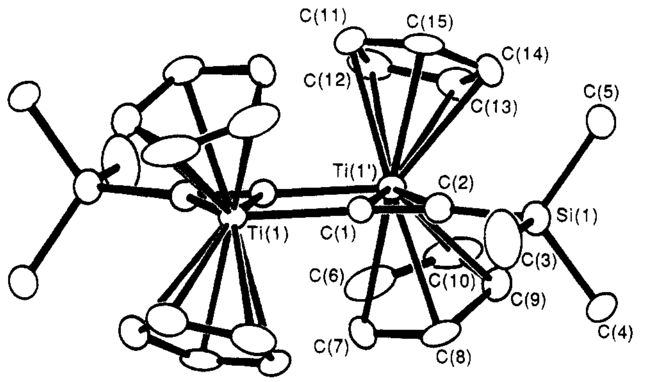

Figure 1. ORTEP representation of $[Cp_2TiC\equiv CSi(CH_3)_3]_2$ (**3**) with H atoms omitted. Ellipsoids are drawn with 20% probability.

to the $\nu_{C\equiv C}$ stretch. The mass spectrum confirms the proposed formulation.

The assignment of the ^{13}C NMR is consistent with those of other alkynyltitanium complexes[4] where the downfield signal is assigned to the carbon directly bonded to the metal. It should be noted that Wrackmeyer and co-workers reported the ^{13}C NMR spectrum for a compound that was believed to be **2**.[4] The ^{13}C NMR data reported by Wrackmeyer do not agree with the values reported here for **2**, but do agree well with the values for **3**.[11]

The dimer, **3**, is comprised of dark burgundy crystals that are soluble in organic solvents and can be handled in ambient atmosphere for limited periods of time (1–2 h). The infrared spectrum exhibits a medium-intensity absorption at 1789 cm^{-1}, which is assigned to the $\nu_{C\equiv C}$ stretch. The shift to lower wavenumber is consistent with the coordination of the acetylenic group with the adjacent metal atom.[12] The mass spectrum confirms the dimeric structure; both the parent ion (*m/e* 550) and the expected mass for the monomer (*m/e* 275) are observed. The complex is expected to contain two formal titanium(III) centers and, therefore, exhibit paramagnetism; however, it is diamagnetic at room temperature. The observed diamagnetism may be due to an antiferromagnetic coupling since similar behavior is observed in other Ti(III) systems at reduced temperatures.[13] For the compounds $[Cp_2Ti(X)]_2$ (X = Cl, Br), it is found that as the Ti–Ti distance decreases the antiferromagnetic coupling increases. The ^{13}C NMR spectrum exhibits a strongly deshielded signal at 236.79 (s) ppm, which is assigned to C_α. The C_β is assigned to a singlet at 142.85 (s) ppm. The trimethylsilyl carbons appear as a singlet at 2.15 ppm.

The X-ray crystal structure of **3** supports the spectroscopic data. As shown in Figure 1, **3** is a dimeric molecule that exhibits a center of inversion. The titanium atom, in this case, is bonded directly to the C(1) atom and to the adjacent acetylenic group. One interesting feature of **3** is the fact that the acetylenic groups do not couple as in the structure reported by Stucky.[5] The structure indicates that the acetylenes are engaged in both σ and π bonding with the titanium metal. Selected bond distances and angles are shown in Table III.

The Ti(1)–Ti(1)′ distance is 3.550 (3) Å. This is shorter than the reported distance in $[Cp_2Ti(Cl)]_2$ (3.926 (3) Å) or $[Cp_2Ti(Br)]_2$ (4.125 (4) Å).[13] The C(1)–C(1)′ distance is 2.706 (16) Å. The C–C single bond distance in **1** is much shorter, only 1.485 (4) Å.[5] The Ti(1)–C(1) bond is 2.056 (11) Å, which is shorter than the Ti–CH$_3$ bond for $(\eta^5\text{-indenyl})_2Ti(CH_3)_2$, which is 2.21 (2) Å.[14] The Ti–C bond distance of **3** more closely matches those for the sp^2-hybridized carbons of **1** where the distances are 2.107 (7) and 2.230 (7) Å.[5] The Ti–C(1)′ and Ti–C(2)′ bond distances are 2.395 (7) and 2.312 (8) Å, respectively. These distances are longer than the bond distances reported for $Cp_2Ti(CO)(\eta^2\text{-}(C_6H_5)C\equiv C(C_6H_5))$ (**4**) where the Ti–C distances are 2.107 (7) and 2.230 (7) Å.[15] The centroid to metal distances (Cp(1)–Ti and Cp(2)–Ti) are 2.099 (1) and 2.096 (2) Å. These are typical of η^5-Cp bond distances. The Cp–Ti distances for **4** are 2.083 and 2.084 Å.[12] The C(1)–C(2) bond distance is 1.253 (15) Å, which is similar to that reported for **4** where the C≡C bond distance is 1.285 (10) Å.

Table III. Selected Bond Distances and Angles for **3**

A. Bond Distances (Å)			
Ti(1)–C(1)	2.056 (11)	Ti(1)–C(6)	2.410 (8)
Ti(1)–C(7)	2.440 (10)	Ti(1)–C(8)	2.442 (11)
Ti(1)–C(9)	2.415 (11)	Ti(1)–C(10)	2.394 (9)
Ti(1)–C(11)	2.417 (8)	Ti(1)–C(12)	2.408 (8)
Ti(1)–C(13)	2.413 (8)	Ti(1)–C(14)	2.424 (8)
Ti(1)–C(15)	2.427 (9)	Ti(1)–Cp(1)	2.099 (1)
Ti(1)–Cp(2)	2.096 (2)	Ti(1)–C(1)′	2.395 (7)
Ti(1)–C(2)′	2.312 (8)	Si(1)–C(2)	1.844 (11)
Si(1)–C(3)	1.881 (13)	Si(1)–C(4)	1.852 (12)
Si(1)–C(5)	1.845 (10)	C(1)–C(2)	1.253 (15)
C(1)–Ti(1)′	2.395 (7)	C(2)–Ti(1)′	2.312 (8)
Ti(1)–Ti(1)′	3.550 (3)	C(1)–C(1)′	2.706 (16)

B. Bond Angles (deg)			
C(1)–Ti(1)–Cp(1)	104.5 (2)	C(1)–Ti(1)–Cp(2)	105.1 (2)
C(1)–Ti(1)–C(1)′	74.5 (3)	C(1)–Ti(1)–C(2)′	105.3 (3)
Cp(1)–Ti(1)–Cp(2)	129.0 (1)	Cp(1)–Ti(1)–C(1)′	114.3 (2)
Cp(1)–Ti(1)–C(2)′	105.4 (2)	Cp(2)–Ti(1)–C(1)′	113.1 (2)
Cp(2)–Ti(1)–C(2)′	105.6 (2)	C(1)′–Ti(1)–C(2)′	30.8 (3)
C(2)–Si(1)–C(3)	106.0 (5)	C(2)–Si(1)–C(4)	112.3 (5)
C(2)–Si(1)–C(5)	112.9 (4)	C(3)–Si(1)–C(4)	108.6 (5)
C(3)–Si(1)–C(5)	109.7 (5)	C(4)–Si(1)–C(5)	107.3 (5)
Ti(1)–C(1)–C(2)	176.1 (7)	Ti(1)–C(1)–Ti(1)′	105.5 (3)
C(2)–C(1)–Ti(1)′	70.9 (6)	Si(1)–C(2)–C(1)	140.3 (8)
Si(1)–C(2)–Ti(1)′	141.4 (5)	C(1)–C(2)–Ti(1)′	78.2 (6)

The Ti(1)–C(1)–C(2) bond angle is essentially linear at 176.1 (7)°. The C(1)–C(2)–Si(1) bond angle is 140.3 (8)°. This distortion is believed to be the result of the side-on bonding of the adjacent titanium atom to the acetylenic group. Such distortion is consistent with the previously reported structure for **4** in which the $C\equiv C(C_6H_5)$ bond angles are 138.8 (7) and 145.8 (7)°. The Cp(1)–Ti–Cp(2) angle is 129.0 (1)° which is smaller than that in **3**, which has a bond angle of 133.5 (5)°.

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Supplementary Material Available: Tables IS and IIS, listing positional and thermal parameters, and Table IIIS, listing distances, angles, and torsion angles (16 pages); Table IVS, listing calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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[11] Wrackmeyer in ref 4 reports the ^{13}C NMR data (C_6D_6, $Si(CH_3)_4$ as follows: C_α, 236.1 ppm; C_β, 143.1 ppm; Cp, 104.1 ppm; $Si(CH_3)_3$, 1.8 ppm.

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Encapsulated Phosphides: $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$, a Molecule with a Six-Coordinate Phosphorus Atom in a Condensed Cluster

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Although an extensive chemistry has been developed for μ_2-diorganophosphido (R_2P)[1] and μ_n-phosphinidene (n = 2–4) (RP)[2]

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Table I. Crystallographic Data for $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$

chem formula	$C_{39}H_{15}O_{21}P_3Ru_8$	Z	4
MW	1721.02	T, K	295 ± 1
cryst syst	monoclinic	λ, Å	0.71069
space group	$P2_1/c$	d_{calc}, g cm^{-3}	2.271
a, Å	15.659 (2)	μ(Mo Kα), cm^{-1}	24.46
b, Å	16.330 (2)	transmissn coeff	0.62–0.76
c, Å	20.699 (3)	R^a	0.028
β, deg	108.05 (1)	R^b	0.033
V, Å^3	5032 (1)		

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$; $w^{-1} = 1.28 - 0.0062|F_o| + 0.00004|F_o|^2$.

Table II. Atomic Coordinates ($\times 10^4$) for $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ (**1**)

atom	x	y	z
Ru(1)	3056.4 (3)	2678.1 (3)	2415.8 (2)
Ru(2)	2510.8 (3)	1299.2 (3)	3049.9 (2)
Ru(3)	2416.0 (3)	1241.7 (3)	1657.0 (2)
Ru(4)	3726.9 (3)	271.3 (3)	2597.8 (3)
Ru(5)	4264.7 (3)	1649.2 (3)	1980.7 (2)
Ru(6)	1819.5 (3)	2890.1 (3)	3153.1 (2)
Ru(7)	96.5 (3)	2668.3 (3)	2040.0 (2)
Ru(8)	527.1 (3)	1681.3 (3)	1030.1 (2)
P(1)	1622.0 (8)	2085.6 (8)	2153.9 (6)
P(2)	3973.6 (9)	1614.2 (9)	3034.1 (7)
P(3)	−839.8 (9)	2234.1 (9)	989.0 (7)
O(1)	4034 (3)	4164 (3)	3180 (3)
O(2)	2561 (4)	3837 (3)	1212 (3)
O(3)	2821 (4)	1330 (4)	4575 (2)
O(4)	1137 (3)	6 (3)	3078 (3)
O(5)	2479 (3)	1738 (4)	265 (2)
O(6)	1729 (3)	−458 (3)	1158 (2)
O(7)	3765 (4)	−921 (4)	1480 (3)
O(8)	2907 (4)	−1014 (4)	3284 (3)
O(9)	5631 (4)	−157 (4)	3417 (4)
O(10)	4525 (4)	526 (4)	890 (3)
O(11)	4308 (6)	3110 (5)	1085 (5)
O(12)	6249 (4)	1811 (7)	2682 (4)
O(13)	3506 (3)	3200 (3)	4350 (2)
O(14)	1537 (4)	4717 (3)	2924 (3)
O(15)	579 (3)	2675 (4)	4016 (2)
O(16)	−379 (3)	1211 (3)	2794 (2)
O(17)	−1064 (3)	3524 (3)	2761 (3)
O(18)	509 (4)	4286 (3)	1424 (3)
O(19)	28 (3)	88 (3)	1610 (2)
O(20)	384 (4)	742 (3)	−256 (2)
O(21)	930 (4)	3210 (3)	298 (2)
C(1)	3678 (4)	3585 (4)	2930 (3)
C(2)	2748 (4)	3400 (4)	1659 (3)
C(3)	2734 (4)	1352 (4)	4010 (3)
C(4)	1649 (4)	499 (4)	3050 (3)
C(5)	2495 (4)	1545 (4)	797 (3)
C(6)	2011 (4)	169 (3)	1363 (3)
C(7)	3749 (5)	−469 (4)	1887 (4)
C(8)	3175 (5)	−492 (5)	3024 (4)
C(9)	4903 (5)	−14 (4)	3118 (4)
C(10)	4418 (4)	923 (5)	1309 (4)
C(11)	4249 (6)	2579 (5)	1429 (5)
C(12)	5500 (5)	1755 (7)	2413 (4)
C(13)	2892 (4)	3059 (4)	3906 (3)
C(14)	1619 (4)	4033 (4)	3015 (3)
C(15)	1043 (4)	2748 (4)	3690 (3)
C(16)	−183 (4)	1713 (3)	2505 (3)
C(17)	−624 (4)	3246 (4)	2478 (3)
C(18)	369 (4)	3690 (4)	1645 (3)
C(19)	221 (3)	673 (3)	1412 (3)
C(20)	435 (4)	1094 (3)	221 (3)
C(21)	801 (4)	2655 (4)	577 (3)
C(22)	4831 (3)	1771 (4)	3846 (3)
C(23)	5395 (4)	2449 (4)	3955 (3)
C(24)	6034 (5)	2563 (5)	4596 (4)
C(25)	6083 (5)	2014 (5)	5126 (4)
C(26)	5523 (5)	1335 (5)	5016 (4)
C(27)	4891 (5)	1212 (4)	4378 (3)
C(28)	−1768 (3)	1532 (3)	936 (3)
C(29)	−2327 (4)	1641 (4)	1336 (3)
C(30)	−3051 (5)	1117 (5)	1253 (4)
C(31)	−3240 (5)	501 (5)	774 (4)
C(32)	−2679 (4)	383 (4)	380 (4)
C(33)	−1943 (4)	893 (4)	461 (3)
C(34)	−1348 (4)	2978 (4)	318 (3)
C(35)	−1650 (5)	3730 (5)	470 (4)
C(36)	−2057 (7)	4283 (6)	−73 (6)
C(37)	−2143 (7)	4061 (6)	−724 (5)
C(38)	−1845 (7)	3311 (7)	−880 (5)
C(39)	−1447 (5)	2755 (5)	−354 (4)

complexes, metal clusters containing fully encapsulated phosphorus atoms are still rare.[3] The earliest examples of phosphorus in a high coordination metal environment within a discrete carbonyl cluster are the rhodium anions $[Rh_9(CO)_{21}P]^{2-}$ and $[Rh_{10}(CO)_{22}P]^{3-}$ in which the main group atom is 9- or 10-coordinate in a capped or bicapped cubic antiprismatic arrangement of metal atoms.[4] Interestingly, the interstitial phosphides in these high nuclearity anions were derived by stripping away phenyl groups from triphenylphosphine under extreme conditions in the presence of rhodium carbonyl anions. The few remaining examples include a μ_8-P ligand in a square antiprismatic cavity $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^2,\eta^6\text{-}CH_2Ph)(\mu_2\text{-}CO)_2(CO)_{17}]$,[5] partially interstitial phosphides with 5-coordination ($[Ru_5(CO)_{16}(\mu_5\text{-}P)(\mu\text{-}PPh_2)]$,[5] $[Fe_5(CO)_{16}(\mu_5\text{-}P)(\mu_4\text{-}P)\ Mn(CO)_2Cp]$)[7] and 6-coordination $[Co_6(CO)_{14}(\mu\text{-}CO)_2(\mu_6\text{-}P)]^-$,[8] and most recently an osmium cluster $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ in which the phosphide occupies a trigonal-prismatic site.[9] There are also a few examples of single phosphorus atoms in trigonal[10] or tetrahedral[11] environments in organometallic molecules although in these cases it is questionable whether the term encapsulated is appropriate. In this paper we define a further coordination environment for a phosphide, that of a μ_6-ligand in a *condensed* Ru_8 polyhedral framework. The cluster $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$ (**1**) also serves as a model for the steps involved in the sequential removal of phenyl groups from triphenylphosphine, incorporating all three of the ligand groups formed in the process.

Experimental Section

General Data. $HRu_3(CO)_{10}(\mu_2\text{-}PPh_2)$ was prepared according to published procedures.[12] Toluene was dried by distillation over $LiAlH_4$ under N_2. Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer. $^{31}P\{^1H\}$ NMR spectra were run on a Bruker AC 200 spectrometer in 10-mm tubes and are referenced to 85% H_3PO_4 (external).

Preparation of $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$. Refluxing a solution of $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}PPh_2)$ (0.62 mmol) in toluene (40 mL) at 120 °C for 2 h gave a complex mixture from which five products were separated and purified by preparative TLC on silica gel with C_7H_{16}–C_6H_6 as eluant. In order of elution, these compounds were $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ (37%), $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$ (7%), $(\mu_3\text{-}H)Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$ (7%), $Ru_7(CO)_{18}(\mu_4\text{-}PPh)_2$ (2%),[13] and dark brown **1** (20%). IR (ν(CO), CCl_4): 2100 vw, 2086 w, 2069 m, 2052 vs, 2037 w, 2016 w, 2011 w, sh

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Table III. Selection of Bond Lengths (Å) and Angles (deg) for $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ (**1**)

(a) Bond Lengths

Ru(1)–Ru(2)	2.8668 (8)	Ru(1)–Ru(3)	2.8283 (6)	Ru(5)–C(12)	1.871 (8)	Ru(5)–C(13)	1.925 (6)
Ru(1)–Ru(5)	2.8758 (6)	Ru(1)–Ru(6)	2.8340 (6)	Ru(6)–C(14)	1.900 (6)	Ru(6)–C(15)	1.898 (6)
Ru(2)–Ru(3)	2.8423 (5)	Ru(2)–Ru(4)	2.9025 (7)	Ru(7)–C(16)	1.952 (6)	Ru(7)–C(17)	1.901 (6)
Ru(2)–Ru(6)	2.8478 (6)	Ru(3)–Ru(4)	2.8354 (7)	Ru(7)–C(18)	1.961 (6)	Ru(8)–C(19)	1.949 (5)
Ru(3)–Ru(5)	2.8409 (6)	Ru(3)–Ru(8)	2.9273 (6)	Ru(8)–C(20)	1.896 (5)	Ru(8)–C(21)	1.961 (6)
Ru(4)–Ru(5)	2.8410 (6)	Ru(6)–Ru(7)	2.9777 (6)	P(2)–C(22)	1.815 (6)	P(3)–C(28)	1.827 (6)
Ru(7)–Ru(8)	2.8802 (6)	Ru(1)–P(1)	2.350 (1)	P(3)–C(34)	1.831 (6)	C(1)–O(1)	1.137 (8)
Ru(1)–P(2)	2.362 (1)	Ru(2)–P(1)	2.330 (1)	C(2)–O(2)	1.132 (8)	C(3)–O(3)	1.136 (7)
Ru(2)–P(2)	2.358 (1)	Ru(3)–P(1)	2.301 (1)	C(4)–O(4)	1.149 (8)	C(5)–O(5)	1.138 (7)
Ru(4)–P(2)	2.358 (1)	Ru(5)–P(2)	2.363 (1)	C(6)–O(6)	1.143 (7)	C(7)–O(7)	1.127 (10)
Ru(6)–P(1)	2.388 (1)	Ru(7)–P(1)	2.514 (1)	C(8)–O(8)	1.152 (10)	C(9)–O(9)	1.140 (10)
Ru(7)–P(3)	2.326 (1)	Ru(8)–P(1)	2.513 (1)	C(10)–O(10)	1.136 (10)	C(11)–O(11)	1.143 (12)
Ru(8)–P(3)	2.300 (1)	Ru(1)–C(1)	1.905 (6)	C(12)–O(12)	1.135 (10)	C(13)–O(13)	1.129 (8)
Ru(1)–C(2)	1.900 (6)	Ru(2)–C(3)	1.910 (6)	C(14)–O(14)	1.133 (8)	C(15)–O(15)	1.141 (8)
Ru(2)–C(4)	1.879 (6)	Ru(3)–C(5)	1.888 (6)	C(16)–O(16)	1.113 (7)	C(17)–O(17)	1.129 (8)
Ru(3)–C(6)	1.898 (6)	Ru(4)–C(7)	1.913 (8)	C(18)–O(18)	1.127 (8)	C(19)–O(19)	1.118 (7)
Ru(4)–C(8)	1.885 (8)	Ru(4)–C(9)	1.881 (8)	C(20)–O(20)	1.124 (7)	C(21)–O(21)	1.125 (7)
Ru(5)–C(10)	1.898 (7)	Ru(5)–C(11)	1.896 (9)				

(b) Bond Angles

Ru(2)–Ru(1)–Ru(3)	59.88 (1)	Ru(2)–Ru(1)–Ru(5)	90.16 (1)	Ru(2)–Ru(6)–C(15)	105.1 (2)	Ru(7)–Ru(6)–C(13)	176.5 (2)
Ru(2)–Ru(1)–Ru(6)	59.94 (1)	Ru(3)–Ru(1)–Ru(5)	59.73 (1)	Ru(7)–Ru(6)–C(14)	86.3 (2)	Ru(7)–Ru(6)–C(15)	81.2 (2)
Ru(3)–Ru(1)–Ru(6)	102.50 (1)	Ru(5)–Ru(1)–Ru(6)	149.97 (1)	Ru(6)–Ru(7)–C(16)	90.2 (2)	Ru(6)–Ru(7)–C(17)	95.7 (2)
Ru(1)–Ru(2)–Ru(3)	59.39 (1)	Ru(1)–Ru(2)–Ru(4)	89.32 (1)	Ru(6)–Ru(7)–C(18)	87.6 (2)	Ru(8)–Ru(7)–C(16)	92.8 (2)
Ru(1)–Ru(2)–Ru(6)	59.46 (1)	Ru(3)–Ru(2)–Ru(5)	59.73 (1)	Ru(8)–Ru(7)–C(17)	158.5 (2)	Ru(8)–Ru(7)–C(18)	92.5 (2)
Ru(3)–Ru(2)–Ru(6)	102.50 (1)	Ru(5)–Ru(2)–Ru(6)	149.97 (1)	Ru(3)–Ru(8)–C(19)	87.4 (2)	Ru(3)–Ru(8)–C(20)	93.3 (2)
Ru(1)–Ru(3)–Ru(2)	60.73 (1)	Ru(1)–Ru(3)–Ru(4)	91.46 (1)	Ru(3)–Ru(8)–C(21)	94.0 (2)	Ru(7)–Ru(8)–C(19)	92.1 (2)
Ru(1)–Ru(3)–Ru(5)	60.96 (1)	Ru(1)–Ru(3)–Ru(8)	100.28 (1)	Ru(7)–Ru(8)–C(20)	162.4 (2)	Ru(7)–Ru(8)–C(21)	91.6 (2)
Ru(2)–Ru(3)–Ru(4)	61.49 (1)	Ru(2)–Ru(3)–Ru(5)	91.37 (1)	P(1)–Ru(1)–P(2)	101.51 (4)	P(1)–Ru(2)–P(2)	102.24 (4)
Ru(2)–Ru(3)–Ru(8)	99.76 (1)	Ru(4)–Ru(3)–Ru(5)	60.07 (1)	P(1)–Ru(7)–P(3)	106.12 (4)	P(1)–Ru(8)–P(3)	106.94 (4)
Ru(4)–Ru(3)–Ru(8)	149.15 (1)	Ru(5)–Ru(3)–Ru(8)	149.65 (1)	P(1)–Ru(1)–C(1)	137.3 (2)	P(1)–Ru(1)–C(2)	94.8 (2)
Ru(2)–Ru(4)–Ru(3)	59.37 (1)	Ru(2)–Ru(4)–Ru(5)	90.14 (1)	P(2)–Ru(1)–C(1)	98.6 (2)	P(2)–Ru(1)–C(2)	149.3 (2)
Ru(3)–Ru(4)–Ru(5)	60.06 (1)	Ru(1)–Ru(5)–Ru(3)	59.30 (1)	P(1)–Ru(2)–C(3)	132.5 (2)	P(1)–Ru(2)–C(4)	97.6 (2)
Ru(1)–Ru(5)–Ru(4)	90.37 (1)	Ru(3)–Ru(5)–Ru(4)	59.87 (1)	P(2)–Ru(2)–C(3)	98.0 (2)	P(2)–Ru(2)–C(4)	148.5 (2)
Ru(1)–Ru(6)–Ru(2)	60.60 (1)	Ru(1)–Ru(6)–Ru(7)	100.08 (1)	P(1)–Ru(3)–C(5)	117.8 (2)	P(1)–Ru(3)–C(6)	121.5 (2)
Ru(2)–Ru(6)–Ru(7)	96.05 (1)	Ru(6)–Ru(7)–Ru(8)	105.66 (1)	P(2)–Ru(4)–C(7)	147.4 (2)	P(2)–Ru(4)–C(8)	118.7 (2)
Ru(3)–Ru(8)–Ru(7)	104.31 (1)	Ru(2)–Ru(1)–P(1)	51.90 (3)	P(2)–Ru(4)–C(9)	89.8 (2)	P(2)–Ru(5)–C(10)	139.9 (2)
Ru(2)–Ru(1)–P(2)	52.53 (3)	Ru(3)–Ru(1)–P(1)	51.77 (3)	P(2)–Ru(5)–C(11)	127.2 (3)	P(2)–Ru(5)–C(12)	91.6 (3)
Ru(3)–Ru(1)–P(2)	75.07 (3)	Ru(5)–Ru(1)–P(1)	111.21 (3)	P(1)–Ru(6)–C(13)	128.8 (2)	P(1)–Ru(6)–C(14)	116.0 (2)
Ru(5)–Ru(1)–P(2)	52.51 (3)	Ru(6)–Ru(1)–P(1)	53.89 (3)	P(1)–Ru(6)–C(15)	120.4 (2)	P(1)–Ru(7)–C(16)	90.2 (2)
Ru(6)–Ru(1)–P(2)	101.56 (3)	Ru(1)–Ru(2)–P(1)	52.54 (3)	P(1)–Ru(7)–C(17)	146.1 (2)	P(1)–Ru(7)–C(18)	92.2 (2)
Ru(1)–Ru(2)–P(2)	52.67 (3)	Ru(3)–Ru(2)–P(1)	51.69 (3)	P(3)–Ru(7)–C(16)	92.6 (2)	P(3)–Ru(7)–C(17)	107.6 (2)
Ru(3)–Ru(2)–P(2)	74.85 (3)	Ru(4)–Ru(2)–P(1)	110.60 (3)	P(3)–Ru(7)–C(18)	91.4 (2)	P(1)–Ru(8)–C(19)	91.7 (2)
Ru(4)–Ru(2)–P(2)	52.00 (3)	Ru(6)–Ru(2)–P(1)	53.81 (3)	P(1)–Ru(8)–C(20)	142.5 (2)	P(1)–Ru(8)–C(21)	92.4 (2)
Ru(6)–Ru(2)–P(2)	101.27 (3)	Ru(1)–Ru(3)–P(1)	53.33 (3)	P(3)–Ru(8)–C(19)	90.2 (2)	P(3)–Ru(8)–C(20)	110.5 (2)
Ru(2)–Ru(3)–P(1)	52.59 (3)	Ru(4)–Ru(3)–P(1)	113.84 (3)	P(3)–Ru(8)–C(21)	90.2 (2)	C(1)–Ru(1)–C(2)	86.2 (3)
Ru(5)–Ru(3)–P(1)	113.99 (3)	Ru(8)–Ru(3)–P(1)	55.91 (3)	C(3)–Ru(2)–C(4)	86.0 (3)	C(5)–Ru(3)–C(6)	93.0 (2)
Ru(2)–Ru(4)–P(2)	52.02 (3)	Ru(3)–Ru(4)–P(2)	75.00 (3)	C(7)–Ru(4)–C(8)	93.6 (3)	C(7)–Ru(4)–C(9)	92.1 (3)
Ru(5)–Ru(4)–P(2)	53.08 (3)	Ru(1)–Ru(5)–P(2)	52.50 (3)	C(8)–Ru(4)–C(9)	94.4 (3)	C(10)–Ru(5)–C(11)	92.3 (3)
Ru(3)–Ru(5)–P(2)	74.82 (3)	Ru(4)–Ru(5)–P(2)	52.91 (3)	C(10)–Ru(5)–C(12)	93.6 (4)	C(11)–Ru(5)–C(12)	91.9 (4)
Ru(1)–Ru(6)–P(1)	52.64 (3)	Ru(2)–Ru(6)–P(1)	51.93 (3)	C(13)–Ru(6)–C(14)	92.5 (3)	C(13)–Ru(6)–C(15)	95.7 (3)
Ru(7)–Ru(6)–P(1)	54.54 (3)	Ru(6)–Ru(7)–P(1)	50.70 (3)	C(14)–Ru(6)–C(15)	95.9 (3)	C(16)–Ru(7)–C(17)	84.5 (2)
Ru(6)–Ru(7)–P(3)	156.68 (3)	Ru(8)–Ru(7)–P(1)	55.03 (3)	C(16)–Ru(7)–C(18)	174.6 (2)	C(17)–Ru(7)–C(18)	90.8 (2)
Ru(8)–Ru(7)–P(3)	51.09 (3)	Ru(3)–Ru(8)–P(1)	49.33 (3)	C(19)–Ru(8)–C(20)	88.3 (2)	C(19)–Ru(8)–C(21)	175.6 (2)
Ru(3)–Ru(8)–P(3)	156.00 (3)	Ru(7)–Ru(8)–P(1)	55.05 (3)	C(20)–Ru(8)–C(21)	87.5 (2)	Ru(1)–P(1)–Ru(2)	75.56 (3)
Ru(7)–Ru(8)–P(3)	51.89 (3)	Ru(2)–Ru(1)–C(1)	121.9 (2)	Ru(1)–P(1)–Ru(3)	74.90 (3)	Ru(1)–P(1)–Ru(6)	73.47 (3)
Ru(2)–Ru(1)–C(2)	146.0 (2)	Ru(3)–Ru(1)–C(1)	170.6 (2)	Ru(1)–P(1)–Ru(7)	132.72 (3)	Ru(1)–P(1)–Ru(8)	130.62 (3)
Ru(3)–Ru(1)–C(2)	95.8 (2)	Ru(5)–Ru(1)–C(1)	110.9 (2)	Ru(2)–P(1)–Ru(3)	75.73 (3)	Ru(2)–P(1)–Ru(6)	74.25 (3)
Ru(5)–Ru(1)–C(2)	97.4 (2)	Ru(6)–Ru(1)–C(1)	85.4 (2)	Ru(2)–P(1)–Ru(7)	126.82 (3)	Ru(2)–P(1)–Ru(8)	131.31 (3)
Ru(6)–Ru(1)–C(2)	109.1 (2)	Ru(1)–Ru(2)–C(3)	117.2 (2)	Ru(3)–P(1)–Ru(6)	140.68 (3)	Ru(3)–P(1)–Ru(7)	144.51 (3)
Ru(1)–Ru(2)–C(4)	149.6 (2)	Ru(3)–Ru(2)–C(3)	172.8 (2)	Ru(3)–P(1)–Ru(8)	74.76 (3)	Ru(6)–P(1)–Ru(7)	74.77 (3)
Ru(3)–Ru(2)–C(4)	99.5 (2)	Ru(4)–Ru(2)–C(3)	115.8 (2)	Ru(6)–P(1)–Ru(8)	144.53 (3)	Ru(7)–P(1)–Ru(8)	69.93 (3)
Ru(4)–Ru(2)–C(4)	98.1 (2)	Ru(6)–Ru(2)–C(3)	80.4 (2)	Ru(1)–P(2)–Ru(2)	74.80 (3)	Ru(1)–P(2)–Ru(4)	118.46 (3)
Ru(6)–Ru(2)–C(4)	110.2 (2)	Ru(1)–Ru(3)–C(5)	101.0 (2)	Ru(1)–P(2)–Ru(5)	74.99 (3)	Ru(2)–P(2)–Ru(4)	75.98 (3)
Ru(1)–Ru(3)–C(6)	165.8 (2)	Ru(2)–Ru(3)–C(5)	161.7 (2)	Ru(2)–P(2)–Ru(5)	118.96 (3)	Ru(4)–P(2)–Ru(5)	74.01 (3)
Ru(2)–Ru(3)–C(6)	105.2 (2)	Ru(4)–Ru(3)–C(5)	123.3 (2)	Ru(7)–P(3)–Ru(8)	77.02 (3)	Ru(1)–P(2)–C(22)	123.3 (2)
Ru(4)–Ru(3)–C(6)	78.6 (2)	Ru(5)–Ru(3)–C(5)	78.5 (2)	Ru(2)–P(2)–C(22)	117.4 (2)	Ru(4)–P(2)–C(22)	118.2 (2)
Ru(5)–Ru(3)–C(6)	120.4 (2)	Ru(8)–Ru(3)–C(5)	82.6 (2)	Ru(5)–P(2)–C(22)	123.6 (2)	Ru(7)–P(2)–C(28)	120.4 (2)
Ru(5)–Ru(3)–C(6)	83.9 (2)	Ru(2)–Ru(4)–C(7)	141.6 (2)	Ru(7)–P(2)–C(34)	120.5 (2)	Ru(8)–P(2)–C(28)	118.0 (2)
Ru(2)–Ru(4)–C(8)	77.9 (2)	Ru(2)–Ru(4)–C(9)	125.6 (2)	Ru(8)–P(2)–C(34)	118.0 (2)	C(28)–P(3)–C(34)	102.7 (2)
Ru(3)–Ru(4)–C(7)	90.4 (2)	Ru(3)–Ru(4)–C(8)	110.6 (2)	Ru(1)–C(1)–O(1)	173.6 (3)	Ru(1)–C(2)–O(2)	179.3 (3)
Ru(3)–Ru(4)–C(9)	154.7 (2)	Ru(5)–Ru(4)–C(7)	94.4 (2)	Ru(2)–C(3)–O(3)	174.4 (3)	Ru(2)–C(4)–O(4)	177.2 (2)
Ru(5)–Ru(4)–C(8)	167.7 (2)	Ru(5)–Ru(4)–C(9)	94.6 (2)	Ru(3)–C(5)–O(5)	175.1 (3)	Ru(3)–C(6)–O(6)	176.1 (2)
Ru(1)–Ru(5)–C(10)	147.0 (2)	Ru(1)–Ru(5)–C(11)	80.4 (3)	Ru(4)–C(7)–O(7)	178.2 (3)	Ru(4)–C(8)–O(8)	172.9 (3)
Ru(1)–Ru(5)–C(12)	118.6 (3)	Ru(3)–Ru(5)–C(10)	91.8 (2)	Ru(4)–C(9)–O(9)	176.5 (3)	Ru(5)–C(10)–O(10)	176.0 (3)
Ru(3)–Ru(5)–C(11)	102.9 (3)	Ru(3)–Ru(5)–C(12)	164.1 (3)	Ru(5)–C(11)–O(11)	173.7 (5)	Ru(5)–C(12)–O(12)	179.0 (4)
Ru(4)–Ru(5)–C(10)	87.5 (2)	Ru(4)–Ru(5)–C(11)	162.8 (3)	Ru(6)–C(13)–O(13)	176.3 (2)	Ru(6)–C(14)–O(14)	176.6 (3)
Ru(4)–Ru(5)–C(12)	105.4 (3)	Ru(1)–Ru(6)–C(13)	83.3 (2)	Ru(6)–C(15)–O(15)	179.0 (3)	Ru(7)–C(16)–O(16)	174.4 (2)
Ru(1)–Ru(6)–C(14)	98.5 (2)	Ru(1)–Ru(6)–C(15)	165.7 (2)	Ru(7)–C(17)–O(17)	173.9 (3)	Ru(7)–C(18)–O(18)	178.3 (3)
Ru(2)–Ru(6)–C(13)	86.3 (2)	Ru(2)–Ru(6)–C(14)	159.1 (2)	Ru(8)–C(19)–O(19)	177.6 (2)	Ru(8)–C(20)–O(20)	180.0 (3)
				Ru(8)–C(21)–O(21)	177.5 (3)		

2002 m, 1956 w cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 554.4 dd (P), 541.8 d (^2J(P–P) = 10.6 Hz, PPh), 213.7 d (^2J(P–P) = 71.3 Hz, PPh_2).

X-ray Structure Analysis. A dark brown crystal of dimensions 0.15 × 0.15 × 0.16 mm grown from heptane was selected for X-ray mea-

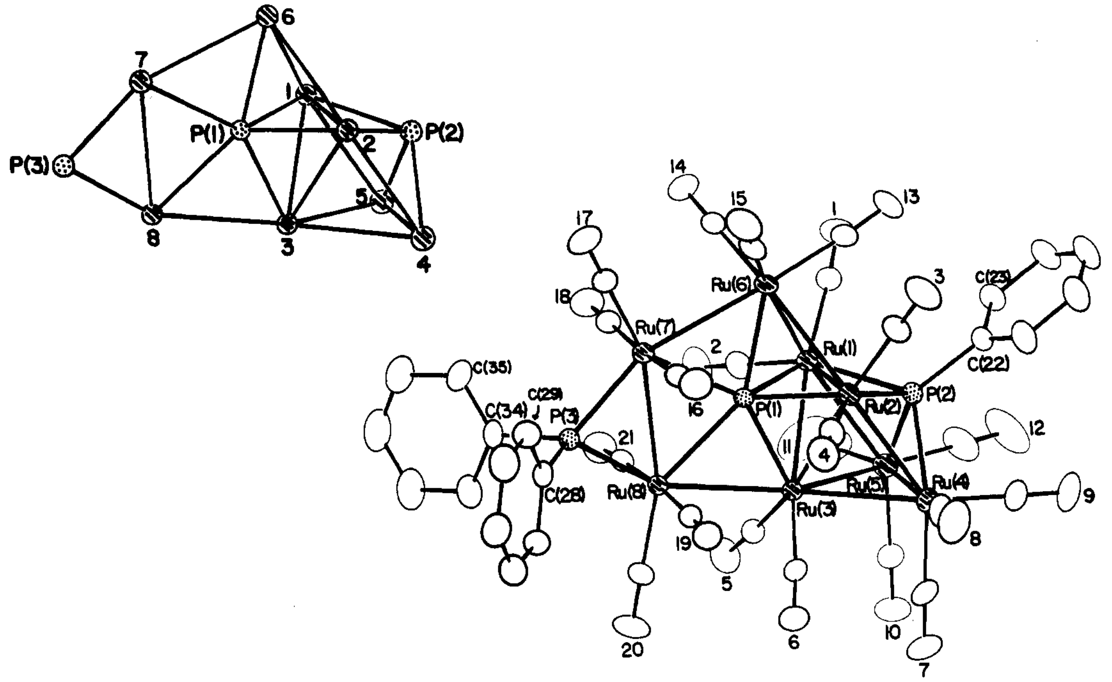

Figure 1. ORTEP plot of the molecular structure of $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ (**1**) showing the atomic numbering. The Ru_8P_3 skeleton of the molecule is also shown.

surements. With use of the Syntex autoindexation and cell refinement procedures, the crystal was identified as belonging to the monoclinic system, space group $P2_1/c$. Crystal data are summarized in Table I. Intensity data were collected at 295 ± 1 K via the $\omega/2\theta$, scan mode within the scan range ($3.2 < 2\theta < 50°$) by using a variable scan rate (2.02–29.3° min^{-1}) on a Syntex $P2_1$ automatic diffractometer. From a total of 9892 reflections measured, 7333 had $I \geq 3\sigma(I)$ and were used in the solution and refinement of the structure. Background counts were measured at the beginning and end of each scan for half of the scan time. Two standard reflections (437 and 497) monitored every 100 reflections indicated no significant loss in scattering power of the crystal. Intensities were corrected for Lorentz and polarization effects, but due to the small, equidimensional crystal and low value of μ (24.46 cm^{-1}), no absorption correction was deemed necessary.

Despite the large number of heavy atoms, a sharpened Patterson map readily revealed positions for all eight ruthenium atoms. Subsequent Fourier syntheses revealed positions for all remaining light atoms. Refinement with anisotropic thermal parameters for all non-hydrogen atoms gave R and R_w values of 0.028 and 0.033. A final difference Fourier map was featureless with maximum residual electron density at the level of 0.65 $Å^3$ in the vicinity of the ruthenium atoms. Scattering factors used were taken from the ref 14 with corrections for anomalous dispersion applied for the ruthenium atoms. All least-squares refinements employed the full matrix with the function minimized being $\sum w(|F_o| - |F_c|)^2$. Calculations were carried out on IBM 4341 systems using a package of programs described elsewhere.[15] Atomic coordinates are listed in Table II and a selection of bond lengths and angles is given in Table III. A complete listing of experimental parameters for data collection, reduction, and refinement (Table S1), anisotropic thermal parameters (Table S2), phenyl ring bond lengths and angles (Table S3), and structure factors (Table S4) have been deposited as supplementary material.

Results and Discussion

The new cluster **1** formed in the condensation of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-PPh}_2)$[12] has two very low-field $^{31}P\{^1H\}$ resonances at δ 554.4 and 541.8 ppm indicative of phosphide or phosphinidene ligands[16] and a higher field resonance (δ 213.7 ppm) typical of an $Ru\text{–}PPh_2\text{–}Ru$ group. Details of the molecular structure were provided by a single-crystal X-ray analysis (Figure 1). The molecule has a novel condensed polyhedral framework consisting of a square pyramid of ruthenium atoms (Ru(1)–Ru(5)) fused via the Ru(1)–Ru(2)–Ru(3) face to an open network of six ruthenium atoms (Ru(1), Ru(2), Ru(3), Ru(6), Ru(7), Ru(8)) linked by eight Ru–Ru bonds. The square face of the pyramid is capped by a μ_4-phosphinidene, and a μ-phosphido group bridges the Ru(7)-Ru(8) edge. As a new member of the interesting class of condensed clusters, the recently proposed counting principles of Mingos[17] should apply. A polyhedral electron count of 118, predicted for a square pyramid (74 e) (Ru(1), Ru(2), Ru(3), Ru(4), Ru(5)) fused to a triangle (Ru(1), Ru(2), Ru(6)) at an edge (+14 e) and to an open rectangle of metal atoms (Ru(3), Ru(6), Ru(7), Ru(8)) (three Ru–Ru bonds) at two vertices (+30 e) is in agreement with the number of cluster valence electrons if the phosphide is a 5-electron donor.

The naked phosphide atom P(1) is located within a cavity of six metal atoms, coordinated via four short (Ru(1)–P(1) = 2.350 (1), Ru(2)–P(1) = 2.330 (1), Ru(3)–P(1) = 2.301 (1), Ru(6)–P(1) = 2.388 (1) Å) and two long (Ru(7)–P(1) = 2.514 (1), Ru(8)–P(1) = 2.513 (1) Å) bonds. The coordination geometry at P(1) is neither octahedral nor trigonal prismatic. In fact the atoms Ru(3), Ru(6), Ru(7), Ru(8), and P(1) lie almost in a plane[18] with Ru(1) and Ru(2) perpendicular to this plane but with an angle Ru(1)–P(1)–Ru(2) of 75.56 (3)°. The most notable feature of the structure however is the striking resemblance of the P(1), Ru(1), Ru(2), Ru(3) and Ru(6) fragment to a butterfly carbide.[19] Indeed the environment of P(1) could be described as that of a Ru_4 butterfly phosphide plus weaker interactions to two other ruthenium atoms. To our knowledge no example of an M_4 butterfly phosphide cluster has yet been described although cluster nitrides are well-known[20] and a butterfly oxo cluster has recently been characterized.[21]

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[18] Deviations from the least squares plane through Ru(3), Ru(6), Ru(7), Ru(8), and P(1) are respectively −0.042, +0.041, −0.063, +0.063, and 0.000 Å. The atoms Ru(1), Ru(2), Ru(4), Ru(5), and Ru(6) are also almost planar. Deviations are −0.040, −0.031, +0.012, +0.020, and +0.038 Å.

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There has been considerable discussion as to the effective radius of an interstitial phosphide and the size of the polyhedron needed to encapsulate a phosphorus atom. In binary phosphides of the transition metals, 9-coordination of phosphorus in a tetrakaidecahedral environment is frequently found.[22] There is evidence however that the radii of main group atoms can be substantially contracted by valence electron transfer to electrophilic metal atoms, resulting in occupation of interstitial cavities much smaller than expected. Earlier work by Chini et al. on $[Co_6(CO)_4(\mu\text{-}CO)_2P]^-$, which has an open semi-interstitial phosphide,[8] implies that a phosphide atom cannot occupy the cavity in a closed octahedron of cobalt atoms. For ruthenium a fully encapsulated phosphorus atom has been found in a closed Ru_8 polyhedron[5] but $Ru_5(CO)_{16}(\mu_5\text{-}P)(\mu\text{-}PPh_2)$ has a partially exposed phosphide in an open framework.[6] Although the phosphide in $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ occupies a 6-fold site, the Ru_6 encapsulating polyhedron has only eight metal–metal contacts, four removed from a *closo* octahedron and one from a trigonal prism. Nevertheless the Ru–P bond lengths (average 2.399 Å) indicate scope for contraction of the M_6 cavity. This, together with the recent characterization of trigonal-prismatic $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (nine Os–Os)[9] suggests that encapsulation of phosphorus in an Ru_6 trigonal-prismatic cluster may be possible. Moreover the structures of $Ru_5(CO)_{16}(\mu_5\text{-}P)(\mu\text{-}PPh_2)$[6] and $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ confirm the ability of the phosphide atom to exist in a greater variety of partially exposed cluster environments than for carbides or nitrides. Since unique reactivity is often associated with low-coordinate exposed main-group atoms[19] the chemical behavior of these cluster phosphides is worthy of investigation.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supplementary Material Available: Table S1 (summary of crystal data, intensity collection, reduction, and refinement), Table S2 (anisotropic thermal parameters), and Table S3 (phenyl ring bond lengths and angles) (5 pages); Table S4 (structure factors) (36 pages). Ordering information is given on any current masthead page.

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