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Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 10.[1] Synthesis and X-ray Crystal Structure of the First Tetraphosphido-Stabilized 48-e Triruthenium Cluster: $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$

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Reaction of 1,2-bis(phenylphosphino)benzene and $Ru_3(CO)_{12}$ gave four products, three of which were characterized by X-ray crystallography as $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$ (2), $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (3), and $Ru_5(CO)_{14}[1\text{-}(\mu_4\text{-}P)\text{-}2\text{-}(\eta\text{-}PPh_2)C_6H_4]$ (4). The yield of the major product 3 was optimized to 36%. Thermolysis of 2 led to 3 in yields of about 50%, in a reaction that did not follow first or second order kinetics. The tetrakis(phosphido)-bridged triruthenium cluster 3 was stable for 24 h in boiling mesitylene (165 °C) in an inert atmosphere, but triethylphosphine readily substituted for a carbonyl ligand in THF at ambient temperature to give two isomeric products in high yield. Crystal structure data (at −100 °C): for 2, monoclinic, $P2_1/c$ (No. 8), $Z = 8$, $a = 8.416(2)$ Å, $b = 32.657(6)$ Å, $c = 19.022(3)$ Å, $\beta = 105.57(2)°$, 11 572 independent reflections measured, $R = 0.0432$, $R_w = 0.0372$ for 725 variables refined vs 7803 reflections with $|F_o| \leq 4\sigma(|F_o|)$; for 3, monoclinic, $P2_1/n$ (No. 8), $Z = 4$, $a = 19.178(2)$ Å, $b = 10.933(2)$ Å, $c = 19.201(2)$ Å, $\beta = 91.18(1)°$, 8968 independent reflections measured, $R = 0.0306$, $R_w = 0.0276$ for 608 variables refined vs 7129 reflections with $|F_o| \leq 4\sigma(|F_o|)$; for 4, triclinic, $P\bar{1}$, (No. 2), $Z = 2$, $a = 9.898(5)$ Å, $b = 12.166(4)$ Å, $c = 16.204(7)$ Å, $\alpha = 76.92(3)°$, $\beta = 83.14(4)°$, $\gamma = 84.05(3)°$, 7383 independent reflections measured, $R = 0.0603$, $R_w = 0.0563$ for 478 variables refined vs 3466 reflections with $|F_o| \leq 4\sigma(|F_o|)$.

Introduction

For more than a decade, interest has been high in heteroatom-bridged transition metal clusters, as it was anticipated that this bridge would stabilize them, particularly under conditions that might be relevant to catalytic reactions mediated by such species.[2] It has been found, however, that even the phosphido group, the most hardy of such moieties, does not protect transition metal clusters from degradation under vigorous reaction conditions.[3] To enhance further the stability of such clusters, chelating diphosphines have been employed.[4] For example, Bonnet and co-workers[4a,b] stabilized triruthenium clusters by using edge-bridging bis(diphenylphosphino)methane (dppm), forming $Ru_3(CO)_8(dppm)_2$ and $Ru_3(CO)_{10}(dppm)$. In addition, they reported that these complexes can undergo thermal, intramolecular oxidative cleavage of the ligand groups to afford phosphido-bridged triruthenium clusters such as $Ru_3(CO)_6(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}PPhCH_2PPh_2)_2$[4a] and $Ru_3(CO)_7(\mu_3\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}CHPPh)(dppm)$.[4b] Recently, a triruthenium carbonyl complex of a 1,2-bis(phenylphosphido)benzene, *i.e.*, $Ru_3(CO)_7[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4](\mu\text{-}PPh_2)(\mu\text{-}H)$ was reported in which the chelating ligand presumably was constructed from coordinated μ-PPh_2 ligands on a Ru_3 framework.[4c]

We have been exploring the utility of linked 1,2-bis(substituted phosphido)benzenes as ligands that might confer extra stability upon transition metal clusters due to the cisoid arrangement of the phosphido groups. In fact, we have reported that such ligands do lead to unusually stable transition metal complexes when com-

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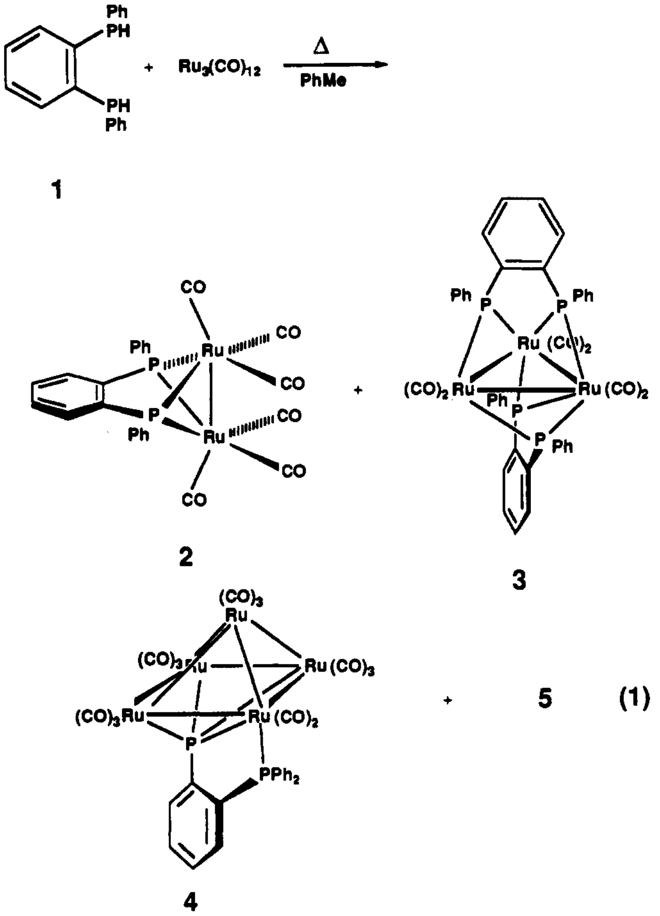
pared to the unlinked diphosphido analogues.[5] We have also described a novel bonding mode by 1,2-phenylene-linked phosphido moieties that stabilized several different transition metal triangles.[6] In addition, we have described recently the unusual catalytic properties of two complexes (2 and 3) described in this report.[1] In particular, evidence was presented that the tetrakis-bridged triruthenium complex 3 could be recovered quantitatively after functioning as a hydrogenation catalyst supported on silica gel for prolonged periods at elevated temperatures.

In this paper, we report the synthesis and crystal structures of three phosphido-stabilized ruthenium clusters: $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$ (2), $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (3), and $Ru_5(CO)_{14}[1\text{-}(\mu_4\text{-}P)\text{-}2\text{-}(\eta\text{-}PPh_2)\text{-}C_6H_4]$ (4).

Results and Discussion

The reaction of 1,2-bis(phenylphosphino)benzene (1) and dodecylcarbonyltriruthenium in toluene under reflux gave rise to four isolable air-stable crystalline products, 2–5 (eq 1). After 72 h, the yield of complex 3 remained constant at about 36%, whereas the other three complexes were isolated in yields in the 3–5% range. Alternatively, the yield of 2 could be optimized by fragmenting $Ru_3(CO)_{12}$ into $Ru(CO)_5$ before the addition of the diphosphine. This was accomplished by heating $Ru_3(CO)_{12}$ in benzene (160 °C) under 80 atm of carbon monoxide,[7] followed by the addition of 1 at 120 °C under 54 atm of carbon monoxide, to give 2 in a 25% yield, with minor amounts of complexes 3–5 observable by HPLC. The purple tetraphosphido-bridged trinuclear compound 3 is the first reported 48-e tetrakis-bridged triruthenium carbonyl complex.[8] The green pentaruthenium complex 4 was fully characterized (*vide infra*), whereas the orange crystalline material 5 never gave crystals suitable for X-ray crystal structure analysis (*vide infra*).



The crystal structure of 2 contains two closely similar symmetry-independent molecules per unit cell. The structure of one these species is given by the coordinates in Table 1 and shown in the thermal ellipsoid plot in Figure 1. Selected bond lengths and angles are given in Table 2. The overall symmetry of each molecule closely approximates C_{2v}, with a mirror plane bisecting the Ru–Ru axis. Each Ru atom is in a slightly distorted octahedral environment, as a consequence of the cisoid diphosphido arrangement. The Ru–Ru bond lengths (2.794, 2.779 Å) are consistent with a Ru–Ru single bond.[9]

The crystal structure of 3 (Table 3) is shown in Figure 2, with selected bond lengths and angles given in Table 4. The molecule has approximately C_2 symmetry with the two 1,2-phenylenediphosphido ligands on opposite sides of the triruthenium plane. Each linked diphosphido unit chelates a different ruthenium center as well as contributing a single bond to each of the remaining metal centers. The result is that two ruthenium atoms, Ru2 and Ru3, are chelated and equivalent, whereas the third, Ru1, is unique; the C_2 axis runs through this unique Ru atom and bisects the bond between the other two identical Ru atoms. One consequence of this bonding arrangement, in which the metals are nonequivalent, is the classical AA′BB′ $^{31}P\{H\}$ NMR spectrum exhibited by 3. This is also reflected in the Ru–Ru bond lengths, two of which are nearly equivalent at 2.841 and 2.846 Å, whereas the third (Ru2–Ru3) is 2.807 Å. Presumably, the contraction is due to the fact that the Ru(2)–Ru(3) bond is doubly phosphido-bridged, whereas the other two bonds are only singly bridged; this latter bond length agrees well with the length(s) observed in 2. Each 1,2-phenylene backbone has a slight tilt with respect to the triruthenium plane, as shown by the dihedral angles: plane (Ru1–Ru2–Ru3)–plane (P1–C1–C2–P2) = 79.6°; plane (Ru1–Ru2–Ru3)–plane (P3–C7–C8–P4) = 81.6°. The 1,2-phenylene backbones are bent toward the center of the ruthenium triangle and are partially staggered with respect to each other. The dihedral angles between the bridging phosphido units and

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Table 1. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $Ru_2(CO)_6[1,2-(\mu-PPh)_2C_6H_4]$ (2)

atom	*x*	*y*	*z*	U^a
		Molecule I		
Ru1	0.28950(5)	0.074820(10)	0.19640(2)	0.0277(2)
Ru2	0.49055(5)	0.134400(10)	0.15283(2)	0.02808(14)
P1	0.2298(2)	0.11074(4)	0.08529(7)	0.0282(5)
P2	0.2977(2)	0.14530(4)	0.22016(7)	0.0280(5)
O7	–0.0414(6)	0.05202(14)	0.2138(3)	0.060(2)
O8	0.4086(6)	0.00260(13)	0.1167(2)	0.052(2)
O9	0.5215(6)	0.05400(14)	0.3481(2)	0.064(2)
O10	0.6803(6)	0.0828(2)	0.0664(3)	0.064(2)
O11	0.7863(5)	0.1370(2)	0.2893(2)	0.057(2)
O12	0.4828(5)	0.21933(14)	0.0858(3)	0.063(2)
C1	0.0769(6)	0.1499(2)	0.0883(3)	0.029(2)
C2	0.1130(6)	0.1681(2)	0.1584(3)	0.027(2)
C3	0.0181(7)	0.2001(2)	0.1717(3)	0.034(2)
C4	–0.1145(7)	0.2133(2)	0.1162(4)	0.043(2)
C5	–0.1520(8)	0.1955(2)	0.0480(3)	0.042(2)
C6	–0.0552(7)	0.1636(2)	0.0337(3)	0.036(2)
C7	0.0870(8)	0.0594(2)	0.2073(3)	0.039(2)
C8	0.3677(7)	0.0283(2)	0.1483(3)	0.034(2)
C9	0.4362(8)	0.0613(2)	0.2920(3)	0.040(2)
C10	0.6106(7)	0.1020(2)	0.0974(3)	0.039(2)
C11	0.6781(7)	0.1364(2)	0.2377(3)	0.035(2)
C12	0.4917(7)	0.1873(2)	0.1111(3)	0.041(2)
C13	0.1774(6)	0.0880(2)	–0.0044(3)	0.030(2)
C14	0.0508(8)	0.0590(2)	–0.0235(3)	0.045(2)
C15	0.0144(9)	0.0400(2)	–0.0908(3)	0.054(3)
C16	0.1024(8)	0.0497(2)	–0.1398(3)	0.047(3)
C17	0.2245(8)	0.0779(2)	–0.1220(3)	0.046(3)
C18	0.2625(7)	0.0977(2)	–0.0545(3)	0.038(2)
C19	0.3293(7)	0.1708(2)	0.3077(3)	0.031(2)
C20	0.2392(7)	0.1585(2)	0.3557(3)	0.036(2)
C21	0.2613(8)	0.1784(2)	0.4219(3)	0.042(2)
C22	0.3701(9)	0.2104(2)	0.4399(3)	0.046(3)
C23	0.4585(9)	0.2230(2)	0.3924(4)	0.049(3)
C24	0.4375(9)	0.2032(2)	0.3268(4)	0.046(3)
		Molecule II		
Ru3	0.46042(5)	–0.080430(10)	0.27521(2)	0.02512(14)
Ru4	0.67463(5)	–0.145970(10)	0.31913(2)	0.02780(14)
P3	0.3869(2)	–0.14740(4)	0.30012(7)	0.0261(4)
P4	0.5982(2)	–0.09766(4)	0.39624(7)	0.0263(4)
O31	0.3498(5)	–0.09796(14)	0.1099(2)	0.051(2)
O32	0.1849(5)	–0.02510(12)	0.2952(2)	0.043(2)
O33	0.7171(5)	–0.01384(12)	0.2743(2)	0.046(2)
O34	0.9868(5)	–0.09632(13)	0.3233(3)	0.055(2)
O35	0.8122(6)	–0.21946(13)	0.4175(3)	0.056(2)
O36	0.6256(6)	–0.1821(2)	0.1654(2)	0.065(2)
C25	0.3405(6)	–0.1480(2)	0.3890(3)	0.026(2)
C26	0.4461(6)	–0.1208(2)	0.4374(3)	0.027(2)
C27	0.4269(7)	–0.1144(2)	0.5061(3)	0.032(2)
C28	0.3037(7)	–0.1363(2)	0.5278(3)	0.040(2)
C29	0.2049(7)	–0.1631(2)	0.4805(3)	0.037(2)
C30	0.2201(7)	–0.1690(2)	0.4098(3)	0.033(2)
C31	0.3890(7)	–0.0902(2)	0.1707(3)	0.036(2)
C32	0.2851(7)	–0.0463(2)	0.2871(3)	0.028(2)
C33	0.6191(7)	–0.0380(2)	0.2726(3)	0.033(2)
C34	0.8755(7)	–0.1166(2)	0.3225(3)	0.036(2)
C35	0.7588(7)	–0.1923(2)	0.3807(3)	0.037(2)
C36	0.6520(7)	–0.1696(2)	0.2230(4)	0.043(2)
C37	0.2432(6)	–0.1811(2)	0.2387(3)	0.026(2)
C38	0.1039(7)	–0.1654(2)	0.1890(3)	0.035(2)
C39	–0.0035(8)	–0.1916(2)	0.1408(3)	0.045(2)
C40	0.0278(9)	–0.2330(2)	0.1418(4)	0.051(3)
C41	0.1643(9)	–0.2484(2)	0.1916(4)	0.053(3)
C42	0.2716(8)	–0.2230(2)	0.2396(4)	0.039(2)
C43	0.7328(6)	–0.0653(2)	0.4644(3)	0.028(2)
C44	0.8831(7)	–0.0800(2)	0.5067(3)	0.040(2)
C45	0.9797(8)	–0.0554(2)	0.5611(4)	0.050(3)
C46	0.9291(8)	–0.0170(2)	0.5746(3)	0.047(3)
C47	0.7811(8)	–0.0022(2)	0.5329(3)	0.046(2)
C48	0.6831(8)	–0.0258(2)	0.4777(3)	0.039(2)

^{a} For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

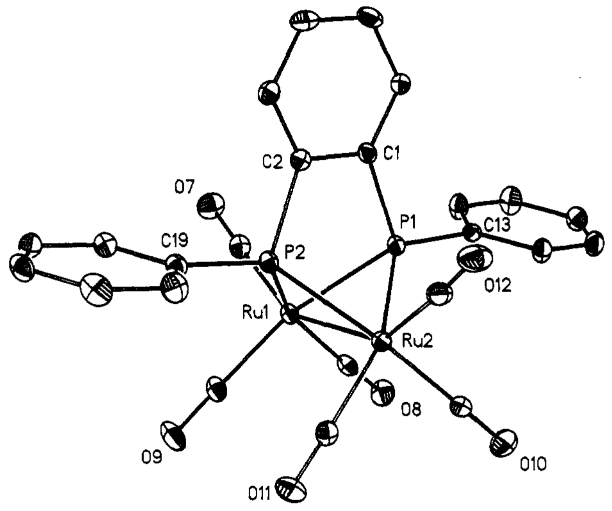

Figure 1. Thermal ellipsoid plot for molecule I of $Ru_2(CO)_6[1,2-(\mu-PPh)_2C_6H_4]$ (2), showing 20% equiprobability ellipsoids. Molecule II is essentially identical, as seen from Table 2. For clarity, only those ring C atoms bonded to P are labeled; carbonyl C atom numbers correspond to those for their bonded O atoms, for which labels are as shown.

the triruthenium plane are similar for P1 and P3 (114.2 and 115.4°, respectively) and for P2 and P4 (127.3 and 126.0°, respectively, Table 4B).

As stated above, in addition to compounds **2** and **3**, two minor products were isolated by alumina chromatography from the reaction mixture. After **3**, an orange compound **5** was eluted, which by $^{31}P\{H\}$ NMR spectroscopy was shown to contain four phosphorus sites; δ 486 (phosphinidino), 251 (presumably phosphido), 80 and 67 (both trisubstituted phosphino). The mass spectrum was consistent with the presence of a $Ru_4(CO)_{11}$ core, but unfortunately the material did not form single crystals so that the detailed structure could not be deduced.

The final fraction to elute from the alumina column gave a green complex **4**, which was fully characterized spectroscopically as well as by single crystal X-ray diffraction. The $^{31}P\{^1H\}$ NMR showed two resonances at δ 460.1 (d, $^3J_{P-P}$ = 10 Hz) and 64.6 (d, $^3J_{P-P}$ = 10 Hz). The downfield resonance was consistent with a phosphinidine capped structure,[10] and the upfield one, with a dative phosphine metal bond.

The crystal structure of **4** (Table 5) is shown in Figure 3, with selected bond lengths and angles given in Table 6. Complex **4** has a pseudooctahedral structure with Ru2, Ru3, Ru3, and Ru5 forming an approximately square equatorial plane with bond lengths ranging from 2.883 to 2.909 Å (average 2.896 Å) and angles ranging from 89.19 to 90.27°. That average bond length is somewhat longer than the average non-edge-bridged Ru–Ru distance of 2.868 Å in the bicapped $Ru_4(\mu_4-PPh)_2(\mu-CO)(CO)_{10}$[10c] but quite like the comparable distances in the monocapped $Ru_5(\mu_4-PPh)\{\mu-PPh(OPr-n)\}(\mu-H)(CO)_{13}$[10c] (average 2.918 Å). This square is slightly distorted from planarity, with

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[10] (a) Gastel, F. V.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1049. (b) Gastel, F. V.; Taylor, N. J.; Carty, A. J. *Ibid.* **1989**, *28*, 384. (c) Field, J. S.; Haines, R. J.; Smit, D. N. *J. Chem. Soc., Dalton Trans.* **1988**, 1315.

[11] Pidcock, A. (Chapter 1); Carty, A. J. (Chapter 10). In *Catalytic Aspects of Metal-Phosphine Complexes*; Alyea, E. C., Meek, D. W., Eds.; ACS Advances in Chemistry Series 196; American Chemical Society: Washington, DC, 1982.

Table 2

A. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$ (**2**)

1	2	3	1–2	2–3	1–2–3
			Molecule I		
Ru2	Ru1	P1	2.7936(6)	2.3498(13)	53.69(3)
Ru2	Ru1	P2		2.3460(14)	53.54(4)
Ru1	P1	Ru2		2.3560(13)	72.83(4)
Ru1	P2	Ru2		2.349(2)	73.03(4)
Ru2	Ru1	C7		1.915(7)	147.6(2)
P1	Ru2	Ru1			53.48(3)
P2	Ru2	Ru1			53.44(3)
C12	Ru2	Ru1	1.902(6)		145.5(2)
P1	Ru2	C10			94.0(2)
C10	Ru2	C11	1.955(7)	1.932(5)	92.5(2)
P1 ...	P2		2.719(2)		
			Molecule II		
Ru3	Ru4	P3	2.7786(5)	2.3512(14)	53.89(3)
Ru3	Ru4	P4		2.3579(15)	53.73(3)
Ru3	P3	Ru4		2.3512(14)	72.36(4)
Ru3	P4	Ru4		2.3579(15)	72.32(4)
Ru3	Ru4	C35		1.927(6)	152.9(2)
P3	Ru3	Ru4	2.7786(5)		53.75(3)
P4	Ru3	Ru4			53.95(4)
C32	Ru3	Ru4	1.911(6)		150.9(2)
P3	Ru3	C31			91.6(2)
C31	Ru3	C33	1.942(6)	1.934(6)	96.8(2)
P3 ...	P4		2.720(2)		

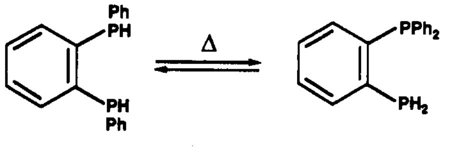
molecule I		molecule II	
atoms in dihedral array	angle	atoms in dihedral array	angle
C9–Ru1–Ru2–C11	9.0(1)	C34–Ru4–Ru3–C33	−1.5(2)
C8–Ru1–Ru2–C10	−1.9(2)	C36–Ru4–Ru3–C31	0.9(3)

molecule I			molecule II		
plane 1	plane 2	angle	plane 1	plane 2	angle
(Ru1–P1–Ru2)	(Ru1–P2–Ru2)	92.0(1)	(Ru4–P3–Ru3)	(Ru4–P4–Ru3)	91.4(1)

Ru3 and Ru5 each about 0.06 Å out of the mean plane toward Ru1, whereas Ru2 and Ru4 are each about 0.06 Å out of the plane away from Ru1. As a consequence of this distortion, the bond lengths from the apical Ru1 to Ru3 and Ru5 (2.801, 2.817 Å, respectively) are somewhat shorter than those to Ru2 and Ru4 (2.913, 2.885 Å, respectively). Concomitantly, the phosphinidene phosphorus (P2) forms the cap of the pseudooctahedral Ru_5P structure, with shorter lengths to Ru2 and Ru4 (2.315, 2.329 Å, respectively) than to Ru3 and Ru5 (2.375, 2.363 Å, respectively). Similarly, in the bicapped complex $Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}$,[10c] each capping phosphorus atom is reported to have two shorter (average 2.39 Å) and two somewhat longer (average 2.48 Å) Ru–P lengths; the monocapped complex $Ru_5(\mu_4\text{-}PPh)\{\mu\text{-}PPh(OPr\text{-}n)\}(\mu\text{-}H)(CO)_{13}$ shows comparable Ru–P distances of 2.318, 2.360, 2.398, and 2.349 Å.[10c]

A few comments regarding the formation of the complexes described above are in order. It is likely that the diruthenium complex **2** does not form via initial ligation of $Ru_3(CO)_{12}$ or some related decarbonylated species, because initial cluster fragmentation favors complex **2**. More interesting, however, is the fact that dinuclear **2**, upon heating above about 100 °C, is transformed into the trinuclear **3** in yields in the range 50–75%, depending upon the conditions used (*vide infra*). Clearly, this is a mechanistically complicated process that must involve fragmentation of the diruthenium complex and the generation of species capable of building up the very stable trinuclear complex **3** relatively efficiently, given the observed yields. Complex **3** is very stable *thermally*, capable of being isolated quantitatively from boiling mesitylene after several hours.

We believe that complexes **4** and **5** are probably artifacts of an impurity in our reactant ligand. We have described elsewhere the equilibrium that is established between ligand **1** and its isomer **6** (ratio, *ca.* 10:1) upon distillation under vacuum (eq 2).[12] Because it is not possible to purify



(2)

1 **6**

the highly oxidizable bis(secondary phosphine) **1** except by distillation, the primary–tertiary diphosphine **6** is always present in small amounts when **1** is utilized. Thus **6** serves as a ready precursor to the phosphinidine moiety found in complex **4** and presumably also **5**.

As stated above, dinuclear **2** is not thermally stable and, at temperatures above 100 °C in aromatic hydrocarbon solution, decomposes to give **3** in substantial yields. When **2** was heated in mesitylene and the rate of reaction was measured by HPLC, the derived rate law did not obey simple first or second order kinetics, as shown in Table 7. The yield of **3** at half-reaction was 54% with respect to the ruthenium balance. In contrast, when **3** was heated at

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[12] Soucek, M. D.; Rines, S. P.; Kyba, E. P. Manuscript in preparation.

Table 3. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $Ru_3(CO)_6[1,2-(\mu-PPh)_2C_6H_4]_2$ (3)

atom	*x*	*y*	*z*	*U*[a]
Ru1	–0.065070(10)	0.15912(2)	0.187240(10)	0.01838(7)
Ru2	0.044960(10)	0.27623(2)	0.262800(10)	0.01863(7)
Ru3	0.014240(10)	0.03010(2)	0.290350(10)	0.01828(7)
P1	–0.07381(4)	0.32096(8)	0.26667(4)	0.0195(2)
P2	0.02298(4)	0.18985(8)	0.37226(4)	0.0213(2)
P3	0.00868(4)	–0.00945(8)	0.17078(4)	0.0198(2)
P4	0.12317(4)	0.11123(8)	0.26131(4)	0.0219(2)
O1	–0.0923(2)	0.2908(3)	0.05235(14)	0.0486(11)
O2	–0.20472(14)	0.0413(3)	0.1634(2)	0.0486(10)
O3	0.1134(2)	0.5110(3)	0.3150(2)	0.0589(10)
O4	0.07089(13)	0.3329(3)	0.10939(13)	0.0376(9)
O5	–0.13877(13)	–0.0163(2)	0.32655(13)	0.0357(8)
O6	0.0621(2)	–0.2146(3)	0.3483(2)	0.0515(11)
C1	–0.1056(2)	0.2959(3)	0.3548(2)	0.0209(9)
C2	–0.0604(2)	0.2419(3)	0.4044(2)	0.0221(9)
C3	–0.0828(2)	0.2221(4)	0.4719(2)	0.0309(12)
C4	–0.1498(2)	0.2546(4)	0.4900(2)	0.0372(13)
C5	–0.1946(2)	0.3067(4)	0.4413(2)	0.0358(12)
C6	–0.1729(2)	0.3285(3)	0.3740(2)	0.0268(10)
C7	0.0954(2)	0.0064(3)	0.1339(2)	0.0224(9)
C8	0.1484(2)	0.0573(3)	0.1761(2)	0.0236(9)
C9	0.2163(2)	0.0659(3)	0.1515(2)	0.0292(11)
C10	0.2312(2)	0.0246(4)	0.0852(2)	0.0335(11)
C11	0.1788(2)	–0.0237(4)	0.0433(2)	0.0323(12)
C12	0.1109(2)	–0.0323(3)	0.0669(2)	0.0273(11)
C13	–0.0826(2)	0.2406(3)	0.1042(2)	0.0277(10)
C14	–0.1508(2)	0.0858(3)	0.1725(2)	0.0291(11)
C15	0.0884(2)	0.4228(3)	0.2947(2)	0.0324(11)
C16	0.0589(2)	0.3094(3)	0.1657(2)	0.0254(10)
C17	–0.0826(2)	0.0037(3)	0.3111(2)	0.0251(11)
C18	0.0445(2)	–0.1225(3)	0.3271(2)	0.0303(11)
C1A	–0.1130(2)	0.4680(3)	0.2461(2)	0.0225(9)
C2A	–0.0895(2)	0.5707(3)	0.2822(2)	0.0332(11)
C3A	–0.1197(2)	0.6838(4)	0.2695(3)	0.0435(13)
C4A	–0.1734(2)	0.6947(4)	0.2215(3)	0.0462(14)
C5A	–0.1973(2)	0.5949(4)	0.1860(2)	0.0410(13)
C6A	–0.1675(2)	0.4801(4)	0.1978(2)	0.0323(11)
C1B	0.0836(2)	0.2027(3)	0.4460(2)	0.0269(11)
C2B	0.1211(2)	0.1024(4)	0.4696(2)	0.0344(12)
C3B	0.1703(2)	0.1165(5)	0.5237(2)	0.047(2)
C4B	0.1801(3)	0.2280(6)	0.5536(2)	0.055(2)
C5B	0.1432(3)	0.3288(5)	0.5317(2)	0.052(2)
C6B	0.0943(2)	0.3161(4)	0.4770(2)	0.0405(15)
C1C	–0.0208(2)	–0.1515(3)	0.1313(2)	0.0227(10)
C2C	–0.0744(2)	–0.1534(4)	0.0820(2)	0.0310(12)
C3C	–0.0936(2)	–0.2614(4)	0.0492(2)	0.0427(14)
C4C	–0.0610(3)	–0.3681(4)	0.0661(2)	0.046(2)
C5C	–0.0084(3)	–0.3689(4)	0.1162(2)	0.044(2)
C6C	0.0121(2)	–0.2605(3)	0.1487(2)	0.0339(12)
C1D	0.2009(2)	0.0907(3)	0.3155(2)	0.0259(10)
C2D	0.2226(2)	–0.0277(4)	0.3321(2)	0.0363(11)
C3D	0.2799(2)	–0.0467(5)	0.3754(2)	0.0464(14)
C4D	0.3159(2)	0.0520(5)	0.4025(3)	0.0505(15)
C5D	0.2952(2)	0.1685(5)	0.3863(3)	0.0527(15)
C6D	0.2373(2)	0.1888(4)	0.3427(2)	0.0397(12)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors. Carbon atoms of the phenyl rings are identified as C1A–C6A, C1B–C6B, etc.

reflux in mesitylene for 24 h in an inert atmosphere, 2 was not observed and 3 was recovered quantitatively.

It is reasonable that 3 can be formed directly from the unfragmented Ru_3 cluster, presumably by an initial loss of CO, but the observations of products 2, 4, and 5 and the observation that 2 gives 3 in substantial yields under the reaction conditions indicate that the formation of 3 is likely a complicated process and not easily unraveled mechanistically.

Although 3 is very stable thermally, it is quite susceptible to attack by a good ligand such as PEt_3 at ambient temperature. Addition of PEt_3 to a THF solution of 3 at ambient temperature results in a change of color from a dark purple to a deep orange (eq 3). After chromatography, two orange compounds were isolated. The major product was $Ru_3(CO)_5[1,2-(\mu-PPh)_2C_6H_4]_2(PEt_3)$ (7), which was isolated in a 52% yield. The $^{31}P\{^1H\}$ NMR spectrum featured five distinct resonances at δ 219 (m), 198 (m), 164 (m), 157 (m), and 53 (s) ppm, and the ^1H NMR spectrum exhibited an aromatic:aliphatic integration ratio of 28:15, consistent with the substitution of only one PEt_3 for a CO. The isomeric minor product 8 was isolated in 38% yield. The $^{31}P\{^1H\}$ NMR spectrum also exhibited five resonances at δ 219 (m), 195 (m), 164 (m), 156 (m), and 53 (s) ppm, and an aromatic:aliphatic integration in the ^1H NMR spectrum of 28:15. We have assigned the structures of the two complexes as shown in eq 3, with the predominant isomer corresponding to substitution onto the two identical ruthenium centers and the minor isomer corresponding to substitution onto the unique metal site. It cannot be ruled out that the unique metal site is more reactive than the other two, in which case the structural assignment would be reversed.

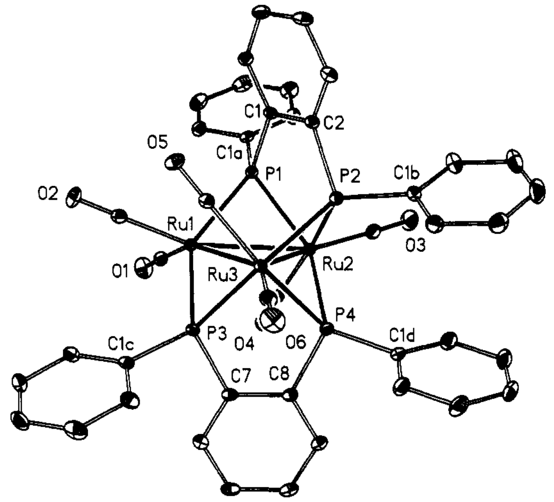
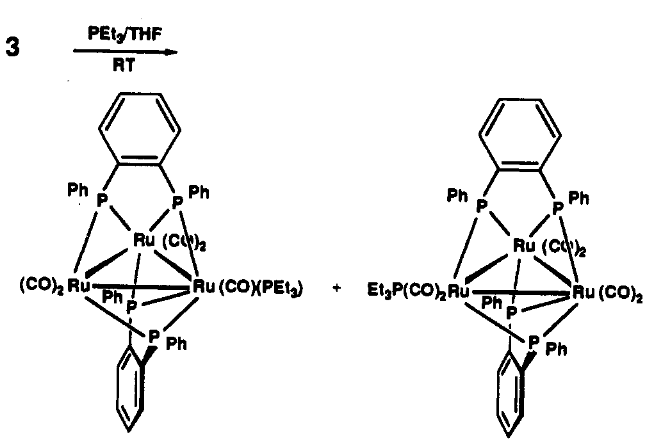


Figure 2. Thermal ellipsoid plot for $Ru_3(CO)_6[1,2-(\mu-PPh)_2C_6H_4]_2$ (3), showing 20% equiprobability ellipsoids. For clarity, only those ring C atoms bonded to P are labeled; carbonyl groups (identified by labels on the O atoms) are as follows: C13–O1, C14–O2, C15–O3, C16–O4, C17–O5, C18–O6.



7 8 (3)

Table 4

A. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (3)

1		2	3	1–2	2–3	1–2–3
Ru3		Ru2	Ru1	2.8073(5)	2.8410(4)	60.508(9)
Ru2		Ru1	Ru3		2.8459(4)	59.159(12)
Ru1		Ru3	Ru2			60.334(8)
Ru1		P1	Ru2	2.3442(9)	2.3324(8)	74.82(3)
Ru1		P3	Ru3	2.3485(9)	2.3365(8)	74.81(3)
Ru2		P2	Ru3	2.3502(8)	2.3540(9)	73.28(2)
Ru2		P4	Ru3	2.3466(9)	2.3473(9)	73.46(3)
P1		Ru1	P3			136.98(3)
P1		Ru2	P4			141.86(3)
P3		Ru3	P2			142.66(3)
P1	···	P2		3.075(1)		
P2	···	P4		3.023(1)		
P3	···	P4		3.070(1)		

B. Angles between Planes (deg) for the Non-Hydrogen Atoms of $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (3)

plane 1	plane 2	angle
(Ru1–Ru2–Ru3)	(P1–C1–C2–P2)	79.6(2)
(Ru1–Ru2–Ru3)	(P3–C7–C8–P4)	81.6(2)
(Ru1–Ru2–Ru3)	(Ru1–P1–Ru2)	114.2(2)
(Ru1–Ru2–Ru3)	(Ru1–P3–Ru3)	114.4(2)
(Ru1–Ru2–Ru3)	(Ru2–P2–Ru3)	127.3(2)
(Ru1–Ru2–Ru3)	(Ru2–P4–Ru3)	126.0(2)
(Ru2–P2–Ru3)	(Ru2–P4–Ru3)	106.7(2)

Conclusion

Four compounds were isolated from the thermal reaction of $Ru_3(CO)_{12}$ and 1,2-bis(phenylphosphino)benzene (1), three of which were identified as $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$ (2), $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (3), and $Ru_5(CO)_{14}[1\text{-}(\mu_4\text{-}P)\text{-}2\text{-}(PPh_2)C_6H_4]$ (4). Complex 3 is the first example of a 48-e tetrakis(phosphido)-stabilized triruthenium cluster.[8] The yield of the diruthenium compound 2 was maximized by adding the diphosphine to the mononuclear $Ru(CO)_5$ instead of to $Ru_3(CO)_{12}$. The thermolysis of 2 gave 3 in substantial yields, and the reaction did not follow simple kinetics. Although 3 was stable in mesitylene at 165 °C, it reacted with $P(Et)_3$ at ambient temperature to form two isomers of $Ru_3(CO)_5[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2(PEt_3)$. Thus, while the four phosphido bridges do impart stability to the triangular ruthenium skeleton, carbonyl substitutions can occur with ease.

Experimental Section

General Information. Proton and ^{31}P NMR spectra were obtained on a Nicolet NT-360. All spectra were determined in $CDCl_3$ at ambient temperature unless otherwise stated. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and to 85% H_3PO_4 for ^{31}P NMR spectra. IR spectra were recorded in NaCl solution cells in toluene or CH_2Cl_2 using a FT-IR Matteson Cygnus 100. Mass spectra were obtained on a Finnegan MAT TSQ70 triple sector quadrupole (CI^+) methane/(CI^-) methane via a direct probe with the rapid thermal desorption technique. Melting points were measured in sealed capillaries under nitrogen and are uncorrected. Analytical HPLC determinations were carried out on a Waters ALC 204 instrument, equipped with a Waters μ-Porasil 10μ, 3.9-mm-i.d. × 30-cm column. HPLC quantitative analyses were performed using a digital integrator (Hewlett-Packard 3390A Reporting Integrator). Responsive factors were determined at 280 nm utilizing pure samples.

Table 5. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for the Non-Hydrogen Atoms of $Ru_5(CO)_{14}[1\text{-}(\mu_4\text{-}P)\text{-}2\text{-}(\eta\text{-}PPh_2)C_6H_4]$ (4)

atom	*x*	*y*	*z*	U^a
Ru1	0.20235(13)	0.07874(10)	0.23813(8)	0.0664(5)
Ru2	0.17182(11)	0.28580(9)	0.30258(7)	0.0561(5)
Ru3	0.22127(12)	0.28699(10)	0.12215(7)	0.0645(5)
Ru4	0.46577(13)	0.13781(10)	0.15216(8)	0.0687(5)
Ru5	0.40477(13)	0.12057(10)	0.33292(7)	0.0672(5)
P1	0.2263(4)	0.4615(3)	0.3144(2)	0.0564(14)
P2	0.3808(4)	0.2823(3)	0.2216(2)	0.0589(15)
O1	−0.0625(15)	0.0763(11)	0.3476(10)	0.148(8)
O2	0.0553(15)	0.0238(12)	0.1012(9)	0.141(8)
O3	0.261(2)	−0.1690(11)	0.3187(10)	0.161(9)
O4	0.0607(12)	0.2303(10)	0.4880(7)	0.106(6)
O5	−0.1169(12)	0.3757(10)	0.2690(7)	0.099(6)
O6	0.289(2)	0.5226(11)	0.0275(8)	0.166(9)
O7	−0.079(2)	0.322(2)	0.0984(9)	0.177(10)
O8	0.2642(12)	0.1916(9)	−0.0368(6)	0.100(6)
O9	0.5926(14)	0.2667(10)	−0.0167(8)	0.126(7)
O10	0.418(2)	−0.0749(12)	0.0940(10)	0.169(9)
O11	0.752(2)	0.059(2)	0.1953(11)	0.204(12)
O12	0.5560(14)	−0.1094(10)	0.3428(9)	0.140(7)
O13	0.264(2)	0.0336(14)	0.5074(9)	0.191(9)
O14	0.6361(14)	0.2145(11)	0.3951(9)	0.139(8)
C1	0.039(2)	0.0869(14)	0.3089(12)	0.100(9)
C2	0.115(2)	0.0486(15)	0.1497(11)	0.103(9)
C3	0.244(2)	−0.0769(14)	0.2902(12)	0.108(9)
C4	0.1082(14)	0.2468(12)	0.4178(9)	0.067(6)
C5	−0.007(2)	0.3451(13)	0.2772(9)	0.071(7)
C6	0.266(2)	0.4368(14)	0.0596(10)	0.105(9)
C7	0.032(2)	0.314(2)	0.1106(11)	0.121(11)
C8	0.252(2)	0.2268(12)	0.0239(9)	0.076(7)
C9	0.545(2)	0.2168(12)	0.0480(9)	0.073(7)
C10	0.428(2)	0.004(2)	0.1189(11)	0.107(9)
C11	0.643(2)	0.083(2)	0.1806(13)	0.128(11)
C12	0.501(2)	−0.0251(13)	0.3347(11)	0.102(8)
C13	0.314(2)	0.070(2)	0.4409(11)	0.106(9)
C14	0.548(2)	0.1788(14)	0.3737(11)	0.091(8)
C15	0.3926(13)	0.4922(12)	0.2572(8)	0.056(6)
C16	0.4640(14)	0.4126(10)	0.2166(8)	0.056(6)
C17	0.5923(14)	0.4304(12)	0.1744(8)	0.065(6)
C18	0.649(2)	0.5312(14)	0.1712(9)	0.074(7)
C19	0.575(2)	0.6152(12)	0.2084(9)	0.068(6)
C20	0.4481(14)	0.5949(11)	0.2524(8)	0.061(6)
C21	0.2515(14)	0.4818(12)	0.4197(8)	0.063(6)
C22	0.3261(14)	0.3954(12)	0.4729(9)	0.070(7)
C23	0.3628(15)	0.4131(13)	0.5498(9)	0.078(7)
C24	0.323(2)	0.5144(14)	0.5730(9)	0.077(7)
C25	0.2479(14)	0.5991(13)	0.5212(10)	0.075(7)
C26	0.2134(14)	0.5825(11)	0.4454(8)	0.064(6)
C27	0.1096(15)	0.5816(10)	0.2698(9)	0.060(6)
C28	−0.010(2)	0.6067(13)	0.3153(10)	0.079(7)
C29	−0.098(2)	0.6968(14)	0.2828(11)	0.083(8)
C30	−0.068(2)	0.7611(14)	0.2026(12)	0.095(9)
C31	0.053(2)	0.7353(13)	0.1556(10)	0.085(8)
C32	0.143(2)	0.6452(11)	0.1888(9)	0.070(6)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

All reactions were performed under a dry nitrogen atmosphere unless otherwise stated. All concentrations of solutions were carried out on a rotary evaporator under water aspirator pressure unless otherwise noted. Air-sensitive liquids were transferred by Teflon flexneedles using nitrogen or by syringe. The alumina used was neutral, activity 1, 80–200 mesh, and was used as supplied from Fischer Scientific Co. Hexane was dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Toluene and mesitylene were dried over sodium and distilled under nitrogen before use. Ethyl acetate and Ru_3CO_{12} were purchased from Aldrich and used as received. The ligand, 1,2-$(PHPh)_2C_6H_4$ (1), was prepared as previously described.[13]

$Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$ (2), $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (3), $Ru_5(CO)_{14}[1\text{-}(\mu_4\text{-}P)\text{-}2\text{-}(PPh_2)C_6H_4]$ (4), and 5. To diphosphine 1 (190 mg, 0.67 mmol) was added a solution of $Ru_3(CO)_{12}$ (855 mg, 1.30 mmol) in toluene (200 mL), and the mixture was heated at reflux (110 °C) for 72 h. The crude reaction mixture was concentrated to a minimum amount of toluene (25 mL) and loaded onto an alumina column (400 g). Four compounds

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[13] Kyba, E. P.; Liu, S.-T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.

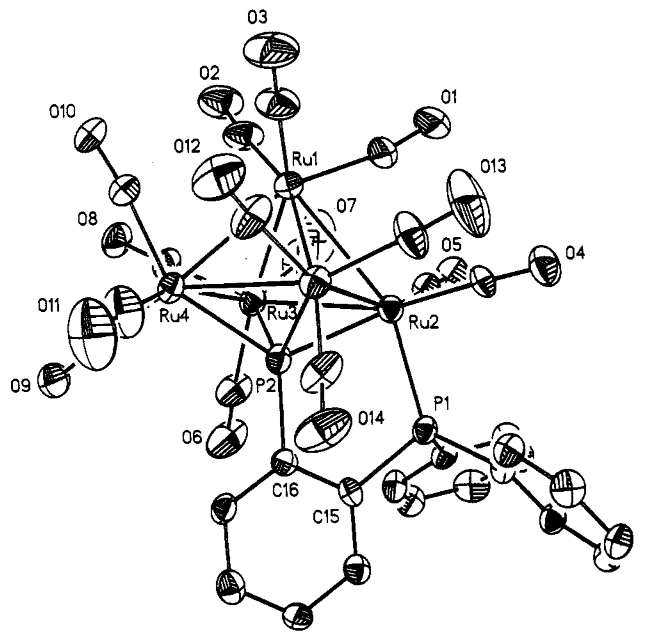

Figure 3. Thermal ellipsoid plot for $Ru_5(CO)_{14}[1-(\mu_4-P)-2-(\eta-PPh_2)C_6H_4]$ (4), showing 20% equiprobability ellipsoids. For clarity, only those ring C atoms bonded to P are labeled; carbonyl C atom numbers correspond to those for their bonded O atoms, for which labels are as shown. The frontmost, unlabeled, Ru atom is Ru5; the frontmost phenyl ring on P1 is C21–26 and the rear phenyl ring is C27–C32.

Table 6

A. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Ru_5(CO)_{14}[1-(\mu_4-P)-2-(PPh_2)C_6H_4]$ (4)

1	2	3	1–2	2–3	1–2–3
Ru4	Ru3	Ru2	2.891(2)	2.903(2)	90.23(6)
Ru5	Ru4	Ru3	2.883(2)		89.93(6)
Ru2	Ru5	Ru4	2.909(2)		90.27(6)
Ru3	Ru2	Ru5	2.903(2)		89.19(6)
P2	Ru4	Ru1	2.329(4)	2.885(2)	72.99(10)
Ru2	P2	Ru4	2.315(4)		124.2(2)
P2	Ru2	Ru1		2.913(2)	72.62(11)
Ru2	Ru1	Ru4			90.16(6)
P2	Ru3	Ru1	2.375(4)	2.801(2)	74.00(10)
Ru3	P2	Ru5		2.363(4)	119.0(2)
P2	Ru5	Ru1		2.817(2)	73.86(11)
Ru3	Ru1	Ru5			93.18(6)
Ru2	Ru1	Ru4			90.16(6)
P1	Ru2		2.312(4)		

B. Dihedral Angles (deg) for the Non-Hydrogen Atoms of $Ru_5(CO)_{14}[1-(\mu_4-P)-2-(PPh_2)C_6H_4]$ (4)

atoms in dihedral array	angle
P1–Ru2–Ru5–C14	9.1(5)
P1–Ru2–Ru3–C6	–6.2(7)
C6–Ru3–Ru4–C10	–131.8(8)
C10–Ru4–Ru5–C14	136.9(8)

Table 7. Thermal Conversion of $Ru_2(CO)_6[1,2-(\mu-PPh)_2C_6H_4]$ (2) into $Ru_3(CO)_6[1,2-(\mu-PPh)_2C_6H_4]_2$ (3)

time (h)	10^{-4}[2] (M) (% Rx)	10^{-4}[3] (M) (% yield)
0	9.36 (0)	0.00 (0)
1	8.48 (9)	0.44 (75)
2	6.32 (32)	1.08 (53)
3	4.64 (50)	1.71 (54)
4	2.72 (71)	2.13 (48)
8	0.39 (96)	2.78 (46)
24	0.00 (100)	2.63 (42)

were eluted using hexane with increasing concentrations of ethyl acetate. Elution with hexane gave a yellow band, which was concentrated and cooled (–10 °C) to afford 2 as pale yellow crystals (20.1 mg, 5.0%); see next section for spectroscopic and other properties.

Elution with 2% ethyl acetate in hexane gave a purple band, which was concentrated and cooled (–10 °C) to afford 3 as purple crystals (120 mg, 36.0%): mp 250 °C; ^1H NMR δ 8.21 (m, 4H), 7.59 (m, 4H), 7.45 (m, 4H), 7.25 (m, 5H), 7.11 (m, 2H), 7.05 (m, 9H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 221.3 (8 lines), 107.7 (8 lines), second order spectrum AA′BB′ pattern; IR (CH_2Cl_2) ν_{CO} 2020 (w), 1998 (s), 1962 (m), 1938 (w) cm^{-1}; MS (CI^+) *m/z* 1056 (MH^+, 100%), 1028 (MH^+ – CO, 8.1%). Anal. Calcd for $C_{42}H_{28}O_6P_4Ru_3$: C, 47.77; H, 2.65. Found: C, 47.64; H, 2.40.

Elution with 5% ethyl acetate in hexane gave an orange band. The solvent was evaporated, leaving an orange powder. The orange powder was dissolved in a minimum of warm toluene (~3 mL), layered with hexane (15 mL), and cooled (–10 °C) to afford 5 as orange crystals (23.7 mg, 3.5%): $^{31}P\{^1H\}$ NMR (C_6D_6) δ 485.8 (t, $^2J_{P-P}$ = 65.4 Hz), 250.6 (d, $^2J_{P-P}$ = 58.1 Hz), 80.1 (d, $^2J_{P-P}$ = 75.0 Hz), 67.4 (s); IR (CH_2Cl_2) ν_{CO} 2075 (m), 2045 (s), 2025 (s), 2010 (s), 1965 (w); MS (CI^-) *m/z* 1294 (M^+, 100), 1266 (M^+ – CO).

Elution with 7% ethyl acetate in hexane gave a green band. The solvent was removed to afford a dark green solid 4 (34.3 mg, 4%). Crystallization from a toluene–hexane (1:1, v/v) solution produced dark green X-ray quality crystals of 4: mp 280 °C; $^{31}P\{H\}$ NMR (C_6D_6) δ 460.1 (d, $^3J_{P-P}$ = 10 Hz), 64.6 (d, $^3J_{P-P}$ = 10 Hz); ^1H NMR ($CDCl_3$) δ 7.448 (4 m, H), 7.471 (10 m, H); IR (CH_2Cl_2) ν_{CO} 2079 (m), 2048 (s), 2033 (s), 2020 (s) cm^{-1}; MS (CI^+) 1190 *m/z* (MH^+, 100), 1162 (MH^+ – CO).

Optimization of the Yield of $Ru_2(CO)_6[1,2-(\mu-PPh)_2C_6H_4]$ (2). Triruthenium dodecacarbonyl (3.284 g, 5.16 mmol) in benzene (350 mL) was stirred at 160 °C under carbon monoxide (80 atm) for 22 h. To this solution at 120 °C under 54 atm of carbon monoxide was added diphosphine 1 (2.69 g, 9.15 mmol) in benzene (50 mL), and the mixture was stirred for 44 h at 120 °C under 68 atm of carbon monoxide. The resulting reaction mixture was concentrated and chromatographed on alumina (150 g) using benzene–hexane (5:95, v/v) as an eluent. Recrystallization from hot hexane afforded pale yellow crystals of $Ru_2(CO)_6[1,2-(\mu-PPh)_2C_6H_4]$ (2) (1.29 g, 25%): mp 179–182 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 100.2 (s); IR ($CDCl_3$) ν_{CO} 2075 (s), 2043 (s), 2013 (s), 1992 (s, br); MS (EI) *m/z* 662 (M^+), 494 (M^+ – 6CO, 100%). Anal. Calcd for $C_{24}H_{14}O_6P_4Ru_2$: C, 43.51; H, 2.13. Found: C, 43.32; H, 2.22.

Thermal Conversion of $Ru_2(CO)_6[1,2-(\mu-PPh)_2C_6H_4]$ (2) into $Ru_3(CO)_6[1,2-(\mu-PPh)_2C_6H_4]_2$ (3). The HPLC response factor for 2 was determined to be 6.126 × 10^{-16} mol/count by making four 5-μL injections of a 0.936 mM solution of 2 in mesitylene onto a silica column using a 2% ethyl acetate–hexane solution as an eluent. The response factor for 3 was similarly calculated to be 2.56 × 10^{-16} mol/count from injections of a 0.573 mM solution of 3 in benzene. The retention volumes of 2 and 3 were 5.36 and 8.08 mL, respectively. The mesitylene solution of 2 (25.0 mL) was degassed and immersed in an oil bath held at 185 °C so that the solution was brought rapidly to reflux. Aliquots were periodically removed and analyzed by making three 5-μL injections on the HPLC. The results are summarized in Table 7. A plot of 1/[2] versus time was not linear, nor was a plot of $\ln([2]_0/[2]_t)$ versus time. In a separate experiment, 2 (38.8 mg, 0.0586 mmol) in mesitylene (6.8 mL) was heated to reflux for 2 h. The resulting red-brown solution was concentrated. The ^{31}P NMR spectrum had resonances corresponding to 2.

Reaction of $Ru_3(CO)_6[1,2-(\mu-PPh)_2C_6H_4]_2$ (3) with PEt_3. Triethylphosphine (0.23 mL, 180 mg, 1.5 mmol) was added to 3 (20 mg, 0.019 mmol) dissolved in THF (100 mL). The reaction mixture was stirred at ambient temperature for 18 h. The resultant mixture was concentrated and loaded onto a silica column (50 g). $Ru_3(CO)_5[1,2-(\mu-PPh)_2C_6H_4]_2(PEt_3)$ (7) was eluted using a 5% EtOAc–hexane (v/v) solution to afford an orange powder (113 mg, 52%): ^1H NMR ($CDCl_3$) δ 8.45 (m, 4H), 8.21 (m, 4H), 7.72 (m, 4H), 7.47 (m, 4H), 7.35 (m, 4H), 7.09 (m, 4H), 6.96 (m, 4H), 1.51 (m, 6H), 0.85 (m, 9H); $^{31}P\{H\}$ NMR (C_6D_6) δ 219.0 (m), 197.8 (m), 164.0 (m), 157.3 (m), 53.0 (s); IR (CH_2Cl_2)

Table 8. Crystallographic Summary for 2–4

	2	3	4
	A. Crystal Data (–100 °C)[a]		
a (Å)	8.416(2)	19.178(2)	9.898(5)
b (Å)	32.657(6)	10.933(2)	12.166(4)
c (Å)	19.022(3)	19.201(2)	16.204(7)
α (deg)			76.92 (3)
β (deg)	105.57(2)	91.18(1)	83.14(4)
γ (deg)			84.05 (3)
V (Å^3)	5036.3	4025.2	1881.0
no. of reflns for cell data	44	45	26
2θ range for cell data (deg)	22.11–24.76	22.03–25.95	24.36–27.81
d_{calcd} (g·cm^{-3})	1.747	1.742	2.101
chem formula	$C_{24}H_{14}O_6P_2Ru_2$	$C_{42}H_{28}O_6P_4Ru_3$	$C_{32}H_{14}O_{14}P_2Ru_5$
fw	662.46	1055.78	1189.76
cryst syst	monoclinic	monoclinic	triclinic
space group, Z	$P2_1/c$, 8	$P2_1/n$, 4	$P\bar{1}$, 2
F(000) (electrons)	2592	2080	1136
	B. Data Collection (–100 °C)[b]		
radiation; λ (Å)	Mo Kα; 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69
data collection mode	ω scan	ω scan	ω scan
scan range	symmetrically over 1° about K$\alpha_{1,2}$ maximum	symmetrically over 1° about K$\alpha_{1,2}$ maximum	2°, Wyckoff method, 3 steps with 6 additional offset
backgrounds	offset +1.0 and –1.0° in ω from K$\alpha_{1,2}$ maximum	offset +1.0 and –1.0° in ω from K$\alpha_{1,2}$ maximum	offset +1.0 and –1.0° in ω from center of scan
scan rate (deg·min^{-1})	3–6	3–6	26
2θ range (deg)	4.0–55.0	4.0–55.0	4.0–52.0
exposure time (h)	121.0	119.6	23.6
instability correction range (on I)	0.991–1.000	0.994–1.004	0.983–1.015
total no. of reflns measd	11 572	8968	7383
data cryst vol (mm^3)	0.0152	0.0087	0.0058
data cryst faces	{010}, {011}, {12$\bar{1}$}	{001}, {010}, {100}	{100}, {010}, {001}, 10$\bar{1}$, $\bar{1}$0$\bar{1}$
abs coeff, μ(MoKα) (mm^{-1})	1.34	1.29	2.07
transm factor range	0.723–0.821	0.938–0.957	0.685–0.849
	C. Structure Refinement[c]		
ignorance factor, p	0.02	0.02	0.02
no. of reflns used, $\lvert F_o\rvert \leq 4\sigma(\lvert F_o\rvert)$	7803	7129	3466
no. of variables	725	608	478
R, R_w	0.0432, 0.0372	0.0306, 0.0276	0.0603, 0.0563
R, R_w for all data	0.0849, 0.0397	0.0491, 0.0293	0.1325, 0.0689
goodness of fit, S	1.48	1.22	1.45
max shift/esd	0.39	0.07	0.148
min, max peaks in diff map (e·Å^{-3})	–0.66, 0.95	–0.49, 0.47	–1.15, 0.68

[a] Unit cell parameters were obtained by least squares refinement vs the number of reflections shown, in the 2θ range given. [b] Siemens *R*3*m*/*V* autodiffractometer with a graphite monochromator and a Siemens LT-1 inert-gas (N_2) low-temperature delivery system. For **2** and **3**, data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections; instability corrections were obtained and applied as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *31*, 1511. For **4**, four check reflections were remeasured after every 196 reflections; data processing was carried out with *SHELXTL-PLUS* (Sheldrick, G. M., *SHELXTL-PLUS*, Version 4.1; Siemens X-Ray Analytical Instruments, Inc.: Madison, WI, 1989). All structures were refined with *SHELXTL-PLUS*. [c] All structures were refined with *SHELXTL-PLUS* (reference in footnote *b*). Relevant expressions are as follows: function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma|F_o|)^{-2}$, $R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

ν_{CO} 2003 (w), 1984 (s), 1946 (m), 1906 (w) cm^{-1}; MS (CI$^+$) (HRMS (CI$^+$) isotope peak cluster pattern matches that calculated for $C_{47}H_{43}O_5P_5Ru_3$) *m*/*z* 1148 (MH$^+$, 100).

$Ru_3(CO)_5[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2(PEt_3)$ (**8**) was eluted from silica using a 20% EtOAc–hexane (v/v) solution to afford an orange powder (83 mg, 38%): ^{1}H NMR (CDCl$_3$) δ 8.45 (m, 4H), 8.21 (m, 4H), 7.72 (m, 4H), 7.21 (m, 4H), 6.95 (m, 4H), 6.73 (m, 4H), 6.55 (m, 4H), 1.4 (m, 6H), 0.80 (t, $^2J_{H-H}$ = 6.9 Hz, 5H), 0.71 (m, 4H); ^{31}P{H} δ 219.0 (m), 195.1 (m), 164.0 (m), 156.0, 53.0 (s); IR (CH$_2$Cl$_2$) ν_{CO} 1950 (s), 1995 (s), 2024 (m), 2065 (w) (m) cm^{-1}; MS (CI$^+$) *m*/*z* 1148 (MH$^+$, 100).

Crystallographic Analysis. For each substance, a single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Nicolet *R*3*m* autodiffractometer, where it was maintained in a cold (–100 °C) stream of dry nitrogen for the duration of the diffraction experiments. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystals for intensity data collection.[14] A summary of the pertinent crystal data and details of the X-ray diffraction data collection and processing are presented in Table 8. Crystallographic coordinates for **2**–**4** were given in Tables 1, 3, and 5, respectively. The measured intensities were reduced and assigned standard deviations, including corrections for absorption based on the measured crystal shape.[14]

The structures were solved by the heavy-atom method, using heavy-atom positions determined from sharpened Patterson maps. All three structures were refined by the full-matrix least-squares method, using the program *SHELXTL-PLUS*.[15] Neutral atom scattering factors for H, C, O, P, and Ru were used, including

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(14) Crystals of **2** and **3** were of excellent quality and gave X-ray diffraction peaks that were symmetrical and sharp. However, compound **4**, which was available as only a minor product, formed poor crystals. The best crystal of **4** that was obtained from numerous recrystallization attempts gave diffraction maxima that were both wider and less symmetrical than desired, so the intensity data collection was carried out with wider ω-scans than we usually employ. These intensity data were collected at a rapid constant scan speed to allow us to elucidate the structure, in hopeful (but unrealized) anticipation of later availability of better crystals for recollection data. Because of the unusual nature of this structure (monocapped square pyramidal Ru_5 cluster, not edge-bridged), we report here the results based on this rapid data collection. As can be seen from the internal agreement of crystallographically independent but chemically similar structural parameters, the quality of structural results is perhaps better than might have been anticipated.

real and imaginary corrections for anomalous dispersion. In the structure refinement of 4, each hydrogen atom was constrained to ride on the C atom to which it was attached, with isotropic *U* values fixed at 0.08 Å^2.

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths, angles, and torsion angles for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters, and bond lengths and angles for hydrogen atoms for structures 2–4 (46 pages). Ordering information is given on any current masthead page.

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(15) Data reductions for 2 and 3 were carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr., Cryst. Chem.* **1976**, *B32*, 381. Data reduction for 4 was carried out with *SHELXTL-PLUS*, Version 4.1 (Siemens X-ray Analytical Instruments, Inc.: Madison, WI, 1989). Other crystallographic calculations employed the *SHELXTL-PLUS* program package.