO_4 (0 ppm). IR spectra were recorded on a Bomem Michelson 120 spectrometer.

Preparation of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}[\mu\text{-P}(\text{H})\text{Ph}]$ (1**).** Phenylphosphine (17 μL , 0.15 mmol) was added to a solution of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ (100 mg, 0.15 mmol) in 2 mL of acetonitrile and 6 mL of CH_2Cl_2 . The color of the solution changed immediately from yellow to dark orange. The volume of the solution was reduced to ca. 1 mL, causing precipitation of an orange crystalline solid. The solution was cooled to -20 °C to ensure complete precipitation, and the solid was collected by filtration and dried under vacuum. Isolated yield: 45 mg (45%). Infrared and proton NMR data agree with those reported by Mays and co-workers.^{3a} Previously unreported ³¹P NMR (CD_2Cl_2 ; δ , ppm): 81 (dd, $\text{P}(\text{H})\text{Ph}$, $J_{\text{PH}} = 385$ Hz, $^2J_{\text{PH}} = 27$ Hz).

Reaction of H_2PPh with $\text{Ru}_3(\text{CO})_{11}(\text{NCMe})$. Phenylphosphine (8 μL , 0.08 mmol) was added by microliter syringe to a stirred solution of $\text{Ru}_3(\text{CO})_{11}(\text{NCMe})$ (50 mg, 0.07 mmol). The color of the solution darkened immediately, and after the solution was stirred 1 h, **1** was observed as the only product in the ³¹P NMR spectrum.

Preparation of $[\text{PPN}][(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-PPh})]^-$ (3a**).** A mixture of $\text{Ru}_3(\text{CO})_{12}$ (200 mg, 0.32 mmol) and [PPN]Cl (180 mg, 0.32 mmol) was dissolved in 1 mL of dichloromethane and 30 mL of THF. This mixture was stirred, and the reaction was monitored by IR spectroscopy until the

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Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for [PPN][$(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-P}(t\text{-Bu)))$] (**3b**)^a

Ru-Ru			
Ru(1)-Ru(2)	2.948 (3)	Ru(1)-Ru(3)	2.848 (3)
Ru(2)-Ru(3)	2.845 (4)		
Ru-P			
Ru(1)-P(1)	2.295 (8)	Ru(2)-P(1)	2.306 (7)
Ru(3)-P(1)	2.261 (8)		
Ru-CO			
Ru(1)-C(11)	1.88 (3)	Ru(1)-C(12)	1.88 (3)
Ru(1)-C(13)	1.91 (3)	Ru(2)-C(21)	1.86 (3)
Ru(2)-C(22)	1.90 (3)	Ru(2)-C(23)	1.86 (3)
Ru(3)-C(31)	1.90 (4)	Ru(3)-C(32)	1.89 (3)
Ru(3)-C(33)	1.91 (3)		
P-t-Bu			
P(1)-C(41)	1.78 (3)	C(41)-C(42)	1.58 (5)
C(41)-C(43)	1.60 (5)	C(41)-C(44)	1.52 (4)
C-O			
O(11)-C(11)	1.16 (5)	O(12)-C(12)	1.13 (3)
O(13)-C(13)	1.12 (4)	O(21)-C(21)	1.17 (4)
O(22)-C(22)	1.13 (4)	O(23)-C(23)	1.12 (4)
O(31)-C(31)	1.17 (5)	O(32)-C(32)	1.16 (3)
O(33)-C(33)	1.14 (3)		
Ru-Ru-Ru			
Ru(2)-Ru(1)-Ru(3)	58.78 (8)	Ru(1)-Ru(2)-Ru(3)	58.86 (8)
Ru(1)-Ru(3)-Ru(2)	62.36 (8)		
Ru-Ru-P			
Ru(2)-Ru(1)-P(1)	50.3 (2)	Ru(3)-Ru(1)-P(1)	50.8 (2)
Ru(1)-Ru(2)-P(1)	50.0 (2)	Ru(3)-Ru(2)-P(1)	50.8 (2)
Ru(1)-Ru(3)-P(1)	51.8 (2)	Ru(2)-Ru(3)-P(1)	52.2 (2)
Ru-P-Ru			
Ru(1)-P(1)-Ru(2)	79.7 (2)	Ru(1)-P(1)-Ru(3)	77.4 (3)
Ru(2)-P(1)-Ru(3)	77.1 (2)		
Ru-Ru-C			
Ru(2)-Ru(1)-C(11)	107.7 (9)	Ru(2)-Ru(1)-C(12)	146.0 (7)
Ru(2)-Ru(1)-C(13)	103.9 (9)	Ru(3)-Ru(1)-C(11)	101.1 (9)
Ru(3)-Ru(1)-C(12)	92.3 (7)	Ru(3)-Ru(1)-C(13)	153.1 (9)
Ru(1)-Ru(2)-C(21)	105.7 (10)	Ru(1)-Ru(2)-C(22)	104.1 (9)
Ru(1)-Ru(2)-C(23)	144.0 (7)	Ru(3)-Ru(2)-C(21)	93.2 (9)
Ru(3)-Ru(2)-C(22)	157.5 (8)	Ru(3)-Ru(2)-C(23)	93.1 (8)
Ru(1)-Ru(3)-C(31)	94.2 (10)	Ru(1)-Ru(3)-C(32)	154.4 (9)
Ru(1)-Ru(3)-C(33)	99.4 (7)	Ru(2)-Ru(3)-C(31)	97.5 (10)
Ru(2)-Ru(3)-C(32)	96.2 (8)	Ru(2)-Ru(3)-C(33)	154.8 (8)
P-Ru-C			
P(1)-Ru(1)-C(11)	149.3 (9)	P(1)-Ru(1)-C(12)	98.4 (8)
P(1)-Ru(1)-C(13)	102.5 (9)	P(1)-Ru(2)-C(21)	142.4 (9)
P(1)-Ru(2)-C(22)	107.6 (8)	P(1)-Ru(2)-C(23)	95.5 (7)
P(1)-Ru(3)-C(31)	140.7 (10)	P(1)-Ru(3)-C(32)	104.5 (9)
P(1)-Ru(3)-C(33)	103.3 (8)		
C-Ru-C			
C(11)-Ru(1)-C(12)	94 (1)	C(11)-Ru(1)-C(13)	104 (1)
C(12)-Ru(1)-C(13)	95 (1)	C(21)-Ru(2)-C(22)	106 (1)
C(21)-Ru(2)-C(23)	97 (1)	C(22)-Ru(2)-C(23)	95 (1)
C(31)-Ru(3)-C(32)	103 (1)	C(31)-Ru(3)-C(33)	101 (1)
C(32)-Ru(3)-C(33)	96 (1)		
Ru-C-O			
Ru(1)-C(11)-O(11)	178 (3)	Ru(1)-C(12)-O(12)	173 (2)
Ru(1)-C(13)-O(13)	177 (3)	Ru(2)-C(21)-O(21)	175 (3)
Ru(2)-C(22)-O(22)	177 (3)	Ru(2)-C(23)-O(23)	177 (2)
Ru(3)-C(31)-O(31)	177 (3)	Ru(3)-C(32)-O(32)	176 (2)
Ru(3)-C(33)-O(33)	176 (2)		
Ru-P-C			
Ru(1)-P(1)-C(41)	130.2 (10)	Ru(2)-P(1)-C(41)	134.0 (11)
Ru(3)-P(1)-C(41)	135.8 (9)		
P-t-Bu			
P(1)-C(41)-C(42)	111 (2)	P(1)-C(41)-C(43)	112 (2)
P(1)-C(41)-C(44)	110 (2)	C(42)-C(41)-C(43)	104 (3)
C(42)-C(41)-C(44)	109 (2)	C(43)-C(41)-C(44)	110 (3)

^a Estimated standard deviations in the least significant digit(s) are given in parentheses.

Table II. Crystallographic Data and Computations for [PPN][$(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-P}(t\text{-Bu)))$] (**3b**)

formula	$\text{C}_{49}\text{H}_{40}\text{NO}_9\text{P}_3\text{Ru}_3$	$F(000)$	589.93
fw	1182.99	d_{calc} , g cm ⁻³	1.55
temp, °C	25	$\mu(\text{Mo K}\alpha)$, cm ⁻¹	10.1
cryst system	triclinic	no. of reflns	4697 unique
space group	$P1$		2650 ($I \geq 2.5\sigma(I)$)
a , Å	10.508 (8)	no. of lst sqr	304
b , Å	11.057 (6)	params	
c , Å	11.699 (5)	data/param	8.7
α , deg	84.92 (4)	R^a	0.075
β , deg	88.66 (5)	R_w^b	0.097
γ , deg	69.11 (5)	error in observn	2.11
V , Å ³	1265 (1)	of unit wt	
Z	1		

$$^a R = (\sum |F_o| - |F_c|) / \sum |F_o| \quad ^b R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w(|F_o|)^2]^{1/2}$$

Table III. Selected Atomic Coordinates^a and Isotropic Thermal Parameters^b for [PPN][$(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-P}(t\text{-Bu)))$] (**3b**)

atom	x	y	z	B_{iso} , Å ²
Ru(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)	4.1 (1)
Ru(2)	0.0065 (2)	0.2626 (2)	0.0139 (2)	4.4 (1)
Ru(3)	-0.0416 (2)	0.1165 (2)	0.2119 (2)	4.4 (1)
P(1)	0.1456 (8)	0.0655 (7)	0.1003 (5)	4.7 (4)
O(11)	-0.291 (3)	0.032 (3)	-0.061 (2)	10.0 (7)
O(12)	0.080 (2)	-0.267 (2)	0.122 (2)	6.9 (5)
O(13)	0.158 (2)	-0.093 (2)	-0.215 (2)	7.3 (5)
O(21)	-0.286 (3)	0.450 (2)	0.001 (2)	8.7 (6)
O(22)	0.137 (2)	0.321 (2)	-0.207 (2)	8.4 (6)
O(23)	0.111 (2)	0.425 (2)	0.147 (2)	8.2 (6)
O(31)	-0.354 (3)	0.215 (3)	0.197 (2)	10.0 (7)
O(32)	0.001 (2)	0.285 (2)	0.389 (2)	6.4 (4)
O(33)	0.016 (2)	-0.123 (2)	0.382 (2)	7.4 (5)
C(11)	-0.179 (3)	0.018 (3)	-0.038 (2)	6.1 (6)
C(12)	0.042 (3)	-0.167 (2)	0.074 (2)	4.4 (5)
C(13)	0.101 (3)	-0.057 (3)	-0.135 (2)	5.3 (6)
C(21)	-0.175 (3)	0.375 (3)	0.003 (2)	5.5 (6)
C(22)	0.091 (3)	0.295 (3)	-0.125 (2)	5.5 (6)
C(23)	0.071 (3)	0.363 (2)	0.100 (2)	4.4 (5)
C(31)	-0.235 (3)	0.178 (3)	0.200 (3)	6.8 (7)
C(32)	-0.011 (3)	0.220 (3)	0.320 (2)	4.8 (5)
C(33)	-0.007 (3)	-0.036 (3)	0.316 (2)	4.7 (5)
C(41)	0.325 (3)	-0.009 (3)	0.124 (2)	5.7 (6)
C(42)	0.379 (4)	0.078 (4)	0.196 (3)	8.0 (9)
C(43)	0.408 (4)	-0.019 (4)	0.006 (3)	8.8 (9)
C(44)	0.358 (3)	-0.142 (3)	0.187 (3)	7.1 (7)

^a Estimated standard deviations in the least significant digit(s) are given in parentheses. ^b B_{iso} is the mean of the principal axes of the thermal ellipsoid.

formation of [PPN][$\text{Ru}_3(\text{CO})_{11}\text{Cl}$] was complete. Phenylphosphine (45 μL , 0.41 mmol) was added by microliter syringe. The color of the solution immediately began to lighten from red to an orange-red, and a gas was evolved. The solution was stirred for 1 h, the volume was reduced to ca. 10 mL, and 25 mL of *i*-Pr₂O was layered onto the solution. The excess [PPN]Cl that precipitated was separated by filtration, and the solvent was removed under vacuum. The resulting oily solid was triturated with hexanes (15 mL) to yield a yellow-orange powder. The supernatant was removed by cannula, and the solid was dried under vacuum for 2 h. Isolated yield: 232 mg (61%). IR (ν_{CO} , cm⁻¹; Et₂O): 2050 (w), 2017 (s), 1989 (s), 1972 (ms), 1952 (m), 1915 (w). ¹H NMR (δ , ppm; CD₂Cl₂): -19.1 (d, ² $J_{\text{P-H}}$ = 17.2 Hz, hydride), 7.32 (m, Ph). ³¹P{¹H} NMR (δ , ppm; CD₂Cl₂): 299 (s, *P*-Ph). Anal. Calcd (found) for C₅₁H₃₆NO₉P₃Ru₃: C, 50.92 (50.58); H, 3.02 (2.57); N, 1.16 (1.06).

Preparation of [PPN][$(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-P}(t\text{-Bu)))$] (3b**).** [PPN][$\text{Ru}_3(\text{CO})_{11}\text{Cl}$] (0.32 mmol) was prepared as described above. *tert*-Butylphosphine (61 μL , 0.50 mmol) was added by microliter syringe to the stirred solution of [$\text{Ru}_3(\text{CO})_{11}\text{Cl}$]⁻. The solution slowly lightened in color from a deep red to an orange-red. After the solution was stirred for 1.5 h, the volume was reduced to ca. 10 mL, and 25 mL of diisopropyl ether was layered on the solution. The excess [PPN]Cl that precipitated was separated by filtration, and the solvent was removed under vacuum. The resulting orange oily solid was triturated with hexanes (15 mL) to yield a yellow-orange solid. Yield: 200 mg (51%). IR (ν_{CO} , cm⁻¹; Et₂O): 2046 (w), 2014 (s), 1984 (s), 1968 (ms), 1948 (m), 1914 (w). ¹H NMR (δ , ppm; CD₂Cl₂): -19.3 (d, ² $J_{\text{P-H}}$ = 16 Hz, hydride), 1.56 (d, ³ J_{PH} =

17 Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (δ , ppm; CD_2Cl_2): 391 (s, *P-t*-Bu). Anal. Calcd (found) for $C_{49}H_{40}NO_9P_3Ru_3$: C, 49.75 (48.63); H, 3.41 (3.28); N, 1.18 (1.06).

Reaction of 1 with [PPN]Cl. A solution of [PPN]Cl (21 mg, 0.04 mmol) in 0.5 mL of CH_2Cl_2 was added to a stirred solution of 1 (25 mg, 0.04 mmol) in 2 mL of THF. The color immediately lightened, and complete formation of 3a was confirmed by infrared spectroscopy.

Crystal Structure of [PPN][$(\mu-H)Ru_3(CO)_9(\mu_3-P(t-Bu))$] (3b). Crystals suitable for analysis by X-ray diffraction were obtained by slow diffusion of pentane into an ether solution of 3b. Crystallographic data and computational results are summarized in Table II. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the cluster anion in 3b may be found in Table III. Data were collected on a Rigaku AFC6S diffractometer utilizing graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were determined by least-squares refinement of the setting angles of 22 high-angle reflections ($2\theta = 20-25^\circ$). The data collection ($2\theta = 2.5-50^\circ$; $-h, \pm k, \pm l$) was monitored by measuring the intensities of two control reflections that showed no significant intensity variation over the course of the data collection. An empirical absorption correction was applied to the raw data utilizing the intensity profiles from ψ scan data (range of transmission factors 0.53-0.81). All computations were performed using the NRCVAX computing package.¹² The structure was solved by direct methods in the space group *P1*. Attempts to find an alternate higher symmetry cell were not successful. Least-squares refinement on *F* minimized the function $\sum w(|F_o| - |F_c|)^2$. A multiplicative factor for the imaginary component of the structure factor was refined and converged at a value of 1 indicating that the original enantiomorph choice was correct.

The metal cluster anion was positioned in two different orientations in the crystal lattice. The minor orientation is inverted relative to the

major one so the Ru_3 plane lies just below the phosphorus atom of the major orientation. This disorder was modeled by refining all atoms of the major orientation at 93% occupancy and the three ruthenium atoms and the phosphorus atom of the minor orientation at 7% occupancy. The occupancy values were refined in a least-squares cycle in which the thermal parameters of the atoms were fixed. No other atoms belonging to the minor orientation could be found in the difference maps. Several carbonyl groups on the major cluster did not refine well with anisotropic thermal parameters, presumably due to the disorder problem. Consequently only the three ruthenium atoms and the phosphorus atom of the major orientation and the two phosphorus atoms of the PPN cation were refined anisotropically. Hydrogen atoms on the PPN cation and the *t*-Bu group were included in calculated positions.

Acknowledgment. Partial financial support provided by a Presidential Young Investigator Award from the National Science Foundation (CHEM-8958027), and the Department of Chemistry at The University of North Carolina at Chapel Hill is gratefully acknowledged. Partial funds for equipping the single-crystal X-ray diffraction facility at UNC-CH were provided by the National Science Foundation (Grant CHE-8919288). Deborah L. Sunico is acknowledged for assisting in the acquisition of variable-temperature ^{31}P NMR data, and the reviewers are thanked for helpful comments.

Supplementary Material Available: Complete crystallographic data and results for 3b including the complete crystallographic experiment and computations (Table S-I) and fractional atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles not included in the text (Tables S-II-S-IV, respectively) (8 pages); tables of calculated and observed structure factors (Table S-V) (16 pages). Ordering information is given on any current masthead page.

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