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Syntheses and ^{31}P NMR studies of ruthenium(II), rhodium(I), and rhodium(III) complexes containing η^5-$P_2C_3{}^tBu_3$ and η^5- and η^1-$P_3C_2{}^tBu_2$ ligated ring systems. Crystal structures of [Rh(η^5-$P_2C_3{}^tBu_3$)(η^4-COD)] (COD = 1,5-cyclooctadiene) and the novel hydrido-η^1-triphosphacyclopentadienyl complex [RhH(η^1-$P_3C_2{}^tBu_2$)(η^5-C_5Me_5)PPh_3] *

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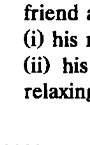
Abstract

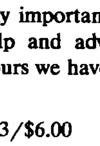
Complexes of the di- and triphosphacyclopentadienyl ring systems of the type [Ru(η^5-$P_2C_3{}^tBu_3$)(η^5-C_8H_{11}), [Ru(η^5-$P_3C_2{}^tBu_2$)(PPh_3)$PPh_2C_6H_4$], [Rh(η^5-$P_2C_3{}^tBu_3$)(η^4-diene)], (diene = hexa-1,5-diene, 1,5-cyclooctadiene), and the novel hydrido complex [RhH(η^1-$P_3C_2{}^tBu_2$)(η^5-C_5Me_5)(PPh_3)], are described, and ^{1}H, ^{31}P, and ^{13}C NMR data reported and discussed. The structures of [Rh(η^5-$P_2C_3{}^tBu_3$)(η^4-COD)] and [RhH(η^1-$P_3C_2{}^tBu_2$)(η^5-C_5Me_5)PPh_3] have been determined by X-ray diffraction studies.

1. Introduction

The di- and triphosphacyclopentadienyl ring systems $P_2C_3{}^tBu_3{}^-$ (**A**) and $P_3C_2{}^tBu_2{}^-$ (**B**) [1,2] are proving to be versatile in their behaviour towards transition metals [3–7]. To date, η^5- and η^1-ligating behaviour has been reported for **B** and η^5- and η^3-bonding for **A**. We present below the results of further studies of the reactions of these ring systems with Rh^I and Ru^{II} chloro-complexes which give products resulting from a variety of pathways.



(A)



(B)

2. Results and discussion

Treatment of a mixture containing roughly equimolar amounts of the sodium salts of the $P_2C_3{}^tBu_3{}^-$ and $P_3C_2{}^tBu_2{}^-$ anions with [Rh_2Cl_2(η^4-diene)$_2$] (diene = 1,5-cyclooctadiene or 1,5-hexadiene), in monoglyme, affords [Rh(η^5-$P_2C_3{}^tBu_3$)(η^4-COD)] (**1**) and [Rh(η^5-$P_2C_3{}^tBu_3$)(η^4-hexadiene)] (**2**), respectively (Scheme 1). Complexes **1** and **2** are the first examples of 'half-sandwich' rhodium(I) complexes containing η^5-bonded $P_2C_3{}^tBu_3$ ring systems, and their structures have been established by ^{31}P{^{1}H}, ^{13}C, ^{1}H NMR and mass spectroscopic studies, and in the case of the former, by elemental analysis and a single crystal *X*-ray diffraction study (see below). Previously when we used the lithium salt of the $P_3C_2{}^tBu_2$/$P_2C_3{}^tBu_3$ anions (richer in $P_3C_2{}^tBu_2{}^-$), and [Rh_2Cl_2(COD)$_2$], we obtained only the complex [Rh(η^5-$P_3C_2{}^tBu_2$)(η^4-COD)], whose identity was confirmed by an X-ray diffraction study [8].

Three very different types of reactions occur, however, when the mixture of the two ring anions **A** and **B** are treated in dme at room temperature with (i) [RuCl(η^4-COD)]; (ii) [$RuCl_2$(η^6-C_6H_6)(PPh_3)]; and

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* This paper is dedicated to Professor Michael Lappert, FRS, my friend and colleague at Sussex for over 25 years, in recognition of (i) his many important contributions to organometallic chemistry, (ii) his help and advice during my career, and (iii) the many relaxing hours we have spent together on the tennis court! (J.F.N.)

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(iii) $[Rh(\eta^5\text{-}C_5Me_5)Cl_2(PPh_3)]$, respectively (see Scheme 1).

In (i), the yellow sublimable sandwich complex $[Ru(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}C_8H_{11})]$ (**3**) is formed by both NaCl and HCl elimination reactions. In reaction (ii), the assumed intermediate complex $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)Cl(PPh_3)_2]$ undergoes spontaneous elimination of HCl *via ortho*-metallation to afford the complex $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)(C_6H_4)PPh_2(PPh_3)]$ (**4**). Complex **4** was also formed directly from **A** and **B** and $[RuCl_2(PPh_3)_4]$.

In (iii), an unexpected abstraction of hydrogen occurs (presumably from the ether solvent), to afford the novel Rh^{III} hydrido complex $[Rh(\eta^5\text{-}C_5Me_5)H(\eta^1P_3C_2{}^tBu_2)(PPh_3)]$ (**5**).

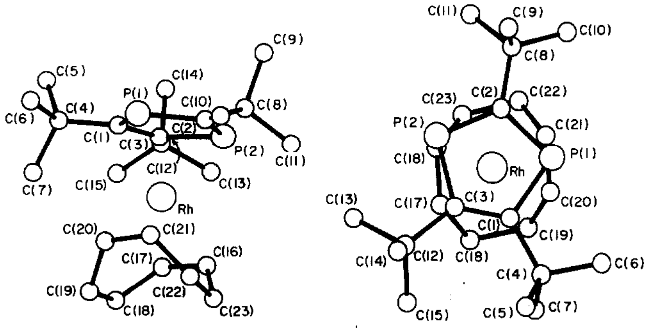
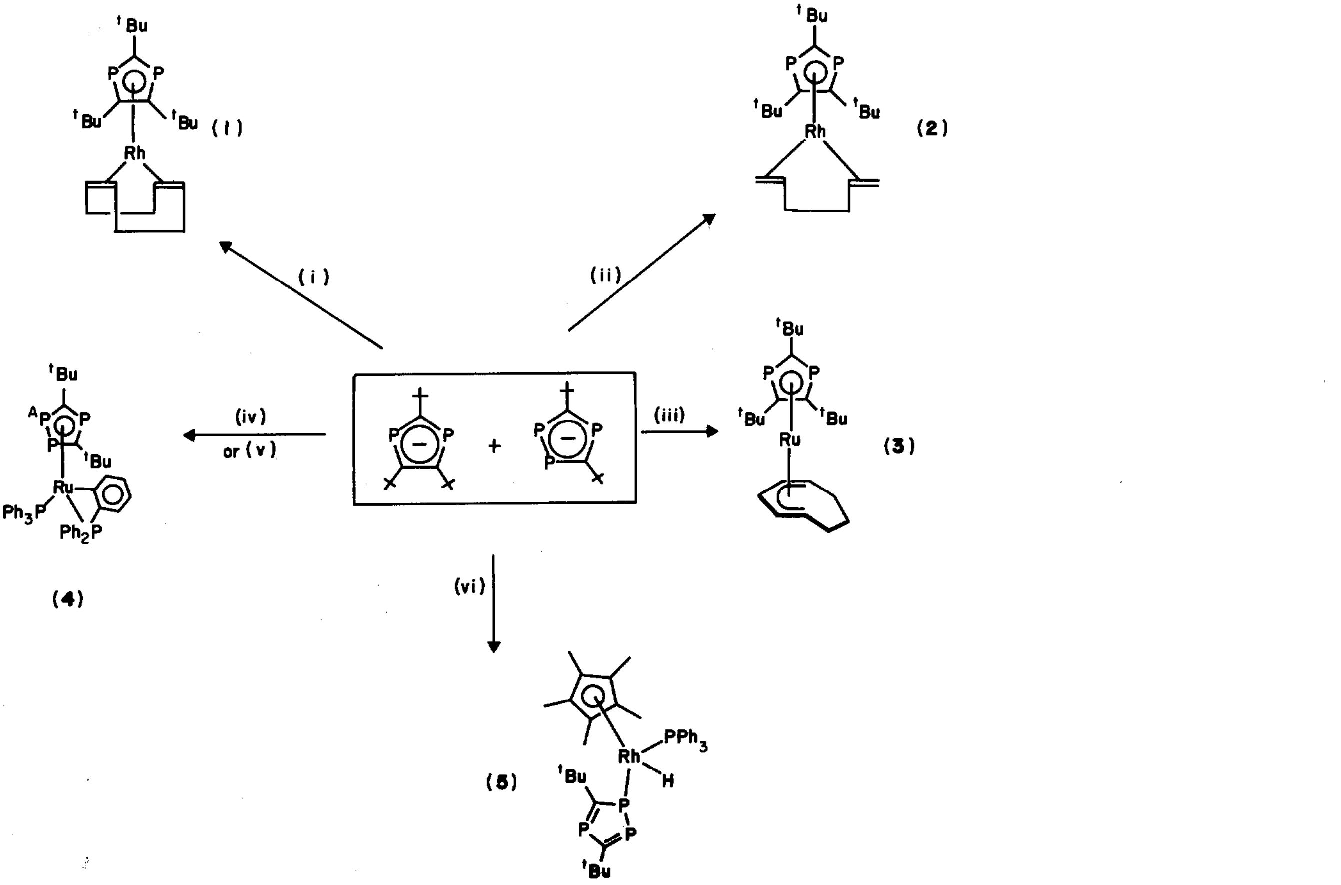


Fig. 1. Two views of the molecular structure of $[Rh(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^4\text{-}COD)]$ (**1**).

The molecular structure of $[Rh(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^4\text{-}COD)]$ (**1**) (Fig. 1) revealed that, as expected, the $\eta^5\text{-}P_2C_3{}^tBu_3$ ring system is planar and bond lengths and angles within the $P_2C_3{}^tBu_3$ ring system are similar to those found for related η^5-complexes such as $[Mo(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^3\text{-indenyl})(CO)_2]$ [9], $[Fe(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ [3], and $[Fe(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}P_3C_2{}^tBu_2)W(CO)_5]$ [10], while the bond lengths within the η^4-coordinated 1,5-cyclooctadiene lie within the range expected [11,12]. Table 1 lists selected bond lengths and bond angles for **1**, and Table 2 the atomic coordinates.

Unlike the analogous $[Rh(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^4\text{-}COD)]$ complex we described previously [8], in which the COD molecule is in a boat conformation, complex **1** contains an asymmetrically skewed diene ring similar to those



Scheme 1. (i) $[Rh_2Cl_2(COD)_2]$ in dme; (ii) $[Rh_2Cl_2(\text{hexadiene})_2]$ in dme; (iii) $[RuCl_2(COD)]_n$ in dme; (iv) $[RuCl_2(\eta^6\text{-}C_6H_6)(PPh_3)]$ in dme; (v) $[RuCl_2(PPh_3)_4]$ in dme; (vi) $[Rh(\eta^5\text{-}C_5Me_5)Cl_2(PPh_3)]$ in dme.

found in complexes of the type $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^4\text{-COD})]$ (M = Rh, Ir) [11,13,14].

As expected, the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of both $[\mathrm{Rh}(\eta^5\text{-}\mathrm{P_2C_3{}^tBu_3})(\eta^4\text{-COD})]$ (**1**) and $[\mathrm{Rh}(\eta^5\text{-}\mathrm{P_2C_3{}^tBu_3})(\eta^4\text{-hexadiene})]$ (**2**) are very simple, consisting of the expected doublet arising from an $[\mathrm{A_2X}]$ spin system ($\mathrm{A} = {}^{31}\mathrm{P}$, $I = \frac{1}{2}$, 100%; $\mathrm{X} = {}^{103}\mathrm{Rh}$, $I = \frac{1}{2}$, 100%) (δ_P 95 ppm (**1**); δ_P 101 ppm (**1**)), while $[\mathrm{Ru}(\eta^5\text{-}\mathrm{P_2C_3{}^tBu_3})(\eta^5\text{-}\mathrm{C_8H_{11}})]$ (**3**) exhibits a singlet (δ_P 60 ppm). Of particular interest are the small $^1J(\mathrm{RhP})$ coupling constants observed for complexes **1** (10.7 Hz) and **2** (11.7 Hz), confirming the η^5-bonding mode in both cases. Interestingly, $^1J(\mathrm{RhP})$ is too small to be observed in the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of the previously reported $[\mathrm{Rh}(\eta^5\text{-}\mathrm{P_3C_2{}^tBu_2})(\eta^4\text{-COD})]$ [8], but $^1J(\mathrm{RhP})$ values of ~ 30 Hz are observed for rhodium(I) complexes containing the neutral η^4-bonded 1,3-diphosphacyclobutadiene ligand, *e.g.* $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^4\text{-}\mathrm{P_2C_2{}^tBu_2})]$ (R = H or Me) [15].

TABLE 1. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses [a]

(a) Bonds			
Rh–M1	1.919	Rh–M2	2.037
Rh–M3	2.024	Rh–P(1)	2.413(1)
Rh–P(2)	2.468(1)	Rh–C(1)	2.381(4)
Rh–C(2)	2.384(4)	Rh–C(3)	2.377(4)
Rh–C(16)	2.153(4)	Rh–C(17)	2.152(4)
Rh–C(20)	2.156(5)	Rh–C(21)	2.129(5)
P(1)–C(1)	1.815(4)	P(1)–C(2)	1.760(4)
P(2)–C(2)	1.738(4)	P(2)–C(3)	1.809(4)
C(1)–C(3)	1.413(6)	C(1)–C(4)	1.574(5)
C(2)–C(8)	1.531(6)	C(3)–C(12)	1.559(6)
C(4)–C(5)	1.539(6)	C(4)–C(6)	1.547(7)
C(4)–C(7)	1.536(6)	C(8)–C(9)	1.518(6)
C(8)–C(10)	1.532(7)	C(8)–C(11)	1.534(6)
C(12)–C(13)	1.553(7)	C(12)–C(14)	1.534(7)
C(12)–C(15)	1.530(7)	C(16)–C(17)	1.393(7)
C(16)–C(23)	1.527(8)	C(17)–C(18)	1.499(7)
C(18)–C(19)	1.489(9)	C(19)–C(20)	1.506(7)
C(20)–C(21)	1.400(7)	C(21)–C(22)	1.493(7)
C(22)–C(23)	1.474(9)		
(b) Angles			
M1–Rh–M2	137.1	M1–Rh–M3	137.1
M2–Rh–M3	85.9	C(1)–P(1)–C(2)	97.7(2)
C(2)–P(2)–C(3)	97.8(2)	P(1)–C(1)–C(3)	114.3(3)
P(1)–C(1)–C(4)	114.3(3)	C(3)–C(1)–C(4)	131.4(4)
P(1)–C(2)–P(2)	114.5(2)	P(1)–C(2)–C(8)	123.2(3)
P(2)–C(2)–C(8)	122.3(3)	P(2)–C(3)–C(1)	115.6(3)
P(2)–C(3)–C(12)	112.6(3)	C(1)–C(3)–C(12)	131.2(4)
C(1)–C(4)–C(5)	111.0(4)	C(1)–C(4)–C(6)	110.3(3)
C(1)–C(4)–C(7)	112.5(3)	C(5)–C(4)–C(6)	105.5(3)
C(5)–C(4)–C(7)	111.4(4)	C(6)–C(4)–C(7)	105.7(4)
C(2)–C(8)–C(9)	108.3(4)	C(2)–C(8)–C(10)	111.3(4)
C(2)–C(8)–C(11)	110.8(4)	C(9)–C(8)–C(10)	109.8(4)
C(9)–C(8)–C(11)	108.8(4)	C(10)–C(8)–C(11)	107.7(4)
C(3)–C(12)–C(13)	111.0(4)	C(3)–C(12)–C(14)	106.8(3)
C(3)–C(12)–C(15)	116.9(4)	C(13)–C(12)–C(14)	106.4(4)
C(13)–C(12)–C(15)	104.7(4)	C(14)–C(12)–C(15)	110.6(4)
C(17)–C(16)–C(23)	123.5(4)	C(16)–C(17)–C(18)	124.0(4)
C(17)–C(18)–C(19)	116.0(5)	C(18)–C(19)–C(20)	113.6(5)
C(19)–C(20)–C(21)	124.3(4)	C(20)–C(21)–C(22)	125.1(5)
C(21)–C(22)–C(23)	114.3(5)	C(16)–C(23)–C(22)	114.8(4)

[a] M1 is the centroid of the P(1), P(2), C(1), C(2), C(3) ring M2 and M3 are the mid-points of the C(16)–C(17) and C(20)–C(21) bonds.

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_eq [a]
Rh	2066.6(3)	1111.2(1)	2112.1(2)	30.8(1)
P(1)	3530.7(9)	1542.2(5)	3675.5(8)	34.3(2)
P(2)	1756.2(10)	338.2(5)	3717.6(9)	37.4(3)
C(1)	4160(4)	769(2)	3048(3)	34(2)
C(2)	2044(4)	1190(2)	4114(3)	35(2)
C(3)	3287(4)	198(2)	3050(3)	36(2)
C(4)	5568(4)	857(2)	2574(3)	43(2)
C(5)	6582(4)	333(3)	3117(4)	59(3)
C(6)	6159(4)	1573(3)	2893(4)	56(2)
C(7)	5486(4)	822(3)	1278(4)	55(2)
C(8)	1105(4)	1586(2)	4831(3)	42(2)
C(9)	1465(6)	1404(4)	6064(4)	77(3)
C(10)	1230(5)	2365(3)	4666(5)	69(3)
C(11)	−358(4)	1386(3)	4508(4)	63(3)
C(12)	3483(4)	−570(2)	2720(3)	44(2)
C(13)	2115(5)	−946(3)	2523(5)	60(3)
C(14)	4245(6)	−919(3)	3742(5)	67(3)
C(15)	4177(5)	−706(3)	1645(4)	62(3)
C(16)	267(4)	815(2)	1105(4)	50(2)
C(17)	1370(5)	581(2)	580(4)	52(2)
C(18)	1869(6)	911(3)	−445(4)	71(3)
C(19)	2275(6)	1646(4)	−323(4)	82(3)
C(20)	2453(5)	1888(2)	886(4)	57(2)
C(21)	1404(5)	2096(2)	1511(4)	53(2)
C(22)	−41(6)	2107(3)	1082(6)	80(3)
C(23)	−577(5)	1434(3)	689(5)	73(3)

[a] U_eq is defined as one third of the trace of the orthogonalised U_{ij} tensor.

The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectroscopic data also readily establish the structures of complexes **1**–**3**. All three complexes exhibit very similar patterns of lines in the $\mathrm{P_2C_3{}^tBu_3}$ ring system region (see Fig. 2). The resonances corresponding to $\mathrm{C^4}$, $\mathrm{C^5}$, and $\mathrm{C^6}$ arise from $[\mathrm{AX_2}]$ spin systems ($\mathrm{A} = {}^{13}\mathrm{C}$, $I = \frac{1}{2}$, 1.1%; $\mathrm{X} = {}^{31}\mathrm{P}$, $I = \frac{1}{2}$, 100%), whereas $\mathrm{C^1}$, $\mathrm{C^2}$, and $\mathrm{C^3}$ resonances arise from $[\mathrm{AXX'}]$ spin systems. A PANIC simulation of $\mathrm{C^1}$, $\mathrm{C^2}$, and $\mathrm{C^3}$ resonances in the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of complex **1** fully reproduces the observed patterns (see Fig. 3) and, interestingly, the cross ring coupling constant $^2J(\mathrm{PP})$ 28.6 Hz can now be measured because of the presence of both $^{12}\mathrm{C}$ and $^{13}\mathrm{C}$ nuclei and their effect upon the adjacent $^{31}\mathrm{P}$ nuclei (3.5×1.0^{-2} ppm). The same behaviour has been observed for complexes **2** and **3**, and, by Mathey and co-workers [16], in the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of 2,2′-diphosphinine, where the $^{13}\mathrm{C}$ isotope shift is 8.5×10^{-2} ppm.

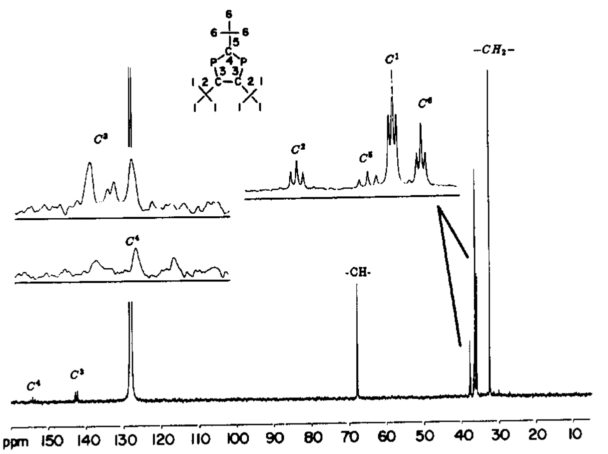


Fig. 2. $^{13}C-\{^1H\}$ NMR spectrum of $[Rh(\eta^5-P_2C_3{}^tBu_3)(\eta^4-COD)]$ (1).

The estimated $^2J(PP)$ coupling constants in complexes **1** (28.6 Hz), **2** (28.6 Hz), and **3** (29.2 Hz) are in accord with those found for unsymmetrical diphospholyl anions such as $P_2C_3{}^iPr_2{}^tBu^-$ (16.5 Hz), $P_2C_3{}^iPr{}^tBu_2^-$ (27.4 Hz) [17], and $P_2C_3HMe{}^tBu^-$ (19.5 Hz) [18], and for the complexes $[M(\eta^5-P_2C_3{}^tBu_3)(\eta^5-P_3C_2{}^tBu_2)W(CO)_5]$ (M = Fe (32.9 Hz) [10]; M = Ru (30 Hz) [19]). Values of $^{13}C-^{31}P$ coupling constants for atoms within the η^5-bonded $P_2C_3{}^tBu_3$ ring system in **1–3** are comparable with those found for complexes containing η^5-bonded $PC_4H_2Me_2$ [20,21]. The $^{13}C-\{^1H\}$ NMR spectrum of complexes **1–3**, in the region corresponding to the η^4-bonded 1,5-cyclooctadiene, 1,5-hexadiene, and the η^5-cyclooctadienyl, also provide structural information. $[Rh(\eta^5-P_2C_3{}^tBu_3)(\eta^4-COD)]$ exhibits the expected patterns for two types of carbon within the η^4-COD; *i.e.* a singlet ($-CH_2-$) and a doublet ($-CH=$) with characteristic value of $^1J(RhC)$ (12.6 Hz). Use of $^{13}C-\{^1H\}$, ^{13}C, and DEPT NMR experiments in $[Rh(\eta^5-P_2C_3{}^tBu_3)(\eta^4-hexadiene)]$ (**2**) allowed the full assignment of the resonances corresponding to the carbons in the η^4-hexadiene. This region of the $^{13}C-\{^1H\}$ NMR spectrum consists of two doublets (43.5 ($CH_2=$) and 67.9 ppm ($=CH-$)) with typical $^1J(RhC)$ coupling constants (12.4 and 11.6 Hz, respectively) and a singlet (33.5 ppm ($-CH_2-$)).

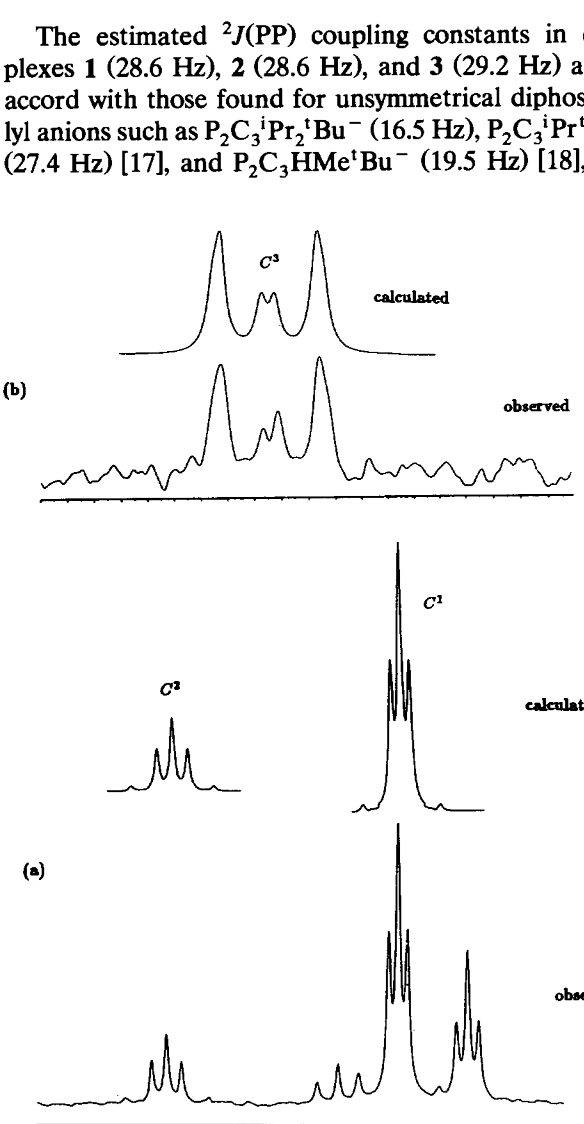


Fig. 3. Observed and calculated $^{13}C-\{^1H\}$ NMR resonances in $[Rh(\eta^5-P_2C_3{}^tBu_3)(\eta^4-COD)]$ (1) for: (a) C^1 and C^2; (b) C^3.

In the case of $[Ru(\eta^5-P_2C_3{}^tBu_3)(\eta^5-C_8H_{11})]$ (**3**), the $^{13}C-\{^1H\}$ NMR spectrum provided definitive information for the presence of a cyclooctadienyl ligand, since the presence of five different types of carbon ($2CH_2$ and 3CH, as evidenced by the ^1H coupled spectrum) ruled out an η^4-bonded cyclooctadiene (see Fig. 4). Interestingly, one of the carbon atoms of the η^5-cyclooctadienyl ligand shows a $^2J(CP)$ coupling constant of 4.7 Hz, but its unambiguous assignment to C^8 or C^9 could not be made without both ^1H and 2D $^1H-^{13}C$ correlation shift studies. The ^1H NMR spectrum of **3** in C_6D_6 did not prove particularly useful, since the CH protons on C^8 and C^9 have identical chemical shifts. However, in CD_2Cl_2, **3** exhibited two separated signals which could be fully analysed.

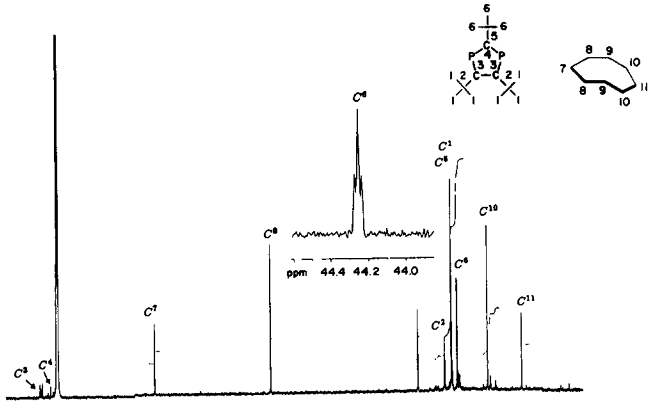
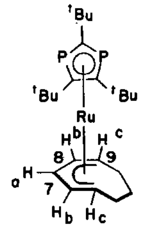


Fig. 4. $^{13}C-\{^1H\}$ NMR spectrum of $[Ru(\eta^5-P_2C_3{}^tBu_3)(\eta^5-C_8H_{11})]$ (3) (in C_6D_6).



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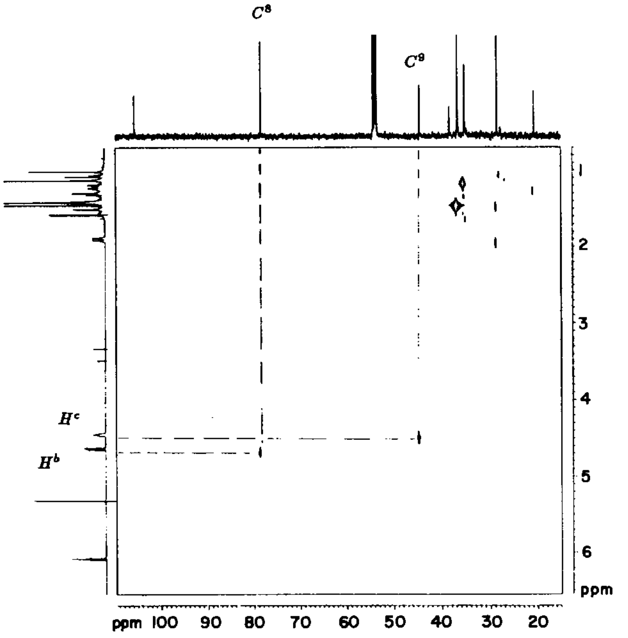
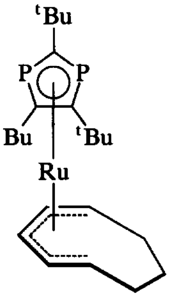


Fig. 5. ²D ¹H–¹³C chemical shift correlation spectrum of $[Ru(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}C_8H_{11})]$ (3) (in CD_2Cl_2).

Selective decoupling at δ4.63 allows an unambiguous assignment of H^b and H^c, since it does not affect the proton resonance of the CH_2 groups. Therefore, H^b (δ4.63) must be attached to C^8, and H^c (δ4.48) is attached to C^9. The $2D\,{}^1H\text{–}{}^{13}C$ chemical shift correlated spectrum (Fig. 5), in a CD_2Cl_2 solution, reveals the interactions $C^8 \cdots H^b$ and $C^9 \cdots H^e$, confirming the attributions of the triplet to C^9 and the singlet to C^8. From the ^{31}P, $^{13}C\text{-}\{^1H\}$, and ^1H NMR spectroscopic results, the structure shown below can be proposed for $[Ru(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}C_8H_{11})]$ (3). ^{13}C and ^1H NMR data found for 3 are similar to those found for analogous complexes containing the η^5-bonded cyclooctadienyl ligand, *e.g.* $[Ru(\eta^5\text{-}C_8H_{11})(\eta^6\text{-}C_6H_6)]$ and $[Ru(\eta^5\text{-}C_8H_{11})(\eta^6\text{-}C_6Me_6)]$ [22].



(3)

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the ruthenium(II) complex $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)PPh_2C_6H_4(PPh_3)]$ (4) provides strong evidence for a *cyclo*-metallated complex consisting of a pattern of lines arising from an [ABCDM] spin system (A, B, C, D, $M = {}^{31}P$, $I = \frac{1}{2}$, 100%) (Fig. 6). The presence of two types of 'triphenylphosphane' ligands with very distinct chemical shifts

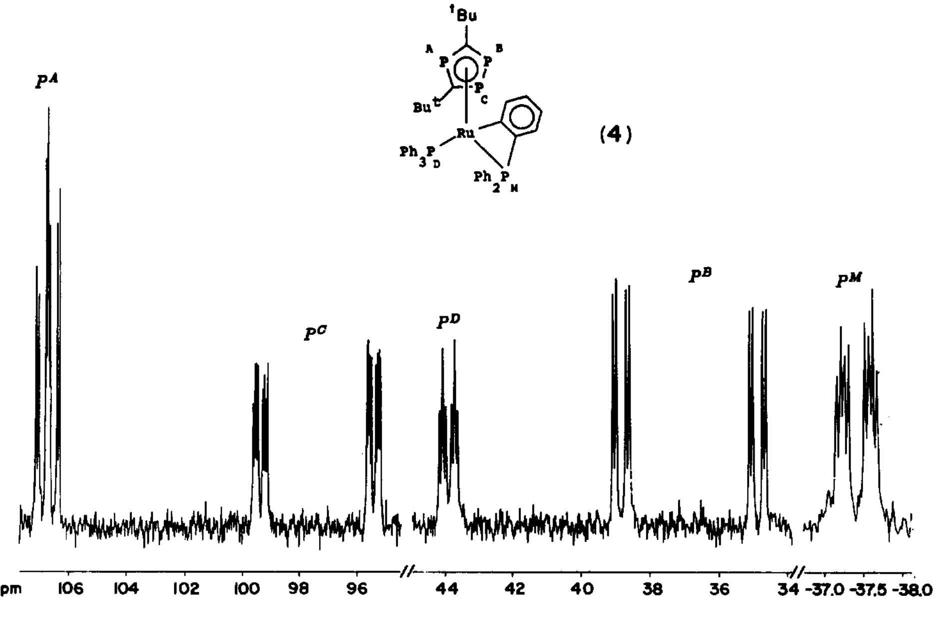


Fig. 6. $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[Ru(\eta^5\text{-}P_2C_3{}^tBu_2)(PPh_2C_6H_4)(PPh_3)]$ (4).

(43.9 and −37.4 ppm) reflects significant differences in the phosphorus environments.

Large differences in the ^{31}P chemical shifts of coordinated phosphanes have been attributed by Garrou to *ortho*-metallation [23]. The ^{31}P resonance for an *ortho*-metallated phosphane usually appears at a lower frequency than that for a normal coordinated phosphane [24–28], and Shaw and co-workers [24] have reported several platinum complexes of the type *trans*-[PtX(P^{t}Bu$_2$C$_6$H$_4$)P^{t}Bu$_2$Ph] (X = Cl, Br, I, NO$_3$) in which coordinated P^{t}Bu$_2$Ph ligands exhibit higher chemical shifts (δ_P 53–48 ppm), than do the metallated P^{t}Bu$_2$Ph ligands (δ_P −19 to −30 ppm). More recently, Bennett and co-workers [25] showed that the ^{31}P-{^{1}H} NMR spectrum of a platinum(II) complex containing two *ortho*-metallated triphenylphosphanes, [Pt(PPh$_2$C$_6$H$_4$)$_2$], exhibits a singlet (with ^{195}Pt satellites) at −52.3 ppm. Likewise, ruthenium complexes of the type [RuR(PPh$_2$C$_6$H$_4$)(PPh$_3$)$_2$L] (R = H or Me, and L = Et$_2$O, THF, or MeCN) also exhibit high-field ^{31}P resonances for the *ortho*-metallated triphenylphosphane [26]. The fully structurally characterised, closely related complex [Ru(η^5-C$_5$R$_5$)(PPh$_2$C$_6$H$_4$)(PPh$_3$)] (R = H; R = Me), reported by Lehmkuhl *et al.* [27], exhibits characteristic doublets in the ^{31}P-{^{1}H} NMR spectrum (R = H), corresponding to the *cyclo*-metallated triphenylphosphane (−17.7 ppm) and the normal PPh$_3$ (62.8 ppm) [28].

The ^{31}P-{^{1}H} NMR spectrum of [Ru(η^5-P$_3$C$_2{}^t$Bu$_2$)(PPh$_2$C$_6$H$_4$)(PPh$_3$)] (4) (Fig. 6) exhibits a resonance at −37.4 ppm, which is attributed to the *ortho*-metallated triphenylphosphane (P^M), and another at 43.9 which is assigned to the coordinated triphenylphosphane (P^D).

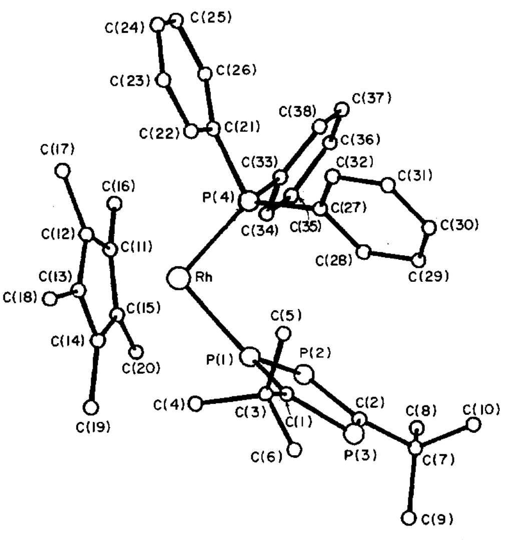
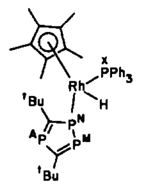


Fig. 7. Molecular structure of [RhH(η^5-C$_5$Me$_5$)(η^1-P$_2$C$_3{}^t$Bu$_2$)(PPh$_3$)] (5).



(5)

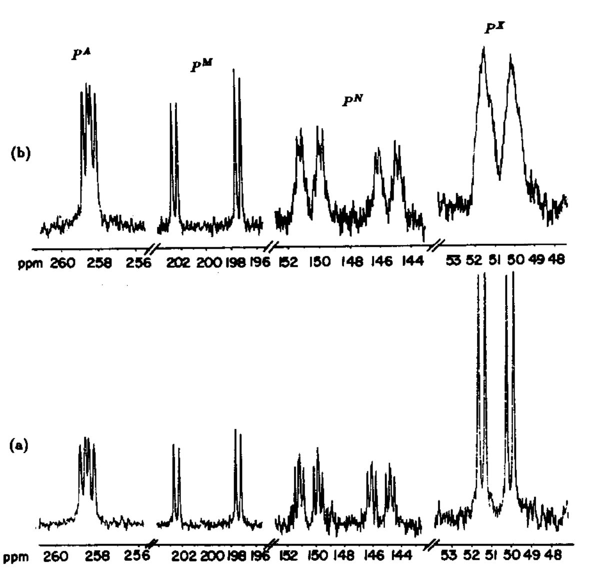


Fig. 8. (a) ^{31}P-{^{1}H} and (b) ^{31}P NMR spectra of [RhH(η^5-C$_5$Me$_5$)(η^1-P$_2$C$_3{}^t$Bu$_2$)(PPh$_3$)] (5).

TABLE 3. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses [a]

(a) Bonds			
Rh–Cp	1.896	Rh–P(1)	2.297(2)
Rh–P(4)	2.262(3)	Rh–C(11)	2.281(9)
Rh–C(12)	2.233(8)	Rh–C(13)	2.224(8)
Rh–C(14)	2.239(11)	Rh–C(15)	2.281(12)
P(1)–P(2)	2.090(4)	P(1)–C(1)	1.712(8)
P(2)–C(2)	1.723(8)	P(3)–C(1)	1.742(8)
P(3)–C(2)	1.743(10)	P(4)–C(21)	1.843(10)
P(4)–C(27)	1.832(10)	P(4)–C(33)	1.826(10)
C(1)–C(3)	1.535(14)	C(2)–C(7)	1.551(12)
C(3)–C(4)	1.549(14)	C(3)–C(5)	1.52(2)
C(3)–C(6)	1.525(12)	C(7)–C(8)	1.53(2)
C(7)–C(9)	1.51(2)	C(7)–C(10)	1.51(2)
C(11)–C(12)	1.45(2)	C(11)–C(15)	1.41(2)
C(11)–C(16)	1.476(14)	C(12)–C(13)	1.411(12)
C(12)–C(17)	1.50(2)	C(13)–C(14)	1.43(2)
C(13)–C(18)	1.49(2)	C(14)–C(15)	1.433(12)
C(14)–C(19)	1.483(15)	C(15)–C(20)	1.49(2)
C(21)–C(22)	1.402(15)	C(21)–C(26)	1.371(12)
C(22)–C(23)	1.36(2)	C(23)–C(24)	1.345(14)
C(24)–C(25)	1.37(2)	C(25)–C(26)	1.42(2)
C(27)–C(28)	1.386(13)	C(27)–C(32)	1.37(2)
C(28)–C(29)	1.41(2)	C(29)–C(30)	1.36(2)
C(30)–C(31)	1.36(2)	C(31)–C(32)	1.39(2)
C(33)–C(34)	1.41(2)	C(33)–C(38)	1.37(2)
C(34)–C(35)	1.37(2)	C(35)–C(36)	1.39(3)
C(36)–C(37)	1.33(3)	C(37)–C(38)	1.37(2)

TABLE 3 (continued)

(b) Angles			
Cp–Rh–P(1)	124.4	Cp–Rh–P(4)	133.5
P(1)–Rh–P(4)	94.46(9)	Rh–P(1)–P(2)	121.2(1)
Rh–P(1)–C(1)	131.2(4)	P(2)–P(1)–C(1)	104.7(3)
P(1)–P(2)–C(2)	96.6(3)	C(1)–P(3)–C(2)	102.8(4)
Rh–P(4)–C(21)	109.0(3)	Rh–P(4)–C(27)	120.5(3)
Rh–P(4)–C(33)	117.2(4)	C(21)–P(4)–C(27)	103.6(5)
C(21)–P(4)–C(33)	104.6(4)	C(27)–P(4)–C(33)	100.1(4)
P(1)–C(1)–P(3)	115.1(5)	P(1)–C(1)–C(3)	125.5(5)
P(3)–C(1)–C(3)	119.4(6)	P(2)–C(2)–P(3)	120.8(5)
P(2)–C(2)–C(7)	121.6(7)	P(3)–C(2)–C(7)	117.7(6)
C(1)–C(3)–C(4)	109.9(9)	C(1)–C(3)–C(5)	110.1(8)
C(1)–C(3)–C(6)	111.1(8)	C(4)–C(3)–C(5)	109.9(8)
C(4)–C(3)–C(6)	106.1(8)	C(5)–C(3)–C(6)	110(1)
C(2)–C(7)–C(8)	112.6(7)	C(2)–C(7)–C(9)	108.3(9)
C(2)–C(7)–C(10)	110(1)	C(8)–C(7)–C(9)	105(1)
C(8)–C(7)–C(10)	106(1)	C(9)–C(7)–C(10)	115(1)
C(12)–C(11)–C(15)	107.7(8)	C(12)–C(11)–C(16)	124(1)
C(15)–C(11)–C(16)	128(1)	C(11)–C(12)–C(13)	108.1(9)
C(11)–C(12)–C(17)	124.1(9)	C(13)–C(12)–C(17)	127(1)
C(12)–C(13)–C(14)	108.1(9)	C(12)–C(13)–C(18)	128(1)
C(14)–C(13)–C(18)	124.1(9)	C(13)–C(14)–C(15)	108.2(8)
C(13)–C(14)–C(19)	125.6(9)	C(15)–C(14)–C(19)	126(1)
C(11)–C(15)–C(14)	108.0(9)	C(11)–C(15)–C(20)	127.5(8)
C(14)–C(15)–C(20)	124.3(9)	P(4)–C(21)–C(22)	117.2(6)
P(4)–C(21)–C(26)	123.9(9)	C(22)–C(21)–C(26)	118.8(9)
C(21)–C(22)–C(23)	120.7(8)	C(22)–C(23)–C(24)	121(1)
C(23)–C(24)–C(25)	121(1)	C(24)–C(25)–C(26)	119.2(9)
C(21)–C(26)–C(25)	119(1)	P(4)–C(27)–C(28)	117(1)
P(4)–C(27)–C(32)	124.8(6)	C(28)–C(27)–C(32)	118.0(9)
C(27)–C(28)–C(29)	120(1)	C(28)–C(29)–C(30)	120.7(9)
C(29)–C(30)–C(31)	120(1)	C(30)–C(31)–C(32)	119(1)
C(27)–C(32)–C(31)	122.3(9)	P(4)–C(33)–C(34)	119.0(8)
P(4)–C(33)–C(38)	121(1)	C(34)–C(33)–C(38)	120(1)
C(33)–C(34)–C(35)	118(1)	C(34)–C(35)–C(36)	121(2)
C(35)–C(36)–C(37)	119(1)	C(36)–C(37)–C(38)	122(2)
C(33)–C(38)–C(37)	119(2)		

[a] Cp is the centroid of the C(11) to C(15) cyclopentadienyl ring.

The P^A, P^B, and P^C chemical shifts of the ring atoms lie, as expected, within the normal range found for other η^5-$P_3C_2{}^tBu_2$ complexes of the type $[M(\eta^5\text{-}P_3C_2{}^tBu_2)L_n]$ ($M = Fe^{II}$, Ru^{II}, Rh^I). Likewise, the coupling-constants $^1J(PP)$ and $^2J(PP)$ within the η^5-bonded $P_3C_2{}^tBu_2$ ring system ($^2J(P^AP^B)$ 39; $^2J(P^AP^C)$ 401 Hz) are similar to those observed for $[M(\eta^5\text{-}P_3C_2{}^tBu_2)(PX_3)_2]$ ($M = Rh$, $X = Ph$ (30 Hz); *p*-tolyl (30 Hz); or Me (36 Hz) [3].

An unprecedented rhodium(III) hydride containing an η^1-bonded $P_3C_2{}^tBu_2$ ring system $[RhH(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}P_3C_2{}^tBu_2)PPh_3]$ (**5**) was unexpectedly obtained by treatment of a mixture of the sodium salts of the $P_3C_2{}^tBu_2{}^-$ and $P_2C_3{}^tBu_3{}^-$ anions with $[RhCl_2(\eta^5\text{-}C_5Me_5)PPh_3]$ in dme at room temperature. The molecular structure of (**5**) (Fig. 7) was established by a single crystal *X*-ray diffraction study, and confirmed the presence of an η^5-bonded C_5Me_5 ring system, a coordinated triphenylphosphane ligand, and the $P_3C_2{}^tBu_2$ ring system bonded in an η^1 fashion. The angles around the rhodium centre in **5** strongly suggest that the metal adopts an approximately octahedral geometry, implying the presence of the hydride, which, however, could not be located. The Rh–P(PPh$_3$) (2.262(3) Å), Rh–C(C$_5$Me$_5$) (average 2.2516 Å) bond lengths and the Rh–cent(C$_5$Me$_5$) distance (1.896 Å) are similar to those listed in the compilation of X-ray data by Orpen *et al.* [29] for related rhodium complexes. Typical bond

TABLE 4. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å$^2 \times 10^3$)

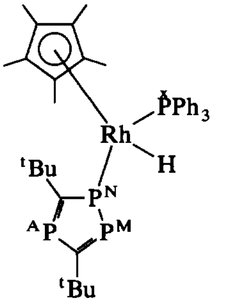
Atom	*x*	*y*	*z*	U_{eq} [a]
Rh	1808.3(7)	2167.2(6)	3549.9(5)	32(1)
P(1)	322(2)	4309(2)	3189(2)	39(2)
P(2)	976(2)	5722(2)	2355(2)	46(2)
P(3)	−2094(3)	6609(2)	2597(2)	48(2)
P(4)	2007(2)	1866(2)	2261(2)	38(2)
C(1)	−1428(8)	5021(8)	3220(6)	40(8)
C(2)	−629(9)	6898(8)	2129(6)	45(8)
C(3)	−2407(9)	4375(9)	3735(6)	48(9)
C(4)	−1939(10)	3600(9)	4627(7)	55(10)
C(5)	−2439(11)	3472(10)	3286(7)	72(11)
C(6)	−3852(11)	5386(11)	3871(8)	73(13)
C(7)	−825(10)	8244(9)	1508(7)	56(10)
C(8)	536(12)	8348(11)	1099(8)	82(13)
C(9)	−1499(16)	9251(11)	2004(12)	120(18)
C(10)	−1588(13)	8484(14)	790(10)	128(15)
C(11)	4011(9)	1252(10)	3878(6)	56(10)
C(12)	3333(10)	377(9)	4303(6)	51(9)
C(13)	2233(9)	971(9)	4862(5)	45(8)
C(14)	2195(9)	2214(8)	4783(6)	44(8)
C(15)	3300(8)	2381(8)	4175(6)	44(8)
C(16)	5331(12)	889(15)	3345(8)	95(15)
C(17)	3898(13)	−1003(11)	4265(8)	83(13)
C(18)	1323(11)	396(11)	5489(7)	73(11)
C(19)	1292(12)	3098(10)	5322(7)	70(11)
C(20)	3660(10)	3520(10)	3962(8)	74(11)
C(21)	2559(10)	123(8)	2369(6)	48(8)
C(22)	1692(10)	−470(9)	2886(6)	50(9)
C(23)	2045(11)	−1756(10)	3015(8)	65(11)
C(24)	3219(12)	−2489(11)	2637(8)	74(12)
C(25)	4130(12)	−1971(11)	2151(7)	71(12)
C(26)	3785(10)	−626(10)	2009(7)	60(10)
C(27)	519(9)	2640(9)	1658(6)	45(9)
C(28)	34(10)	3974(9)	1330(7)	56(9)
C(29)	−1110(10)	4619(10)	868(7)	63(10)
C(30)	−1769(10)	3953(11)	759(7)	67(11)
C(31)	−1300(10)	2645(10)	1076(8)	81(11)
C(32)	−166(9)	2004(9)	1534(7)	56(9)
C(33)	3258(9)	2329(9)	1455(6)	50(9)
C(34)	3903(10)	3007(10)	1625(7)	61(11)
C(35)	4824(12)	3360(13)	1002(10)	95(15)
C(36)	5110(14)	3069(16)	228(10)	119(19)
C(37)	4482(15)	2421(16)	94(9)	107(18)
C(38)	3527(12)	2077(12)	680(7)	77(13)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

lengths and bond angles for **5** are listed in Table 3, and the atomic coordinates in Table 4.

The η^1-$P_3C_2{}^tBu_2$ ring system is planar and the rhodium atom deviates by 0.564 Å from the best plane containing the $P_3C_2{}^tBu_2$ ring. The bond lengths within the η^1-$P_3C_2{}^tBu_2$ ring system show no significant differences from those found in some platinum(II) and palladium(II) η^1-$P_3C_2{}^tBu_2$ complexes [7], and are very similar to those in η^5-bonded $P_3C_2{}^tBu_2$ ring systems [3–5]. The C–P (1.712–1.743 Å) and the P–P (2.090 Å) bond distances lie in the range expected for delocalised systems [30,31].

The retention of the structure of complex **5** in solution was fully established by its ^{31}P-$\{^1H\}$ NMR spectrum, which exhibits the pattern expected for an [AMNXZ] spin system (A, M, N, X, $= {}^{31}P$, $I = \frac{1}{2}$, 100%; $Z = {}^{103}Rh$, $I = \frac{1}{2}$, 100%). The presence of the hydride is readily established by the ^1H coupled ^{31}P NMR spectrum, since the P^N and P^X resonances are broader in the ^{31}P NMR spectrum (Fig. 8(b)) than in the ^{31}P-$\{^1H\}$ spectra, (Fig. 8(a)). Unfortunately, the $^2J(PH)$ coupling constants could not be derived from the ^{31}P NMR spectrum.



(5)

The ^1H NMR spectroscopic studies, which independently established the presence of a hydride resonance (δ-11), consists of five lines arising from an [AMXY] spin system ($A = {}^1H$, $I = \frac{1}{2}$, 100%; $M = {}^{103}Rh$, $I = \frac{1}{2}$, 100%; X, $Y = {}^{31}P$, $I = \frac{1}{2}$, 100%), subsequently simulated using the PANIC program ($^1J(RhH)$ 41.6 Hz; $^2J(P^XH)$ 20 Hz; $^2J(P^NH)$ 20 Hz).

3. Experimental details

3.1. General procedures

All reactions were carried out by use of standard procedures for manipulation of air-sensitive materials, either under dry dinitrogen using standard Schlenk tubes, syringe, and/or high-vacuum techniques. Glassware was flame dried *in vacuo*, and solvents were dried, freshly distilled under dinitrogen, and degassed prior to use.

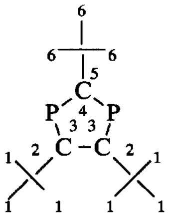
NMR spectra were recorded on Bruker WP80SY, AC-P250, WM360, or AMX500 spectrometers. Unless otherwise indicated, chemical shifts were measured at ambient temperatures, and are quoted in ppm with positive values to low field of the indicated reference, and are corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hz. For variable temperature experiments Bruker B-VT1000 variable temperature units were used.

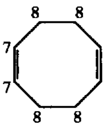
Mass spectra were obtained with Kratos MS25 or MS80RF double-focusing mass spectrometers. Carbon, hydrogen, and nitrogen analyses were carried out by Ms. Mita Patel of this laboratory.

^tBuCP was synthesised from $(Me_3Si)P{=}C$-$^tBu(OSiMe_3)$ and NaOH [32–34]. $Li(P_3C_2{}^tBu_2)$ and Na salts of $P_2C_3{}^tBu_3$ and $P_3C_2{}^tBu_2$ anions were made from ^tBuCP [1,2]. The following metal complexes were made by published methods: $[Rh_2Cl_2(\eta^4\text{-COD})_2]$ [35]; $[Rh_2Cl_2(\eta^4\text{-hexa-1,5-diene})_2]$ [35]; $[RhCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)_2]$ [36]; $[RuCl_2(\eta^6\text{-}C_6H_6)(PPh_3)]$ [37,38]; $[RuCl_2(\eta^4\text{-COD})]_n$ [39]; and $[RuCl_2(PPh_3)_4]$ [40].

3.2. Synthesis of $[Rh(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^4\text{-COD})]$ (1)

A solution of $Na(P_2C_3{}^tBu_3)$ (2 mmol) and $Na(P_3C_2{}^tBu_2)$ (2 mmol) (dme, 5 ml) was added dropwise to a suspension of $[Rh_2Cl_2(\eta^4\text{-COD})]$ (990 mg, 2 mmol) (dme, 2 ml) and the mixture was stirred for 24 h. The solvent was removed and the black residue with petroleum ether 60–80°C. The extract was chromatographed (Kieselgel/petroleum ether 60–80°C) and the product recrystallised from petroleum ether 60–80°C to give crystals of (η^4-1,5-cyclooctadiene)(η^5-2,4,5-tri-t-butyl-1,3-diphosphacyclopentadienyl)rhodium(I) (221 mg, 23%). (Found: C, 56.70%; H, 7.91%. $C_{23}H_{39}P_2Rh$ requires C, 57.5%; H, 8.1%). ^{31}P-$\{^1H\}$ NMR data (101.3 MHz, toluene-d_8, 25°C) δ_P 95.1 ppm, $^1J(RhP)$ 10.7 Hz. ^1H NMR data (360.1 MHz, toluene-d_8, 25°C) δ1.35 (s, 9H, ^tBu); δ1.42 (s, 18H, $2{}^tBu$); δ1.91–2.10 (m, 8H, $4CH_2$); δ4.73 (bs, 4H, 4CH). ^{13}C-$\{^1H\}$ NMR data (125.3 MHz, benzene-d_6, 25°C) δ154.1 ppm (t, $^1J(CP)$ 69.1 Hz, C^4); δ142.6 ppm (m, $^1J(CP)$ 72.9 Hz, C^3); δ67.9 ppm (d, $J(RhC)$ 12.6 Hz, C^7); δ37.8 ppm (m, $^2J(CP)$ 22.7 Hz, $^2J(P^AP^B)$ 28.6 Hz, C^2); δ36.8 ppm (t, $^2J(CP)$ 15.6 Hz, C^5); δ36.4 ppm (t, $^3J(CP)$ 14.3 Hz, C^1); δ36.1 ppm (t, $^3J(CP)$ 8.3 Hz, C^6); δ32.6 ppm (s, C^8).

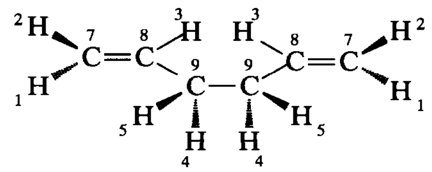


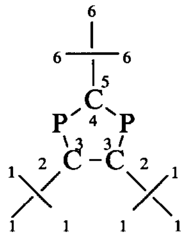


Mass spectrum (FAB) m/z 480 $[RhP_2C_3{}^tBu_3C_8H_{11}]^+$; 423 $[RhP_2C_3{}^tBu_2C_8H_{12}]^+$; 372 $[RhP_2C_3{}^tBu_3]^+$.

3.3. Synthesis of [Rh(η^5-$P_2C_3{}^tBu_3$)(η^4-hexadiene)] (2)

A similar procedure outlined used for [$Rh_2Cl_2(\eta^4$-$C_6H_{10})_2$] (880 mg, 2 mmol), Na($P_2C_3{}^tBu_3$) (2 mmol), and Na($P_3C_2{}^tBu_2$) (2 mmol). The yellow product obtained after chromatography could not be recrystalized, but it was identified as (η^4-1,5-hexadiene)(η^5-2,4,5-tri-t-butyl-1,3-diphosphacyclopentadienyl)-rhodium(I) (300 mg, 16%) on the basis of ^{31}P-{^1H}, ^1H, ^{13}C NMR and mass spectroscopy. ^{31}P-{^1H} NMR data (101.3 MHz, benzene-d_6, 25°C) δ_P 101.0 ppm, J(RhP) 11.7 Hz. ^1H NMR data (500.1 MHz, toluene-d_8, 25°C) δ4.85–4.82 (bm, 2H, H^3); δ3.73 (dd, 2H, $^3J(H^2H^3)$ 8.0 Hz, $^2J(H^1H^2)$. 4 Hz, H^2); δ1.96–1.94 (m, 2H, H^4); δ1.77 (dd, 2H, $^3J(H^1H^3)$ 11.6 Hz, H^1); δ1.67–1.65 (m, 2Hm, H^5); δ1.38 (s, 18H, $2{}^tBu$); δ1.28 (s, 9H, ^tBu).

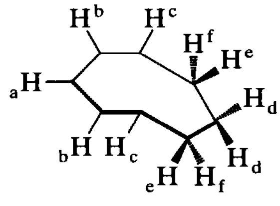




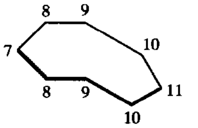
^{13}C-{^1H} NMR data (125.8 MHz, toluene-d_8, 25°C) δ153.6 ppm (t, ^1J(CP) 72.2 Hz, C^4); δ141.2 ppm (m, ^1J(CP) 73.6 Hz, C^3); δ67.9 ppm (d, $^1J(RhC^8)$ 11.6 Hz, C^8); δ43.5 ppm (d, $^1J(RhC^7)$ 12.4 Hz, C^7); δ37.7 ppm (t, ^2J(CP) 22.7 Hz, C^2); δ36.6 ppm (t, ^2J(CP) 15.6 Hz, C^5); δ36.1 ppm (t, ^3J(CP) 14.2 Hz, C^1); δ35.8 ppm (t, ^3J(CP) 8.3 Hz, C^6); δ33.5 ppm (s, C^9). ^{13}C NMR data (125.8 MHz, toluene-d_8, 25°C) δ67.9 ppm (dd, ^1J(RhC) 1.6 Hz, ^1J(CH) 154.2 Hz, C^8); δ43.5 ppm (td, ^1J(CH) 154.9 Hz, C^7); δ33.5 ppm (t, ^1J(CH) 125.2 Hz, C^9). Mass spectrum (FAB) m/z 454 $[RhP_2C_3{}^tBu_3C_6H_{10}]^+$; 397 $[RhP_2C_3{}^tBu_2C_6H_{10}]^+$; 372 $[RhP_2C_3{}^tBu_3]^+$.

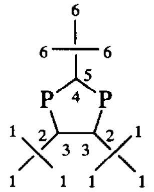
3.4. Synthesis of [Ru(η^5-$P_2C_3{}^tBu_3$)(η^5-C_8H_{11})] (3)

A solution of Na($P_2C_3{}^tBu_3$) (2 mmol) and Na(P_3C_2-^tBu) (2 mmol) (dme, 5 ml) was added at room temperature to a suspension of $[RuCl_2(COD)]_n$ (1680 mg, 3 mmol) (dme, 5 ml). The mixture was stirred for 1 h after which the solvent was removed. The black oil was dissolved in petroleum ether 60–80°C, and the solution filtered throught Celite, and subjected to column chromatography (Kieselgel/petroleum ether 60–80°C) to yield a yellow oil, which was heated under vacuum to 100°C for about 1 h, and then washed with ethanol to give a sublimable yellow solid (125°C, 0.1 mmHg) shown to be (η^5-cyclooctadienyl)(η^5-2,4,5-tri-t-butyl-1,3-diphosphacyclopentadienyl)ruthenium(II) (420 mg, 21%). (Found: C, 58.8%; H, 6.20%. $C_{23}H_{28}P_2Ru$ requires: C, 59.1%; H, 6.0%). ^{31}P-{^1H} NMR data (101.3 MHz, CD_2Cl_2, 25°C) δ_P 60.4 ppm. ^1H NMR data (500.1 MHz, CD_2Cl_2, 25°C) δ6.08 (t, $^3J(H^aH^b)$ 63 Hz, 1H, H^a), δ4.64 (ddd, $^3J(H^bH^c)$ 7.7 Hz, $^4J(H^bH^{(e)f})$ 1.3 Hz, 2H, H^b); δ4.48 (m, $^3J(H^cH^{f(e)})$ 3.5 Hz, 2H, H^c); δ1.92–1.87 (m, $^2J(H^eH^f)$ 15.5 Hz, 2H, H^e or H^f); δ1.42 (s, 18H, ^tBu); δ1.23–1.18 (m, 2H, H^d); δ1.13 (s, 9H, ^tBu); δ1.05–1.02 (m, 2H, H^f or H^e).



^{13}C-{^1H} NMR data (125.8 MHz; C_6D_6; 25°C) δ131.6 ppm (m, ^1J(CP) 76.4 Hz, C^3); δ129.6 ppm (t, ^1J(CP) 72.4 Hz, C^4); δ105.3 ppm (s, C^7); δ78.2 ppm (s, C^8); δ44.3 ppm (t, J(CP) 4.7 Hz, C^9); δ38.2 ppm (t, ^2J(CP) 22.2 Hz, C^2); δ36.6 ppm (t, ^3J(CP) 14.7 Hz, C^1); δ35.3 ppm (t, ^3J(CP) 8.0 Hz, C^6); δ28.4 ppm (s, C^{10}); C^5 is presumed to lie under the C^1 resonance.



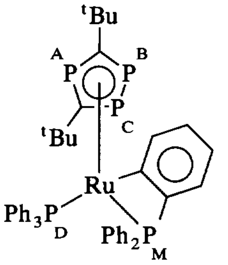


^{13}C NMR data (125.8 MHz, C_6D_6, 25°C) (only the most important resonances are given) δ105.3 ppm (d, J(CH) 159.6 Hz, C^7); δ78.2 ppm (d, J(CH) 162.0 Hz, C^8); δ44.3 ppm (t, J(CH) 145.2 Hz, J(CP) 4.8 Hz, C^9); δ28.4 ppm (t, J(CH) 128.9 Hz, C^{10}); δ20.6 ppm (t, J(CH) 125.9 Hz, C^{11}). Mass spectrum (EI) m/z 478 $[RuP_2C_3{}^tBu_3C_8H_{11}]^+$; 421 $[RuP_2C_3{}^tBu_2C_8H_{11}]^+$; 365 $[RuP_2C_3{}^tBu_2C_4H_7]^+$; 309 $[RuPC{}^tBuC_8H_{11}]^+$; 169 $[PC_2{}^tBu_2]^+$.

3.5. Synthesis of [Ru(η^5-$P_3C_2{}^tBu_2$)($PPh_2C_6H_4$)(PPh_3)] (4)

3.5.1. Method A

To a suspension of [$RuCl_2(\eta^6$-$C_6H_6)(PPh_3)$] (1000 mg, 2 mmol) (dme, 2 ml) was added a solution of Na($P_2C_3{}^tBu_3$) (2 mmol) and Na($P_3C_2{}^tBu_2$) (2 mmol) (dme, 3 ml). The mixture was stirred for 24 h and the solvent then removed to leave a black oil, which was extracted with CH_2Cl_2. The extract was subjected to column chromatography (Kieselgel/CH_2Cl_2) to give a brown oil, which yielded a yellow solid upon washing with petroleum ether 60–80°C. The yellow solid was identified as [2-(diphenylphosphano-κP)-phenyl-κC^1]-(η^5-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)(triphenylphosphane-κP)ruthenium(II) (920 mg, 55%). (Found: C, 64.13%; H, 5.02%. $C_{46}H_{47}P_5Ru$ requires C, 64.5%; H, 5.5%). $^{31}P-\{^1H\}$ NMR data (101.3 MHz, CD_2Cl_2; 25°C). δ_{PA} 106.7 ppm; δ_{PB} 36.9 ppm; δ_{PC} 97.4 ppm; δ_{PM} −37.4 ppm; $^2J(P^AP^B)$ 38.5 Hz; $^2J(P^AP^C)$ 33.4 Hz; $^2J(P^AP^D)$ 8.7 Hz; $^1J(P^BP^C)$ 400.8 Hz; $^2J(P^BP^M)$ 9.9 Hz; $^1J(P^CP^D)$ 11 Hz; $^2J(P^CP^M)$ 5.7 Hz; $^2J(P^DP^M)$ 36.3 Hz.



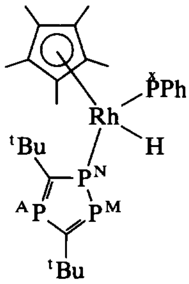
^1H NMR data (500.1 MHz, CD_2Cl_2, 25°C) δ0.74 (s, 9H, ᵗBu); δ0.94 (s, 9H, ᵗBu); δ6.97–7.94 (m, 29H, PPh_3, and $C_6H_4PPh_2$). Mass spectrum (FAB) m/z 856 $[RuC_2{}^tBu_2P_3PPh_3PPh_2C_6H_4]^+$; 594 $RuC_2{}^tBu_2P_3$-$PPh_2C_6H_4]^+$. A better yield (60%) was achieved by carrying out the reaction in the presence of free triphenylphosphane.

3.5.2. Method B

To a suspension of $[RuCl_2(PPh_3)_4]$ (2442 mg, 2 mmol) (dme, 2 ml) was added a solution of $Na(P_3C_2{}^tBu_2)$ (2 mmol) and $Na(P_2C_3{}^tBu_3)$ (2 mmol) (dme, 2 ml). The mixture was stirred for 24 h, and removal of the solvent and purification, by the procedures outlined for Method A, gave the [2(diphenylphosphano-κP)phenyl-κC¹]-(η⁵-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)(triphenylphosphane-κP)ruthenium(II) (354 mg, 20%), whose $^{31}P-\{^1H\}$ NMR spectrum was identical to the previous sample.

3.6. Synthesis of $[RhH(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}C_5Me_5)(PPh_3)]$ (5)

To a suspension of $[RhCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)_2]$ (580 mg, 1 mmol) (dme, 1 ml) was added a solution of $Na(P_2C_3{}^tBu_3)$ (1 mmol) and $Na(P_3C_2{}^tBu_2)$ (1 mmol) (dme, 5 ml). The resulting mixture was stirred for 24 h and the solvent then removed to leave a black oil, which was extracted with toluene. The extract was filtered through Celite and the solvent removed. Recrystallisation of the residue from toluene at −5°C for 3 days gave red crystals of (η¹-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl-κP¹)hydrido(η⁵-pentamethylcyclopentadienyl)triphenylphosphane-rhodium(III) (550 mg, 70%). (Found: C, 63.9%; H, 6.8%. $C_{38}H_{49}P_4Rh$ requires C, 62.3%; H, 6.7%). $^{31}P-\{^1H\}$ NMR data (101.3 MHz, toluene-d_8, 25°C) δ_PA 259.7 ppm; δpN 202.2 ppm; δ_PM 146.9 ppm; δ_PX 51.4 ppm; $^2J(P^AP^M)$ 39.1 Hz; $^2J(P^AP^N)$ 24.4 Hz; $^1J(P^MP^N)$ 512.7 Hz; $^2J(P^MP^X)$ 29.3 Hz; ^1J(RhP)X 146.5 Hz; $^1J(RhP^M)$ 126.9 Hz.



^1H NMR Data (250.1 MHz, toluene-d_8, 25°C) δ7.27–6.86 (s, 18H, Ph); δ1.73 (s, 15H, CH_3); δ1.49 (s, 9H, ᵗBu); δ1.44 (s, 9H, ᵗBu); δ-11 (m, 1H, H). Mass spectrum (FAB) m/z 732 $[RhHP_3C_5Me_5C_2{}^tBu_2PPh_3]^+$; 596 $[RhHP_3C_2{}^tBu_2PPh_3]^+$; 500 $[RhC_5Me_5PPh_3]^+$; 470 $[RhHP_3C_5Me_5C_2{}^tBu_2]^+$.

3.7. X-ray diffraction study

3.7.1. Crystal data

$C_{23}H_{29}P_2Rh$ (1), $M = 480.4$, monoclinic $P2_1/n$, $a = 10.025$ (5), $b = 19.428(9)$, $c = 11.876(7)$ Å, $\beta = 95.06(4)°$, $U = 2304.1$ Å³, $Z = 4$, $D_c = 1.39$ g cm⁻¹. Data were collected on an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation, λ = 0.71069 Å, μ = 8.7 cm⁻¹. A total of 4173 unique reflections were measured and 3186 with $|F^2| > 3\sigma(F^2)$ were used in the refinement. Non-H atoms were located using the heavy atom routines of SHELXS 86 and refinement with anisotropic thermal parameters by full matrix least squares. The refinement converged at $R = 0.039$, $R' = 0.049$. $C_{38}H_{49}P_4Rh$, (5) $M = 732.6$, triclinic, $P\bar{1}$ (No. 2), $a = 10.955(5)$, $b = 11.915(7)$, $c = 16.854(6)$ Å, $\alpha = 70.73(3)$, $\beta = 76.48(4)$, $\gamma = 63.60(4)$, $U = 1850.1$ Å³, $Z = 2$, $D_c = 1.32$ g cm⁻³. Data were collected on an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation, λ = 0.71069 Å, μ = 6.5 cm⁻¹. A total of 4533 unique reflections were measured, and 3507 with $|F^2| > 3\sigma(F^2)$ were used in the refinement. The structure was solved using heavy atom routines, and non-H atoms were refined with aniosotropic thermal parameters by full matrix least squares. The hydride H could not be located; Me and Ph H atoms were held fixed at calculated positions $U_{iso} = 1.3_{eq}$ for the parent atom. Final residuals were $R = 0.056$, $R' = 0.091$.

For both structures full lists of bond lengths and angles and tables of hydrogen atom coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

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