η^6-Triphosphabenzene, η^5-Triphosphacyclohexadienyl, and η^5-Diphosphacyclopentadienyl Complexes of Group 8 and 9 Metals: Heterocycle Transformations at the Metal Center

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The reactivity of a 1,3,5-triphosphabenzene, $P_3C_3Bu^t_3$, and a triphosphacyclohexadienyl anion, $[MeP_3C_3Bu^t_3]^-$, toward a range of group 8 and 9 halide complexes has been investigated. The anion reacts with $FeCl_2$ to give the known tetraphosphaferrocene $[Fe(\eta^5\text{-}1,3\text{-}P_2C_3Bu^t_3)_2]$ and an unusual heterocage complex, $[(\eta^5\text{-}1,3\text{-}P_2C_3Bu^t_3)Fe\{P_2(PMe)_2(CBu^t)_3\}]$, via phosphinidene elimination and intramolecular phosphinidene transfer reactions, respectively. The reactions of $P_3C_3Bu^t_3$ or $[MeP_3C_3Bu^t_3]^-$ with $[Cp^*Ru(NCMe)_3][PF_6]$ have afforded $[Cp^*Ru(\eta^6\text{-}P_3C_3Bu^t_3)][PF_6]$ and the first example of a triphosphacyclohexadienyl−transition metal complex, $[Cp^*Ru\{\eta^5\text{-}(MeP)P_2C_3Bu^t_3\}]$. The latter can also be prepared by treating $[Cp^*Ru(\eta^6\text{-}P_3C_3Bu^t_3)][PF_6]$ with MeLi. Similarly, the reaction of $[Cp^*Ru(\eta^6\text{-}P_3C_3Bu^t_3)][PF_6]$ with $LiAlH_4$ has yielded the 2-H-triphosphacyclohexadienyl complex $[Cp^*Ru\{\eta^5\text{-}P_3C_2Bu^t_2(CHBu^t)\}]$. Treatment of $[Rh(COD)Cl]_2$ with $P_3C_3Bu^t_3$ in the presence of $Na[BAr^f_4]$, $Ar^f = C_6H_3(CF_3)_2$-3,5, gave the complex $[(COD)Rh(\eta^6\text{-}P_3C_3Bu^t_3)][BAr^f_4]$, which when reacted with either water or ethanol afforded the 1,1-addition products $[(COD)Rh\{\eta^5\text{-}[(H)(RO)P]P_2C_3Bu^t_3\}][BAr^f_4]$, R = H or Et. The mechanisms of the various heterocycle transformation reactions are discussed, and the X-ray crystal structures of all new complexes are reported.

Introduction

The coordination chemistry of ligand systems containing low-coordinate λ^3-phosphorus centers has rapidly expanded over the last two decades.[1] It has become clear that these ligands can display many similarities to their classical hydrocarbon counterparts, so much so that phosphorus has been coined "The Carbon Copy" in the title of a recent book devoted to the subject.[1a] Despite these similarities, low-coordinate phosphorus ligands were largely thought of as chemical curiosities that would have little practical application, a result of the reactive nature of their P−C multiple bonds. This view is quickly changing, as it is being realized that the special electronic properties of cyclic and acyclic low-coordinate phosphorus ligands can be harnessed in transition metal complexes that show high activity and selectivity in a variety of catalytic processes.[1c]

Most relevant to the work reported here are complexes of monophosphabenzenes (phosphinines). Examples incorporating kinetically stabilized phosphinines, η^1-P-coordinated to rhodium(I) fragments, have been shown by Breit et al. to be highly active and selective catalysts for the hydroformylation of olefins.[2] In addition, complexes containing η^6-phosphinines are well known, and examples have been utilized as catalysts for the synthesis of pyridines from alkynes and nitriles[3] and the cyclodimerization of 1,3-butadiene.[4] Moreover, treatment of phosphinines with alkyllithium reagents yields 1-R-phosphacyclohexadienyl anions, which in a few cases have been shown to participate in salt elimination reactions with metal halides to give η^5-phosphacyclohexadienyl−transition metal complexes.[1] Le Floch et al. have recently utilized this and other routes to prepare phosphacyclohexadienylrhodium(I) complexes, e.g., $[Rh(COD)(\eta^5\text{-}Bu^tPC_4Ph_4)]$, and have demonstrated their effectiveness as catalysts for the selective hydroformylation of a range of olefins under mild conditions.[5]

Of late, our research interests in low-coordination phosphorus chemistry have stretched to the 1,3,5-triphosphabenzene, $P_3C_3Bu^t_3$, **1**.[6,7] Photoelectron spectroscopic studies have shown that the LUMOs of this heterocycle in the complexes $[M(CO)_3(\eta^6\text{-}P_3C_3Bu^t_3)]$, M = Cr, Mo, or W, are lower in energy than in the cor-

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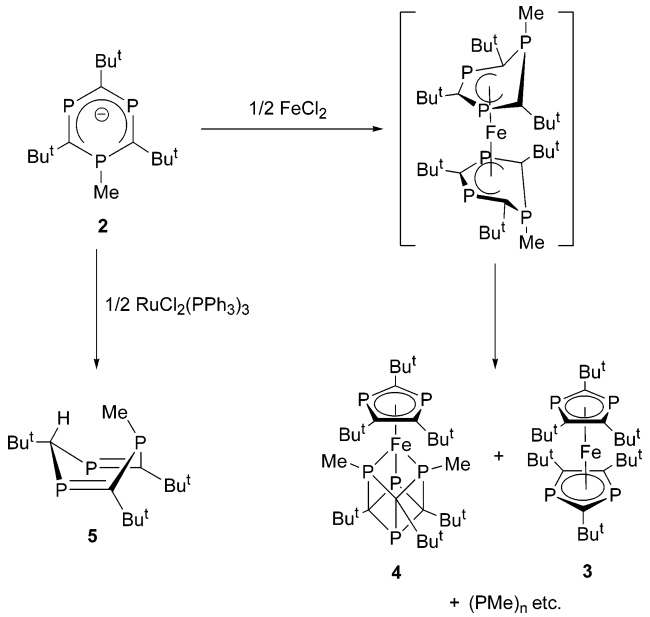
responding arene complexes, $[M(CO)_3(\eta^6\text{-}C_6H_3Bu^t_3)]$.[8] As a result, there is a greater degree of metal to ligand back-bonding in the former, which leads to a stronger coordination of this heterocycle. Despite this, only a handful of spectroscopically characterized $\eta^6\text{-}P_3C_3Bu^t_3$ complexes (with group 6−8 metal fragments) are known,[8,9] and the only crystallographically characterized example has the ligand bridging two scandium(I) centers, $[\{Sc(1,2,4\text{-}P_3C_2Bu^t_3)\}_2(\mu\text{-}\eta^6\text{-}P_3C_3Bu^t_3)]$.[10] In addition to these complexes, several η^1-complexes of **1** with square planar Pt(II) fragments have been reported.[11] One aim of this study was to extend the η^6-coordination chemistry of **1** to the preparation of group 8 and 9 metal complexes, which could possibly lead to catalytic applications (cf. η^6-phosphinine chemistry). It was also thought of sufficient interest to prepare η^5-triphosphacyclohexadienyl complexes of these metals for the same purpose (cf. η^5-phosphacyclohexadienyl chemistry). Such complexes are unknown, but the recently reported syntheses of lithium triphosphacyclohexadienyl salts, e.g., $[Li][RP_3C_3Bu^t_3]$, from **1** and alkyllithium reagents, RLi, lent hope to this cause.[12] It seemed these salts could be reacted with transition metal halides to give the desired complexes. The sometimes unexpected results of our investigations in these areas are reported herein.

Results and Discussion

Group 8 Chemistry. Dimroth et al. reported the synthesis of a range of bis(phosphacyclohexadienyl)iron complexes by reaction of phosphacyclohexadienyl anions with $FeCl_2$ in 1985.[13] A subsequent crystal structure analysis of one of these sandwich complexes, $[Fe(MePC_5Ph_2H_2Bu^t)_2]$, showed the heterocycles to be η^5-coordinated to the metal center.[14] In an attempt to form a hexaphospha analogue of these complexes, the triphosphacyclohexadienyl anion, $[MeP_3C_3Bu^t_3]^-$, **2**,[12] was reacted with $FeCl_2$ in a 2:1 stoichiometry. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture suggested the presence of several products. Upon workup, two were isolated as crystalline solids in low to moderate yields, viz., the known tetraphosphaferrocene, **3**,[15] and the unusual organometallic cage complex, **4** (Scheme 1). It seems likely that the intermediate in this reaction is the expected complex $[Fe(\eta^5\text{-}MeP_3C_3Bu^t_3)_2]$, but this subsequently eliminates 2 equiv of the phosphinidene (PMe) to give **3** or undergoes an intramolecular phosphinidene transfer reaction to give **4**. Both transformations must be facile, as following the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed no evidence of the intermediate. In addition, both **3** and **4** had formed after 5 min

Scheme 1



at 25 °C. The eliminated phosphinidene fragments in the reaction gave rise to the known cyclophosphanes $(PMe)_n$,[16] as evidenced by the presence of multiplet signals centered at ca. δ 10 ppm in the ^{31}P NMR spectrum of the reaction mixture. It is noteworthy that the lithium salt of **2** also eliminates PMe to give the diphosphacyclopentadienyl anion, $[1,3\text{-}P_2C_3Bu^t_3]^-$, but only on heating in THF at reflux for 3 h.[17] Therefore, it seems that coordination of **2** to iron significantly lowers the energy barrier to this elimination process. We have demonstrated similar chemistry with the p-block element halides, TlCl, "GaI", $SnCl_2$, and $PbCl_2$, which react with **2** to give the corresponding mono- or bis(diphosphacyclopentadienyl) complexes $[M(P_2C_3Bu^t_3)_n]$, $n = 1$ or 2, in good yield.[18] This is of synthetic importance because, until recently,[19] synthetic routes to the anion $[P_2C_3Bu^t_3]^-$ were difficult and low yielding, and its homoleptic complexes are still rare.

In contrast to the reaction with $FeCl_2$, when **2** was reacted with $[RuCl_2(PPh_3)_3]$ in THF, the only product recovered (ca. 60% yield) was the known triphosphacyclohexa-1,4-diene, **5**[20] (Scheme 1). This is a recognized hydrolysis product of **2**, but cannot arise from the presence of water in this case because the exclusion of moisture from the reaction mixture was rigorous. Instead, it likely derives from hydrogen abstraction from the THF solvent. Indeed, **5** was also produced in small amounts in the iron reaction. It is not known why these differences occur, but it is worth mentioning that we have seen high yields of **5** arise from reactions of **2** with group 4 to 7 metal halides.[18]

The spectroscopic data for **4** are consistent with its proposed structure. Most informative is its $^{31}P\{^1H\}$ NMR spectrum, which displays four signals, one for the

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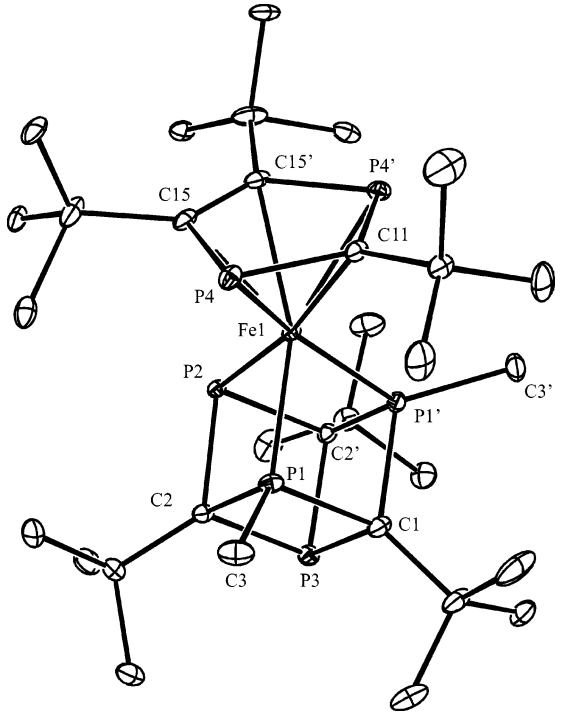
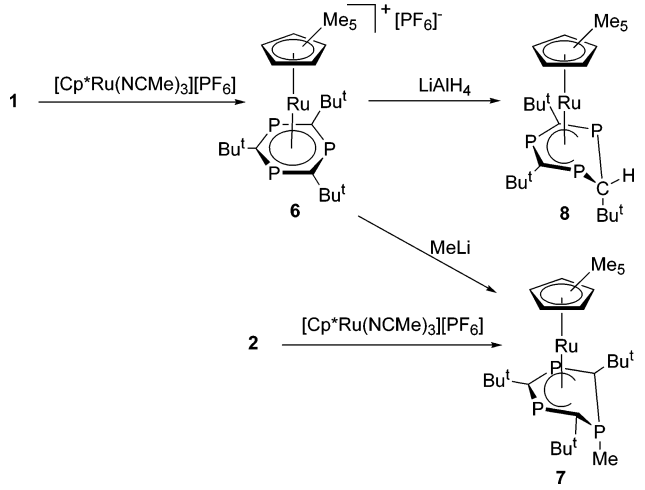


Figure 1. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [(η^5-1,3-$P_2C_3Bu^t_3$)Fe{P_2($PMe)_2$-($CBu^t)_3$}] (**4**); hydrogen atoms are omitted for clarity. Fe(1)−P(1) 2.1570(10), Fe(1)−P(2) 2.3013(13), Fe(1)−P(4) 2.3287(10), Fe(1)−C(11) 2.254(5), Fe(1)−C(15) 2.217(3), P(4)−C(11) 1.742(3), P(4)−C(15) 1.796(4), P(1)−C(3) 1.837(4), P(1)−C(2) 1.855(3), P(1)−C(1) 1.890(4), P(2)−C(2) 1.937(3), P(3)−C(1) 1.881(5), P(3)−C(2) 1.902(4), P(1)−Fe(1)−P(1′ 74.53(5), P(1)−Fe(1)−P(2) 74.38(4), C(2)−P(1)−C(1) 87.23(19), C(2)−P(1)−Fe(1) 100.99(11), C(1)−P(1)−Fe(1) 98.54(11), C(2)−P(2)−C(2′ 85.1(2), C(2)−P(2)−Fe(1) 93.69(11), C(1)−P(3)−C(2) 86.15(15), C(2)−P(3)−C(2′ 87.0(2), P(3)−C(1)−P(1) 93.08(19), P(1)−C(1)−P(1′ 87.4(2), P(1)−C(2)−P(3) 93.54(16), P(1)−C(2)−P(2) 90.65(15), P(3)−C(2)−P(2) 93.78(16). Symmetry transformation used to generate equivalent atoms ′: x, $-y+1/2$, z.

heterocycle (δ 57.2 ppm) and three for the heterocubane moiety. The signal for the two chemically equivalent methylated P-centers, which are coordinated to the iron atom, appears as a singlet, δ 49.1 ppm, while the other tertiary P atom and the iron-coordinated phosphide center resonate at δ 106.5 and 94.0 ppm, respectively. These doublet signals ($^2J_{PP}$ = 18.0 Hz) are at relatively low field due to the strain in the heterocubane fragment, which gives rise to bonds of high p-character to these P atoms. A similar, though more pronounced, phosphorus deshielding has been reported for the tetraphosphacubane, $P_4C_4Bu^t_4$, δ 257 ppm.[21]

The molecular structure of this unusual complex is depicted in Figure 1 (see also Table 1) and shows it to contain a delocalized diphosphacyclopentadienyl ring η^5-coordinated to the iron center which forms one vertex of a P_4C_3Fe heterocubane fragment. The geometry of the heterocycle is similar to that in other complexes incorporating it, e.g., [Cp*Fe(η^5-$P_2C_3Bu^t_3$)],[22] while the geometry of the heterocubane is strained, with intracage angles ranging from 74.38(4) to 100.99(11)°. Its P−C bond lengths are in the normal range,[23] as are the Fe−P bonds. Perhaps surprisingly, however, the dative P(1)−Fe(1) bonds [2.1570(10) Å] are significantly shorter than the phosphide P(2)−Fe(1) interaction [2.3013(13) Å].

Scheme 2



To extend the η^6-coordination chemistry of the triphosphabenzene **1**, and to generate potential precursors for triphosphacyclohexadienyl complexes, **1** was reacted with [Cp*Ru(NCMe)$_3$]PF_6 to give a good yield of the desired complex, **6**, after recrystallization from a dichloromethane/hexane solution (Scheme 2). Surprisingly, treatment of **1** with [Cp*Fe(NCMe)$_3$]PF_6 led to no reaction, perhaps because the smaller covalent radius of iron (1.16 Å) compared to that of ruthenium (1.24 Å)[24] disfavors η^6-coordination of the heterobenzene. When **6** was reacted with 1 equiv of MeLi, the first example of a η^5-triphosphacyclohexadienyl complex, **7**, resulted from nucleophilic attack at a P-center of the heterocycle. This is favored over attack at the C-centers of the heterocycle due to the polarization of its $^{\delta+}$P−C$^{\delta-}$ bonds. The isolated yield from this reaction was low (ca. 10%), and so an alternative synthetic route was devised whereby [Cp*Ru(NCMe)$_3$]PF_6 was treated with the anion **2** in a salt elimination reaction to give **7** in a 40% isolated yield.

An attempt was also made to prepare the secondary phosphine analogue of **7** by treating **6** with a 10-fold excess of a hydride source, $LiAlH_4$. However, after aqueous workup, an isomer of the expected product containing a saturated C-center within the heterocycle was obtained, viz., **8**. Although the isolated yield of this compound was again low (22%), the ^{31}P NMR spectrum of the workup solution suggested **8** was the major product. Presumably, this compound proved difficult to crystallize in high yields because of its high solubility in hexane. It is believed that **8** forms via its expected secondary phosphine isomer, which undergoes a rapid P to C hydrogen migration reaction. Closely related migrations have been proposed for the conversion of the 1-H-phosphacyclohexadienyl complex [CpFe{η^5-(H)$PC_5H_2Ph_3$}] to its 2-H- and 3-H-isomers, [CpFe{η^5-(H)(Ph)$CPC_4H_2Ph_2$}] and [CpFe{η^5-$(H)_2CPC_4HPh_3$}], in the presence of a hydride source.[25] Complex **8** does not arise

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Table 1. Summary of Crystallographic Data for Compounds 4 and 6−11

	4	**6**·CH_2Cl_2	**7**	**8**	**9**	**10**·CH_2Cl_2	**11**
empirical formula	$C_{32}H_{60}FeP_6$	$C_{26}H_{44}Cl_2F_6P_4Ru$	$C_{26}H_{45}P_3Ru$	$C_{25}H_{43}P_3Ru$	$C_{55}H_{51}BF_{24}P_3Rh$	$C_{56}H_{55}BCl_2F_{24}OP_3Rh$	$C_{57}H_{57}BF_{24}OP_3Rh$
fw	686.47	766.46	551.60	537.57	1374.59	1477.53	1420.66
cryst syst	orthorhombic	triclinic	cubic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	*Pnma*	$P\bar{1}$	$Pa\bar{3}$	$Pca2_1$	*Pbca*	$P2_1/c$	$P2_1/n$
a (Å)	19.965(4)	9.610(2)	17.555(2)	17.890(4)	24.974(5)	14.960(3)	12.786(3)
b (Å)	16.184(3)	12.153(2)	17.555(2)	10.162(2)	18.245(4)	17.488(4)	26.238(5)
c (Å)	11.299(2)	14.980(3)	17.555(2)	14.624(3)	25.181(5)	25.741(5)	17.885(4)
α (deg)	90	84.85(3)	90	90	90	90	90
β (deg)	90	74.47(3)	90	90	90	91.23(3)	90.30(3)
γ (deg.)	90	84.90(3)	90	90	90	90	90
vol (Å^3)	3650.9(13)	1675.0(6)	5410.1(11)	2658.6(9)	11474(4)	6733(2)	6000(2)
Z	4	2	8	4	8	4	4
ρ (calcd) (g·cm^{-3})	1.249	1.520	1.354	1.343	1.592	1.458	1.573
μ (mm^{-1})	0.696	0.868	0.769	0.780	0.497	0.507	0.479
F(000)	1472	784	2320	1128	5536	2976	2872
cryst size (mm)	0.20 × 0.20 × 0.15	0.25 × 0.23 × 0.15	0.35 × 0.30 × 0.30	0.40 × 0.30 × 0.15	0.20 × 0.20 × 0.10	0.25 × 0.15 × 0.10	0.20 × 0.15 × 0.10
θ range (deg)	3.26 to 26.02	2.91 to 25.32	3.28 to 26.36	3.03 to 27.48	3.14 to 26.36	2.95 to 26.34	3.04 to 26.33
no. of reflns collected	19 083	23 827	23 185	15 654	71 092	48 820	54 678
R_{int}	0.0501	0.1172	0.0678	0.0411	0.0875	0.1039	0.1025
no. of data/restraints/params	3696/18/233	6065/42/367	1836/12/114	5570/1/277	11 662/24/797	13 602/24/845	12 159/71/963
goodness of fit on F^2	1.117	1.044	1.098	1.034	1.020	1.062	1.024
R1 indices $[I > 2\sigma(I)]^a$	0.0602	0.0498	0.0527	0.0289	0.0534	0.0621	0.0608
*w*R2 indices (all data)^b	0.1544	0.1288	0.1432	0.0605	0.1364	0.1705	0.1498
largest peak and hole (e·A^{-3})	1.926 (near Fe1) and −0.528	0.755 and −0.777	0.756 and −0.401	0.412 and −0.445	0.883 and −0.614	0.879 and −0.908	0.842 and −1.026

^{a} $R1(F) = \{\sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. ^{b} $wR2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o^2|^2\}^{1/2}$ where w is the weight given each reflection.

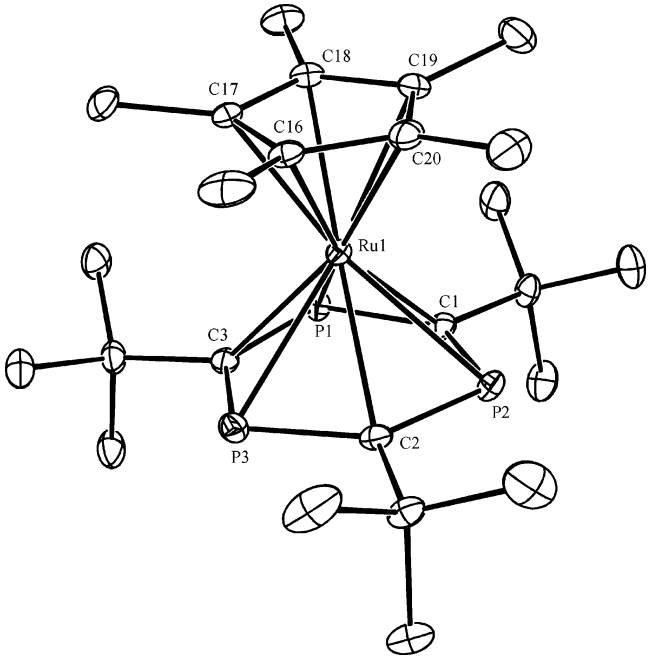

Figure 2. Thermal ellipsoid plot (25% probability surface) of the cationic component of [Cp*Ru(η^6-$P_3C_3Bu^t_3$)][PF_6] (**6**); hydrogen atoms are omitted for clarity. Ru(1)−C(1) 2.341(4), Ru(1)−C(2) 2.353(4), Ru(1)−C(3) 2.357(4), Ru(1)−P(2) 2.4842(13), Ru(1)−P(1) 2.4857(15), Ru(1)−P(3) 2.4908(14), P(1)−C(3) 1.748(5), P(1)−C(1) 1.750(5), P(2)−C(2) 1.744(4), P(2)−C(1) 1.756(5), P(3)−C(2) 1.753(5), P(3)−C(3) 1.756(5), C(3)−P(1)−C(1) 107.7(2), C(2)−P(2)−C(1) 107.0(2), C(2)−P(3)−C(3) 107.4(2), P(1)−C(1)−P(2) 132.6(3), P(2)−C(2)−P(3) 132.9(3), P(1)−C(3)−P(3) 132.0(3).

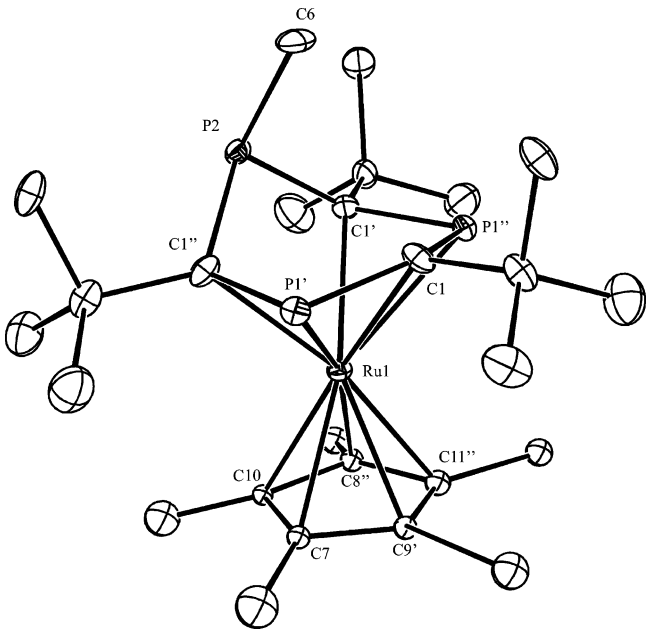

Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [Cp*Ru{η^5-(MeP)$P_2C_3Bu^t_3$}] (**7**); hydrogen atoms are omitted for clarity. Ru(1)−C(1) 2.328(14), Ru(1)−P(1)′ 2.448(10), C(1)−P(1)′ 1.802(5), C(1)−P(1)″ 1.781(5), P(2)−C(1)′ 1.829(6), P(2)−C(1)″ 1.841(6), P(1)′−C(1)−P(1)″ 116.4(3), C(1)−P(1)′−C(2)″ 99.6(3), C(1)′−P(2)−C(1)″ 96.4(3). Symmetry transformations used to generate equivalent atoms ′: y, z, x; ″: z, x, y.

from the aqueous workup of the reaction, as the ^{31}P NMR spectrum of the reaction mixture prior to quenching shows **8** as the major product. In addition, treating **6** with 1 M HCl or NaOH solutions did not yield **8** but gave compound mixtures of unknown identity.

The $^{31}P\{^1H\}$ NMR spectra for the complexes **6**−**8** are compatible with their proposed formulations. That for **6** displays a singlet resonance for the heterocycle at δ 25.3 ppm, considerably upfield of the resonance for the free triphosphabenzene, δ 257 ppm,[6] but close to that of related complexes, e.g., [Ru(η^4-COD)(η^6-$P_3C_3Bu^t_3$)] δ 59.0 ppm.[9] The spectra for **7** and **8** both exhibit AX_2 systems, the signals for which in the spectrum of **7** [δ −35.2 ppm (P_A), 30.9 ppm (P_X)] have shifted significantly from those for the lithium salt of the free anion, **2** [δ −91.5 ppm (P_A), 192.4 ppm (P_X)].[12] In addition, the doublet signal in the spectrum of **8** [δ −111.4 ppm (P_X)] is at much higher field than the triplet resonance [δ 34.9 ppm (P_A)]. Moreover, this signal is at higher field than the region that might be expected for a coordinated P−C multiple bond. There is a precedent for such a high-field shift in the ^{31}P NMR spectrum of the aforementioned 2-H-phospacyclohexadienyl complex, [CpFe{η^5-(H)(Ph)$CPC_4H_2Ph_2$}], the phosphorus center of which resonates at δ −173.0 or −150.1 ppm for its *exo*- and *endo*-isomers, respectively.[25]

The structure of the cationic component of **6** is depicted in Figure 2 and represents the first structural characterization of a nonbridging η^6-triphosphabenzene complex. Its heterocycle is essentially planar, with P−C bond lengths that are similar [1.751 Å av] and suggestive of delocalization within the ring. Not surprisingly, these are longer than those in the free heterocycle [1.723 Å av],[26] but shorter than the P−C bonds in the triphosphabenzene-bridged complex [{Sc(1,2,4-$P_3C_2Bu^t_3$)}$_2$(μ-η^6-$P_3C_3Bu^t_3$)] [1.803 Å av].[10] The distance from the Ru-center to the heterocycle centroid [1.677 Å] is significantly less than the Ru−Cp* ring centroid separation [1.864 Å].

The molecular structures of the triphosphacyclohexadienyl complexes, **7** and **8**, are shown in Figures 3 and 4, respectively. In both, the heterocycle and Cp* ligands are η^5-coordinated to the metal center, while the alkyl substituents of the saturated heterocyclic centers are in *exo*-positions. The P−C bonds within each delocalized heteropentadienyl fragment are similar [**7** 1.781 Å av; **8** 1.767 Å av] and comparable to those in **6**. Moreover, the Cp* centroid−Ru distances and the heteropentadienyl fragment centroid−Ru separations are identical for both complexes. viz., 1.886 and 1.674 Å, respectively.

Group 9 Chemistry. In attempts to prepare group 9-triphosphacyclohexadienyl complexes, a number of reactions were carried out between the anion **2** and group 9 halide complexes, e.g., $CoCl_2$, [RhCl(COD)]$_2$, [IrCl(COD)]$_2$, [$RhCl(PPh_3)_3$], and [Ir(CO)Cl(PPh_3)$_2$]. In all cases, inseparable mixtures of products resulted, which included the triphosphacyclohexadiene **5**. It was believed that an alternative route to such complexes could involve the synthesis of η^6-triphosphabenzene complexes, which could then be treated with nucleophiles or other reagents, cf. the preparation of **7** and **8**. Le Floch et al. have recently demonstrated the effectiveness of this approach with the synthesis of the first Rh-

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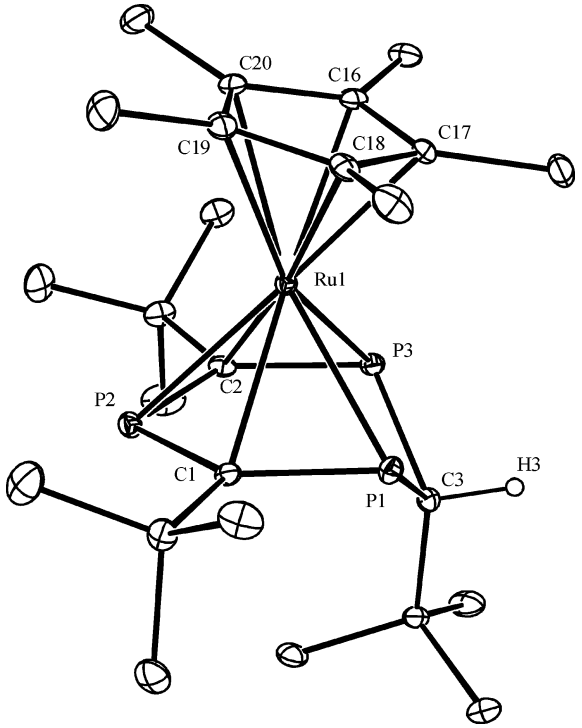
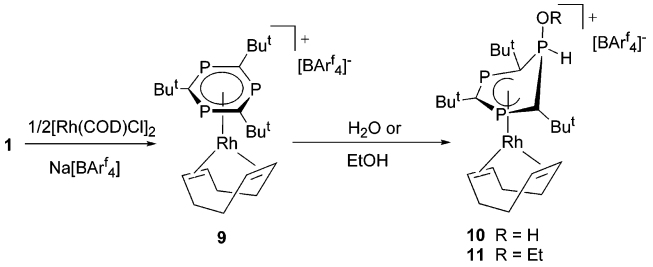


Figure 4. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [Cp*Ru{η^5-$P_3C_2Bu^t_2(CHBu^t)$}] (**8**); methyl hydrogen atoms are omitted for clarity. Ru(1)−C(2) 2.264(3), Ru(1)−C(1) 2.274(3), Ru(1)−P(3) 2.4066(9), Ru(1)−P(1) 2.4118(9), Ru(1)−P(2) 2.4599(10), P(1)−C(1) 1.778(3), P(1)−C(3) 1.857(3), P(2)−C(1) 1.757(3), P(2)−C(2) 1.765(3), P(3)−C(2) 1.768(4), P(3)−C(3) 1.850(3), C(1)−P(1)-C(3) 107.51(14), C(1)−P(2)−C(2) 104.59(14), C(2)−P(3)−C(3) 108.18(13), P(2)−C(1)−P(1) 127.47(17), P(2)−C(2)−P(3) 127.23(16), P(3)−C(3)−P(1) 96.63(15).

(I) and Ir(I) η^6-monophosphabenzene complexes, e.g., [Rh(η^4-COD){η^6-$PC_5H(SiMe_3)_2(Ph)_2$}]$^+$, which undergo 1,1-addition reactions with alcohols or water to give the first examples of Rh(I) and Ir(I) phosphacyclohexadienyl complexes, e.g., [Rh(η^4-COD){η^5-$(H)(EtO)PC_5H(SiMe_3)_2$-$(Ph)_2$}]$^+$.[27] It seemed reasonable that similar chemistry could be carried out starting with the triphosphabenzene **1**.

Initial attempts to prepare the cationic complex [Rh(COD)($P_3C_3Bu^t_3$)]$^+$ by treating a mixture of [RhCl(COD)]$_2$ and $P_3C_3Bu^t_3$ in CH_2Cl_2 with $NaBPh_4$ met with failure and led only to the known complex [(COD)Rh{η^6-$(C_6H_5)BPh_3$}][28] and unreacted triphosphabenzene. This presumably occurs as one phenyl arm of the $[BPh_4]^-$ anion successfully competes with the triphosphabenzene for Rh coordination. As a result, the sodium salt of the more weakly coordinating anion, $[BAr^f_4]^-$, Ar^f = $C_6H_3(CF_3)_2$-3,5, was used in this reaction. Although this anion can also coordinate to the [Rh(COD)]$^+$ fragment,[29] in this case it does not and the first triphosphabenzene−group 9 complex, **9**, was formed cleanly and in good yield (Scheme 3). Surprisingly, attempts to prepare the iridium analogue of this complex by an analogous procedure led only to approximately 50% of the triphosphabenzene being consumed

Scheme 3



and an unidentified mixture of other products. Furthermore, treating a mixture of **1** and [RhCl(PPh_3)$_2$]$_2$ with Na[BAr^f_4] led to no Rh coordination of the triphosphabenzene, most probably because of the greater steric demands of two PPh_3 ligands relative to one COD ligand.

We have begun to examine the further chemistry of **9** and have made some interesting observations. First, the triphosphabenzene ligand is not displaced and the complex remains intact when it is treated with large excesses of arenes, e.g., benzene, or two- or four-electron donors such as PPh_3, CO, or bipyridine. This is in contrast to corresponding [Rh(COD)(arene)]$^+$ complexes, the arene ligands of which are generally readily displaced.[27] In the case of **9**, two factors probably hinder displacement of the triphosphabenzene: the steric protection this bulky ligand affords the rhodium center and a stronger interaction with the rhodium center than is normal for arenes. The latter is reasonable considering the known lower energy LUMOs (and greater M→ring back-bonding) of **1** relative to those of arenes in their respective transition metal complexes.[8]

The coordination of **1** also seems to activate it toward attack at its P-centers, as has been found to be the case with monophosphabenzenes. An excellent example of this is the fact that in the uncoordinated state **1** is resistant toward reaction with water or alcohols.[11] However, one P-center of complex **9** readily reacts at 0 °C with an excess of water or ethanol to give the triphosphacyclohexadienyl complexes **10** and **11** as the only phosphorus-containing products in the reaction mixtures (Scheme 3). These 1,1-addition reactions are completely analogous to those involving the aforementioned monophosphabenzene−rhodium(I) cationic complexes reported by Le Floch et al.[27] A number of other reactions were carried out between **9** and precursors that could potentially oxidatively add to its rhodium center or attack a phosphorus center of its heterocyclic ligand. Little success has so far been had here, as **9** was found to be unreactive to excesses of H_2 (5 atm/50 °C) or MeI, while reactions with excess anhydrous HCl, triflic acid, or Et_3SiH led to intractable mixtures of phosphorus-containing products. In addition, and in contrast to other cationic Rh(I) complexes,[30] complex **9** was found to be unreactive toward the oxidative addition of bis(catecholato)diborane.

The $^{31}P\{^1H\}$ NMR spectrum of the triphosphabenzene complex **9** displays a singlet resonance, δ 108.3 ppm, which is considerably downfield of that for the ruthenium complex, **6** (δ 25.3 ppm), but close to the position of the signals in related monophosphabenzene−rho-

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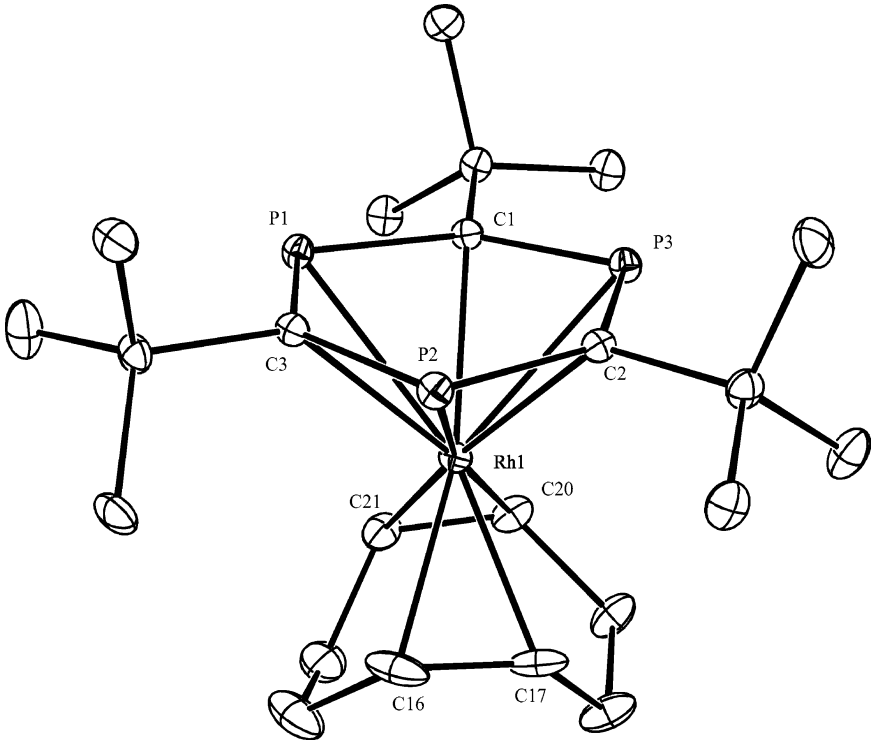

Figure 5. Thermal ellipsoid plot (25% probability surface) of the structure of the cationic component of [(COD)Rh(η^6-$P_3C_3Bu^t_3$)][BAr^f_4] (**9**); hydrogen atoms are omitted for clarity. Rh(1)−C(1) 2.321(4), Rh(1)−C(2) 2.372(4), Rh(1)−C(3) 2.445(4), Rh(1)−P(2) 2.5220(11), Rh(1)−P(3) 2.5293(12), Rh(1)−P(1) 2.5683(12), P(1)−C(3) 1.739(4), P(1)−C(1) 1.766(4), P(2)−C(3) 1.758(4), P(2)−C(2) 1.761(4), P(3)−C(2) 1.745(4), P(3)−C(1) 1.753(4), C(3)−P(1)−C(1) 107.13(18), C(3)−P(2)−C(2) 109.48(18), C(2)−P(3)−C(1) 106.51(18), P(3)−C(1)−P(1) 134.1(2), P(3)−C(2)−P(2) 131.6(2), P(1)−C(3)−P(2) 131.0(2).

dium(I) complexes, e.g., δ 101.4 ppm for [Rh(COD)-{η^6-$PC_5Me_2(SiMe_3)_2$}]$^+$.[27] However, unlike the latter complexes, which generally exhibit small $^1J_{RhP}$ couplings (ca. 10 Hz), no such coupling was observed in the spectrum of **9**. Similarly no Rh−P couplings were seen in the ^{31}P NMR spectra of the 1,1-addition products **10** and **11**, both of which exhibit AX_2 spin systems with the doublet signals (δ 117.0 and 121.1 ppm, respectively) close to the position of the resonance in the spectrum of **9**. The triplet resonances (δ −13.0 and −8.5 ppm, respectively) are at considerably higher field and exhibit large $^1J_{PH}$ couplings (560 and 578 Hz, respectively). The presence of P−H bonds in these complexes was confirmed by the observation of characteristic stretching absorptions in their IR spectra.

An examination of the structure of the cationic component of **9** (Figure 5) showed it to have no significant interaction with the [BAr^f_4]$^-$ anion and to contain an effectively planar triphosphabenzene ligand η^6-coordinated to the rhodium center. The intracyclic P−C bond lengths are similar [1.754 Å av] and close to those in the ruthenium complex, **6**. There is, however, a significant difference between the M−heterocycle centroid distances in the two compounds [**6** 1.677 Å; **9** 1.734 Å], which mirrors the expected smaller covalent radius of Ru(II) relative to Rh(I).

The structures of the cations of the closely related complexes **10** and **11** are very similar and are depicted in Figures 6 and 7, respectively. Both display significant positional disorder within the heterocycles, which, although successfully modeled, does not allow definitive comment to be made on the geometries of those heterocycles. Saying that, it is clear that the diphosphapentadienyl fragments of each are essentially planar and η^5-coordinated to the rhodium centers, as has been seen in the structure of the related iridium(I) complex [Ir(COD){η^5-(H)(EtO)$PC_5(Me)_2(SiMe_3)_2$}]$^+$.[27]

Conclusions

In summary, reactions of the 1,3,5-triphosphabenzene $P_3C_3Bu^t_3$ or the triphosphacyclohexadienyl anion [$MeP_3C_3Bu^t_3$]$^-$ toward a series of group 8 and 9 halide complexes have been investigated. These have given rise to the first examples of triphosphacyclohexadienyl−transition metal complexes and the first structurally characterized complexes containing a nonbridging η^6-coordinated triphosphabenzene ligand. The facility of heterocycle transformations at metal centers has been demonstrated with the nucleophilic attack of a triphosphabenzene within the coordination sphere of a ruthenium(II) fragment to yield either 1-R- or 2-H-triphosphacyclohexadienyl complexes. Formal 1,1-additions of water or ethanol to a phosphorus center of the same heterobenzene, but within the coordination sphere of a rhodium(I) fragment, have yielded related complexes containing zwitterionic triphosphacyclohexadienyl ligands. Evidence has also been presented to show that in the coordination sphere of an iron(II) center the triphosphacyclohexadienyl ligand [$MeP_3C_3Bu^t_3$]$^-$ readily eliminates a phosphinidene fragment, PMe, to give η^5-1,3-diphosphacyclopentadienyl complexes. Taken as a whole, this study has highlighted both similarities and differences in the reactivity of triphosphaheterocycle complexes, compared to that of their monophospha counterparts. Considering the emerging importance of the latter in a range of catalytic applications, there is much scope to extend investigations into the chemistry of the

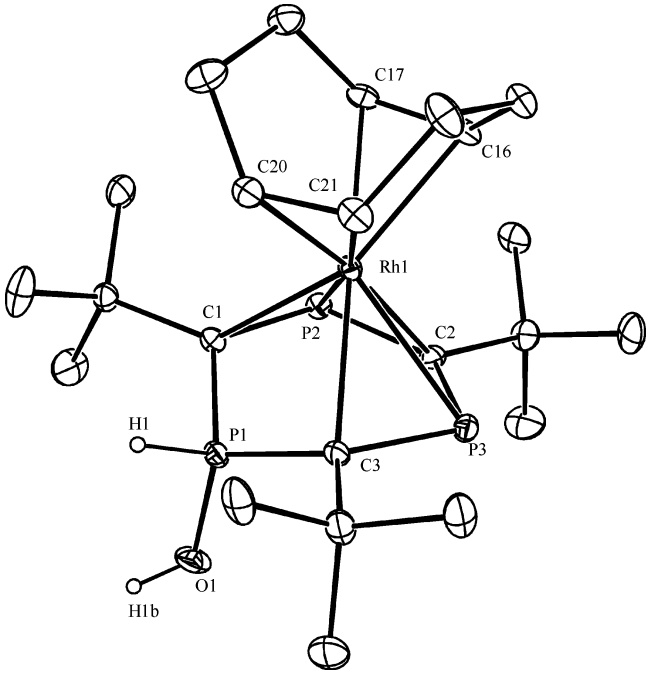

Figure 6. Thermal ellipsoid plot (25% probability surface) of the structure of the cationic component of [(COD)Rh-{η^5-[(H)(HO)P]$P_2C_3Bu^t_3$}][BAr^f_4] (**10**); methyl hydrogen atoms are omitted for clarity. Rh(1)−C(3) 2.300(4), Rh(1)−C(2) 2.331(4), Rh(1)−C(1) 2.410(4), Rh(1)−P(3) 2.4389(13), Rh(1)−P(2) 2.4918(18), P(1)−O(1) 1.565(5), P(1)−C(3) 1.727-(4), P(1)−C(1) 1.749(4), P(2)−C(1) 1.731(4), P(2)−C(2) 1.739(4), P(3)−C(2) 1.766(4), P(3)−C(3) 1.772(4), O(1)−P(1)−C(3) 115.6(2), O(1)−P(1)−C(1) 115.0(2), C(3)−P(1)−C(1) 108.5(2), C(1)−P(2)−C(2) 109.4(2), C(2)−P(3)−C(3) 104.67(19), P(2)−C(1)−P(1) 120.6(2), P(2)−C(2)−P(3) 132.9-(2), P(1)−C(3)−P(3) 124.2(3).

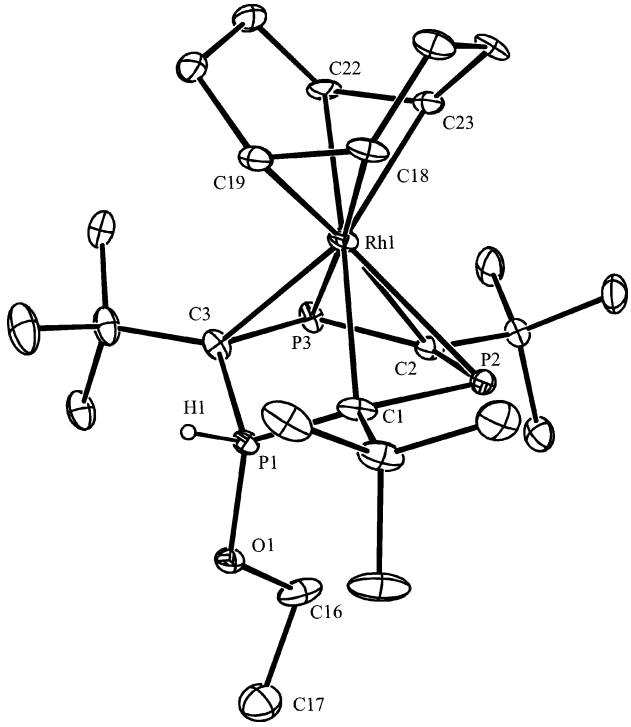

Figure 7. Thermal ellipsoid plot (25% probability surface) of the structure of the cationic component of [(COD)Rh-{η^5-[(H)(EtO)P]$P_2C_3Bu^t_3$}][BAr^f_4] (**11**); carbon bound hydrogen atoms are omitted for clarity. Rh(1)−C(1) 2.312(4), Rh(1)−C(3) 2.361(4), Rh(1)−C(2) 2.389(4), Rh(1)−P(3) 2.4898(14), Rh(1)−P(2) 2.520(1), P(1)−O(1) 1.579(5), P(1)−C(1) 1.628(5), P(1)−C(3) 1.801(5), P(2)−C(2) 1.781(5), P(2)−C(1) 1.857(6), P(3)−C(2) 1.752(5), P(3)−C(3) 1.753(4), O(1)−P(1)−C(1) 119.0(3), O(1)−P(1)−C(3) 116.2(2), C(1)−P(1)−C(3) 108.8(2), C(2)−P(2)−C(1) 99.9(2), C(2)−P(3)−C(3) 108.0(2), P(1)−C(1)−P(2) 125.1(3), P(3)−C(2)−P(2) 135.8-(3), P(3)−C(3)−P(1) 117.4(3).

former. Such studies are ongoing in our laboratory and will be reported in due course.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon. Diethyl ether, hexane, and THF were distilled over Na/K alloy, while CH_2Cl_2 was distilled over CaH_2. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on either Bruker DPX400 or JEOL Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^1H or ^{13}C resonances of the solvent used (^1H and ^{13}C NMR) or external 85% H_3PO_4, δ 0.0 ppm (^{31}P NMR). Mass spectra were recorded using a VG Fisons Platform II instrument operating under APCI conditions or were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were obtained from Medac Ltd. Reproducible microanalyses for compounds **4** and **6**−**8** could not be obtained, but the NMR spectra of bulk samples of these compounds suggested a purity of greater than 95% in each case (see Supporting Information). $P_3C_3Bu^t_3$,[6] [Cp*Ru(NCMe)$_3$]-[PF_6],[31] [Rh(COD)Cl]$_2$,[32] and Na[BAr^f_4][33] were synthesized by literature procedures. All other reagents were used as received.

Preparation of [(η^5-1,3-$P_2C_3Bu^t_3$)Fe{P_2(PMe)$_2$(CBu^t)$_3$}] (4). $P_3C_3Bu^t_3$ (0.150 g, 0.5 mmol) was dissolved in a mixture of THF (10 mL)/tmeda (1 mL) and cooled to −78 °C. To this solution was added a diethyl ether solution of MeLi (0.55 mmol) over 5 min. After 30 min, the reaction mixture was warmed to ambient temperature and stirred for 1 h. Volatiles were removed to give an orange powder. This was dissolved in THF (5 mL) and added over 5 min to a suspension of $FeCl_2$ (32 mg, 0.25 mmol) in THF (15 mL) at −78 °C. The resultant solution was warmed to room temperature and stirred overnight. Volatiles were then removed in vacuo, and the residue was extracted with hexane and filtered. Concentration and slow cooling of the filtrate to −30 °C afforded **4** as deep red crystals (46 mg, 27%). Mp: 286−288 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K): δ 0.93 (s, 9 H, Bu^t), 1.07 (s, 18 H, 2 × Bu^t), 1.25 (s, 9 H, Bu^t), 1.75 (s, 18 H, 2 × Bu^t), 2.42 (m, 6 H, PMe). $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 300 K): δ 49.1 (s, 2 × PMe), 57.2 (s, $P_2C_3Bu^t_3$), 94.0 (d, P(CBu^t)$_2$Fe, $^2J_{PP}$ = 18.0 Hz), 106.5 (br d, P(CBu^t)$_3$, $^2J_{PP}$ = 18.0 Hz). IR ν/cm^{-1} (Nujol): 1262-(s), 1202(s), 919(sh), 883(sh), 829(s), 775(w), 760(w), 721(s), 669(w). MS/EI: *m/z* 686 [M^+, 100%]. Acc. Mass EI$^+$: calc for $C_{32}H_{60}FeP_6$ 686.2465, found 686.2456. NB: after crystallization of **4** from the reaction mixture, chromatography of the mother liquor (silica gel/hexane) yielded [Fe(η^5-$P_2C_3Bu^t_3$)$_2$], **3**, as a blue-green solid in 17% yield. The NMR data for this sample were found to be in agreement with those previously reported.[15]

Preparation of [Cp*Ru(η^6-$P_3C_3Bu^t_3$)][PF_6] (6). To a solution of [Cp*Ru(NCMe)$_3$][PF_6] (0.30 g, 0.59 mmol) in dichloromethane (15 mL) was added a solution of $P_3C_3Bu^t_3$ (0.185 g, 0.62 mmol) in dichloromethane (5 mL) over 5 min at

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0 °C. The resultant solution became orange and was stirred for 4 h at ambient temperature. Volatiles were removed in vacuo, and the residue was washed with hexane and dried in vacuo, leaving a pale yellow solid. This was dissolved in CH_2Cl_2 (1 mL), and the solution slowly diffused into hexane to give **6** as yellow-orange crystals (220 mg, 55%). Mp: 220−222 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.60 (s, 27 H, Bu^t), 1.89 (s, 15 H, Me). ^{13}C NMR (101.6 MHz, CD_2Cl_2, 300 K): δ 12.7 (Me), 35.4 (C(CH_3)$_3$, $^3J_{PC}$ = 12.7 Hz), 43.5 ($C(CH_3)_3$, $^2J_{PC}$ = 23.0 Hz), 101.7 ($C(CH_3)$), CP resonance not observed. ^{31}P{^{1}H} NMR (121.7 MHz, CD_2Cl_2, 300 K): δ 25.3 (s, $P_3C_3Bu^t_3$), −143.9 (sept., PF_6, $^1J_{PF}$ = 712 Hz). IR ν/cm^{-1} (Nujol): 1078(s), 1021(s), 838(s), 721(m). MS/APCI: *m/z* 555 [Cp*Ru($P_3C_3Bu^t_3F$)$^+$, 25%], 536 [M − PF_6, 40%]. Acc. Mass ES$^+$: calc for M − PF_6 ($C_{25}H_{42}P_3Ru$) 537.1537, found 537.1543.

Preparation of [Cp*Ru{η^5-(MeP)$P_2C_3Bu^t_3$}] (7). $P_3C_3Bu^t_3$ (0.150 g, 0.5 mmol) was dissolved in a mixture of THF (10 mL)/tmeda (1 mL) and cooled to −78 °C. To this solution was added a diethyl ether solution of MeLi (0.55 mmol) over 5 min. After 30 min, the reaction mixture was warmed to ambient temperature and stirred for 1 h. Volatiles were removed in vacuo to give an orange powder. This was dissolved in THF (10 mL) and the solution added to a suspension of [Cp*Ru(CH_3CN)$_3$][PF_6] (0.252 g, 0.5 mmol) in THF (15 mL) at −78 °C. The mixture was warmed to ambient temperature and stirred overnight. Volatiles were then removed in vacuo, and the residue was extracted with hexane (5 mL). Placement of this extract at −30 °C overnight yielded **7** as yellow crystals (110 mg, 40%). Mp: 118−121 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.62 (d, 3 H, PMe, $^2J_{PH}$ = 6.1 Hz), 1.48 (s, 18 H, Bu^t), 1.60 (s, 15 H, Me), 1.64 (s, 9 H, Bu^t). ^{13}C NMR (101.6 MHz, C_6D_6, 300 K): δ 10.1 (PMe), 12.7 (Me), 31.9 (m, $P_ACC(CH_3)_3P_X$), 35.5 (tr, $P_XCC(CH_3)_3P_X$, $^3J_{PC}$ = 13.3 Hz), 38.9 (m, $P_ACC(CH_3)_3P_X$), 41.5 (tr, $P_XCC(CH_3)_3P_X$, $^2J_{PC}$ = 19.6 Hz), 93.0 ($C(CH_3)$), CP resonances not observed. ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 300 K): δ 30.9 (d, P_X, $^2J_{PP}$ = 8.9 Hz), −35.2 (tr, P_A, $^2J_{PP}$ = 8.9 Hz). IR ν/cm^{-1} (Nujol): 1261(s), 1213(s), 1022(s), 844(m). MS/APCI: *m/z* 553 [M$^+$, 100%]. Acc. Mass ES$^+$: calc for M$^+$ ($C_{26}H_{45}P_3Ru$) 553.1850, found 553.1851.

Preparation of [Cp*Ru{η^5-$P_3C_2Bu^t_2$(CHBu^t)}] (8). To a suspension of **6** (0.22 g, 0.33 mmol) in diethyl ether (10 mL) was added a solution of $LiAlH_4$ (0.l2 g, 3 mmol) in diethyl ether (25 mL). The resultant mixture was stirred overnight, after which it was quenched with an excess of degassed 1 M HCl (aq). A solution of degassed $NaHCO_3$ (aq) was then added with rapid stirring until the pH was approximately 8. The ether layer was separated, dried over $MgSO_4$, and evaporated. The residue was extracted with hexane (10 mL) and filtered, and the filtrate was placed at −30 °C overnight to give **8** as yellow crystals (39 mg, 22%). Mp: 147−149 °C. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 0.84 (s, 9 H, Bu^t), 1.43 (s, 18 H, Bu^t), 1.77 (s, 15 H, Me), methine resonance obscured. ^{13}C NMR (101.6 MHz, C_6D_6, 300 K): δ 12.1 (Me), 28.5 (br s, $P_XCC(CH_3)_3P_X$), 31.8 (tr, $P_XCC(CH_3)_3P_X$, $^1J_{PC}$ = 38.9 Hz), 34.1 (m, $P_ACC(CH_3)_3P_X$), 35.6 (br s, $P_XCC(CH_3)_3P_X$), 39.9 (m, $P_ACC(CH_3)_3P_X$), 95.6 ($C(CH_3)$), P_ACP_X resonance not observed. ^{31}P NMR (121.7 MHz, C_6D_6, 300 K): δ 34.9 (tr, P_A, $^2J_{PP}$ = 24.0 Hz), −111.4 (d of d, P_X, $^2J_{PP}$ = 24.0 Hz, $^2J_{PH}$ = 15.0 Hz). IR ν/cm^{-1} (Nujol): 1260(s), 1095(s), 1023(s), 802(m). MS/APCI: *m/z* 538 [M$^+$, 100%]. Acc. Mass EI$^+$: calc for M$^+$ ($C_{25}H_{43}P_3Ru$) 538.1616, found 538.1609.

Preparation of [(COD)Rh(η^6-$P_3C_3Bu^t_3$)][BAr^f_4] (9). To a mixture of $P_3C_3Bu^t_3$ (0.15 g, 0.50 mmol) and Na[BAr^f_4] (0.44 g, 0.50 mmol) in dichloromethane (5 mL) at 25 °C was added a solution of [Rh(COD)Cl]$_2$ (0.12 g, 0.25 mmol) in dichloromethane (10 mL). The resultant suspension was stirred overnight, whereupon volatiles were removed in vacuo. The residue was washed with hexane, extracted into dichloromethane (1 mL), and layered with hexane to give red-brown crystals of **9** over 2 days (0.31 g, 46%). Mp: 122−126 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.54 (s, 27 H, Bu^t), 2.16 (m, 8 H, CH_2), 4.84 (s, 4 H, CH), 7.45 (s, 4 H, *p*-ArH), 7.61 (s, 8H, *o*-ArH). ^{13}C NMR (101.6 MHz, CD_2Cl_2, 300 K): δ 31.6 (br s, CH_2), 35.1 (t,$^3J_{PC}$ = 13.1 Hz, CH_3), 44.8 (m, $C(CH_3)_3$), 84.1 (d, CH, $^1J_{RhC}$ = 9.0 Hz), 117.5 (s, *p*-ArC), 124.6 (q, CF_3, $^1J_{CF}$ = 272.2 Hz), 128.7 (q, *m*-ArC, $^2J_{CF}$ = 31.5 Hz), 134.8 (s, *o*-ArC), 161.8 (q, *ipso*-ArC, $^1J_{BC}$ = 50.1 Hz), 163.5 (m, CP). ^{31}P{^{1}H} NMR (121.7 MHz, CD_2Cl_2, 300 K): δ 108.3 (s, $P_3C_3Bu^t_3$). ^{11}B{^{1}H}NMR (94.4 MHz, CD_2Cl_2, 300 K): δ −7.6. ^{19}F{^{1}H} NMR (282.8 MHz, CD_2Cl_2, 300 K): δ −62.71. IR ν/cm^{-1} (Nujol): 1353(s), 1279(s), 1161(s), 888(s), 837(m). MS/EI: *m/z* 511 [M − BAr^f_4, 13%]; 300 [$P_3C_3Bu^t_3{}^+$, 100%]. Anal. Calc for $C_{55}H_{51}BF_{24}P_3Rh$: C 48.06, H 3.74. Found: C 47.23, H 3.70.

Preparation of [(COD)Rh{η^5-[(H)(HO)P]$P_2C_3Bu^t_3$}][BAr^f_4] (10). To a solution of **9** (150 mg, 0.11 mmol) in dichloromethane (10 mL) at −78 °C was added H_2O (10 μL, 0.55 mmol). After 10 min the solution was warmed to room temperature and stirred overnight. Volatiles were then removed in vacuo, and the residue was washed with hexane, extracted into dichloromethane (1 mL), and layered with hexane (10 mL) to give red-brown crystals of **10** after 2 days (0.09 g, 52%). Mp: 86−92 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.33 (s, 9 H, Bu^t), 1.45 (s, 18 H, Bu^t), 2.21 (m, 8 H, CH_2), 4.62 (s, 4H, CH), 7.42 (d, 1 H, PH, $^1J_{PH}$ = 560 Hz) 7.45 (s, 4 H, *p*-ArH), 7.62 (s, 8H, *o*-ArH), OH resonance not observed. ^{13}C NMR (101.6 MHz, CD_2Cl_2, 300 K): δ 31.5 (br s, CH_2), 33.0 (m, $P_ACC(CH_3)_3P_X$), 34.4 (t,$^3J_{PC}$ = 11.1 Hz, $P_XCC(CH_3)_3P_X$), 39.4 (m, $P_ACC(CH_3)_3P_X$), 43.2 (m, $P_XCC(CH_3)_3P_X$), 80.3 (d, CH, $^1J_{RhC}$ = 12.1 Hz), 117.5 (s, *p*-ArC), 124.6 (q, CF_3, $^1J_{CF}$ = 272.2 Hz), 128.9 (q, *m*-ArC, $^2J_{CF}$ = 31.1 Hz), 134.8 (s, *o*-ArC), 161.5 (q, *ipso*-ArC, $^1J_{BC}$=50.4 Hz), PC resonances not observed. ^{31}P{^{1}H} NMR (121.7 MHz, CD_2Cl_2, 300 K): δ 117.3 (d, P_x, $^2J_{PP}$ = 14.9 Hz), −13.1 (t, P_A, $^2J_{PP}$ = 14.9 Hz). ^{11}B{^{1}H} NMR (94.4 MHz, CD_2Cl_2, 300 K): δ −7.6. ^{19}F{^{1}H} NMR (282.8 MHz, CD_2Cl_2, 300 K): δ −62.73. IR ν/cm^{-1} (Nujol): 2358(m), P−H. MS/EI: *m/z* 529 [M − BAr^f_4, 100%]. Acc. Mass ES$^+$: calc for M − BAr^f_4 ($C_{23}H_{41}OP_3Rh$) 529.1420, found 529.1424. Anal. Calc for $C_{55}H_{53}BF_{24}OP_3Rh$ (vacuum-dried sample): C 47.44, H 3.84. Found: C 47.02, H 3.78.

Preparation of [(COD)Rh{η^5-[(H)(EtO)P]$P_2C_3Bu^t_3$}][BAr^f_4] (11). To a solution of **9** (150 mg, 0.11 mmol) in dichloromethane (10 mL) at −78 °C was added ethanol (30 μL, 0.55 mmol). After 10 min the solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed in vacuo, and the residue was washed with hexane, extracted into dichloromethane (1 mL), and layered with hexane (10 mL) to give red-brown crystals of **11** after 2 days (0.10 g, 58%). Mp: 166−168 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.04 (tr, 3 H, CH_3, $^3J_{HH}$ = 7.1 Hz), 1.34 (s, 9 H, Bu^t), 1.43 (s, 18 H, Bu^t), 2.23 (m, 8 H, CH_2), 3.05 (q, 2 H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 4.67 (s, 4 H, CH), 7.45 (s, 4 H, *p*-ArH), 7.60 (d, 1 H, PH, $^1J_{PH}$ = 578 Hz), 7.63 (s, 8 H, *o*-ArH). ^{13}C NMR (101.6 MHz, CD_2Cl_2, 300 K): δ 15.1 (br, CH_3), 31.5 (br s, CH_2), 32.7 (m, $P_ACC(CH_3)_3P_X$), 34.6 (t,$^3J_{PC}$ = 11.1 Hz, $P_XCC(CH_3)_3P_X$), 39.4 (m, $P_ACC(CH_3)_3P_X$), 43.4 (m, $P_XCC(CH_3)_3P_X$), 62.7 (br, OCH_2), 80.9 (d, CH, $^1J_{RhC}$ = 9.2 Hz), 117.5 (s, *p*-ArC), 124.6 (q, CF_3, $^1J_{CF}$ = 272.5 Hz), 129.0 (q, *m*-ArC, $^2J_{CF}$ = 31.4 Hz), 134.8 (s, *o*-ArC), 161.0 (q, *ipso*-ArC, $^1J_{BC}$ = 50.4 Hz), PC resonances not observed. ^{31}P{^{1}H} NMR (121.7 MHz, CD_2Cl_2, 300 K): δ 121.7 (d, P_x, $^2J_{PP}$ = 18.2 Hz), −8.4 (t, P_A, $^2J_{PP}$ = 18.2 Hz). ^{11}B{^{1}H} NMR (94.4 MHz, CD_2Cl_2, 300 K): δ −7.6. ^{19}F{^{1}H} NMR (282.8 MHz, CD_2Cl_2, 300 K): δ −62.75. IR ν/cm^{-1} (Nujol): 2363(m), P−H. MS/EI: *m/z* 557 [M − BAr^f_4, 86%]. Acc. Mass EI$^+$: calc for M − BAr^f_4 ($C_{25}H_{44}OP_3Rh$) 557.1733, found 557.1730. Anal. calc for $C_{57}H_{57}BF_{24}OP_3Rh$ (vacuum-dried sample): C 48.19, H 4.04. Found: C 47.83, H 3.81.

X-ray Crystallography. Crystals of **4** and **6**−**11** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 150 K, and the structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[34]

using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Crystal data, details of data collections, and refinement are given in Table 1.

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Supporting Information Available: Crystallographic data as CIF files for **4** and **6**−**11**; ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra for compounds **4** and **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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