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Use of 1,3-Diphosphacyclobutadiene Complexes in the Synthesis of Mixed Metal Aggregates Containing Cobalt, Rhodium, and Platinum: Structure of a Hexarhodium Complex

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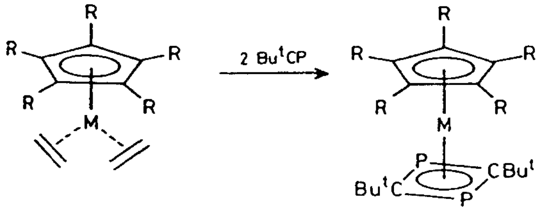
ABSTRACT

The η^4-diphosphacyclobutadiene complexes $[M(\eta^5\text{-}C_5R_5)(\eta^4\text{-}P_2C_2Bu^t_2)]$ (M = Co, Rh; R = H, Me), react with Rh(I), Pt(O), and Pt(II) centers via the phosphorus lone pairs of the rings to afford mixed metal complexes. The crystal and molecular structure of the novel hexarhodium complex $[Rh_2Cl_2\{Rh(P_2C_2Bu^t_2)\}]_4]$ (Cp = η^5-C_5H_5) is presented and discussed.

INTRODUCTION

The chemistry and ligating ability of phosphaalkynes, RC≡P, is developing rapidly [1–4]. In addition to complexes containing η^1- and η^2-ligated phosphaalkynes, it is also possible to induce cycloaddition reactions at transition metal centers to afford η^4-1,3-diphosphacyclobutadiene complexes [5–8]. Thus, Nixon and coworkers and Binger et al. have independently shown that $[M(\eta^5\text{-}C_5R_5)(C_2H_4)_2]$ (R = H, M = Co, Rh: R = Me, M = Co, Rh, Ir) or $[M(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ (C_9H_7 = indenyl, M = Co, Rh), afford the 'sandwich' compounds $[M(\eta^5\text{-}C_5R_5)(P_2C_2R'_2)]$ and $[M(\eta^5\text{-}C_9R_7)(P_2C_2R'_2)]$ (R′ = Bu^t, isopropyl), which have been fully structurally characterized. A typical example is shown below:



Following our original report of the first 1,3-diphosphacyclobutadiene metal complexes [5], Binger and coworkers [6, 7] briefly reported the synthesis of $[Co(Cp)(\eta^4\text{-}P_2C_2R_2)]$ (R = Bu^t, *i*-Pr) and its further reactions with $[Co(Cp)(C_2H_4)_2]$ to give the di- and trimetallic compounds **1** and **2**, respectively, utilizing the lone pairs of electrons on the two phosphorus atoms of the diphosphacyclobutadiene rings.

More recently, the same authors have reported [8] syntheses and crystal structures of the polynuclear indenyl rhodium complexes **3** and **4**. We now describe our own results in this area including the synthesis and structural characterization of hexametallic metal aggregate complexes containing both η^4- and η^1-ligated diphosphacyclobutadiene rings. A brief report of part of this work has already appeared [9].

RESULTS AND DISCUSSION

Reaction of $[Rh(Cp)\eta^4\text{-}(Bu^tCP)_2]$ with $[\{RhCl(C_2H_4)_2\}_2]$

$[Rh(Cp)\eta^4\text{-}(Bu^tCP)_2]$ reacts with $[Rh\{Cl(C_2H_4)_2\}_2]$ to afford the red brown complex **5**, which was

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This paper is dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

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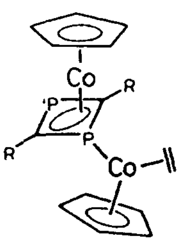

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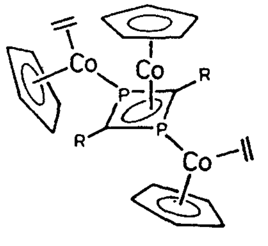
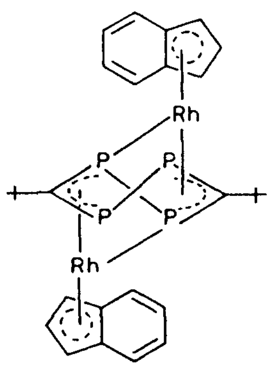


: R = tert-Bu
b: R = iso-Pr

2



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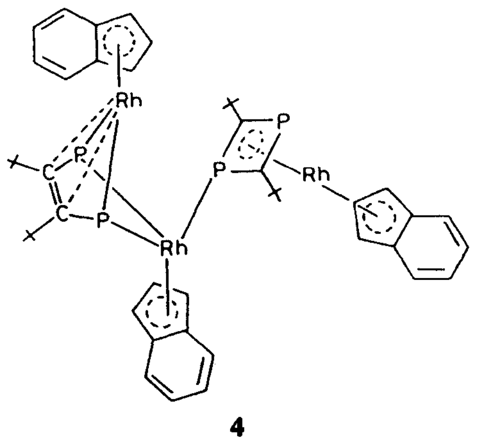

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formulated as the hexarhodium complex $[\mathrm{Rh_2Cl_2\{Rh(Cp)(P_2C_2Bu^t_2)\}_4}]$ on the basis of its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum, and its structure was subsequently confirmed by a single crystal X-ray diffraction study, vide infra.

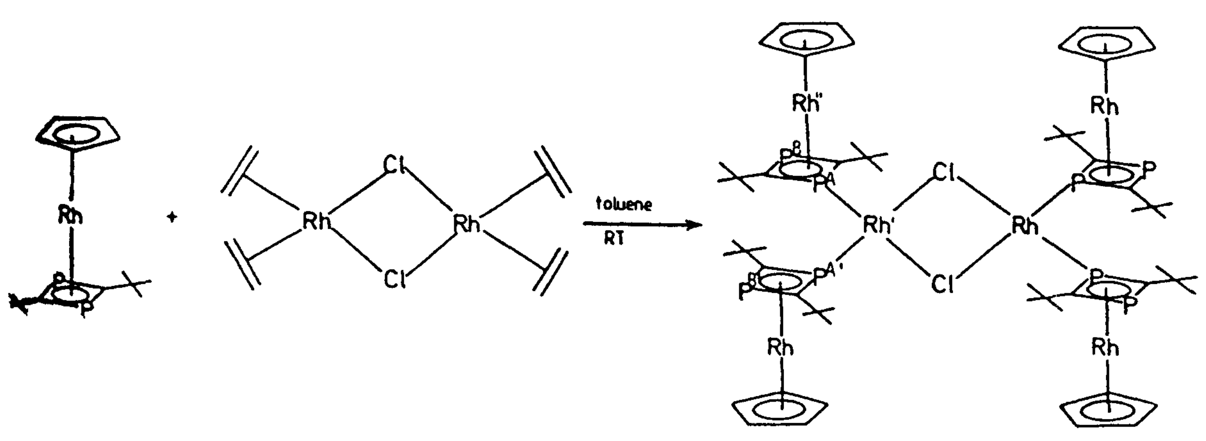
The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **5** is shown in Figure 1 and chemical shift and coupling constant data are summarized in Table 1. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum exhibits a doublet of doublets of doublets ($\delta(\mathrm{P^A}) = -26.4$ $^1J(\mathrm{Rh'P^A}) = 232.2$ Hz, $^1J(\mathrm{Rh''P^A}) = 35.7$ Hz, $^2J(\mathrm{P^AP^B}) = 8.9$ Hz) and another doublet of doublets ($\delta(\mathrm{P^B}) = -152.0$, $^1J(\mathrm{Rh''P^B}) = 35.7$ Hz, $^2J(\mathrm{P^AP^B}) = 8.9$ Hz). On the assumption that the rhodium atoms of the $[\mathrm{Rh(Cp)\{\eta^4\text{-}(Bu^tCP)_2\}}]$ groups are equivalent, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum is expected to exhibit an $[[\mathrm{ABM}]_2\mathrm{X}]_2$ pattern (A,B = ^{31}P; M,X = ^{103}Rh) with the observation of long range couplings, e.g. $^3J(\mathrm{Rh'P^B})$, $^4J(\mathrm{P^AP^{B'}})$. The low resolution of the spectrum, however, makes these coupling constants impossible to measure accurately. The observed $^1J(\mathrm{Rh'P^A})$ coupling constant (232.2 Hz) is large and lies within the range normally observed for η^1-bonded rhodium–phosphine complexes. $^1J(\mathrm{Rh''P^A})$ or $^1J(\mathrm{Rh''P^B})$ are small (35.7 Hz), as expected for a π-bonded rhodium complex.

TABLE 1 $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR parameters for complexes **5**, **6**, and **7**

Compound	5	6	7
δ (P^A)^a	−26.4	−45.5	−67.9
δ (P^B)^a	−152.0	−135.0	−150.6
^1J(Rh′P^A)^b	232.2	233.8	144.3
^1J(Rh″P^A) = ^1J(Rh″P^B)^b	35.7	36.8	—
^2J(P^{A}P^B)^b	8.9	6.9	not resolved

[a] Relative to trimethyl phosphite.
[b] In Hz.

The large $^1J(\mathrm{Rh'P^A})$ coupling constant indicates that the phosphorus atoms, P^A or P$^{A'}$, are bound directly to the metal via the lone pair electrons and that one of the ring phosphorus atoms in **5** acts as a donor site for further ligation to interlink the metal–ligand fragments. This hexarhodium complex is structurally related to other well known chloro-bridged complexes $[\{\mathrm{RhClL_2}\}_2]$ (L = CO, PF$_3$) [10, 11, 12], but it is the first time that such systems have been utilized in metal aggregate synthesis.



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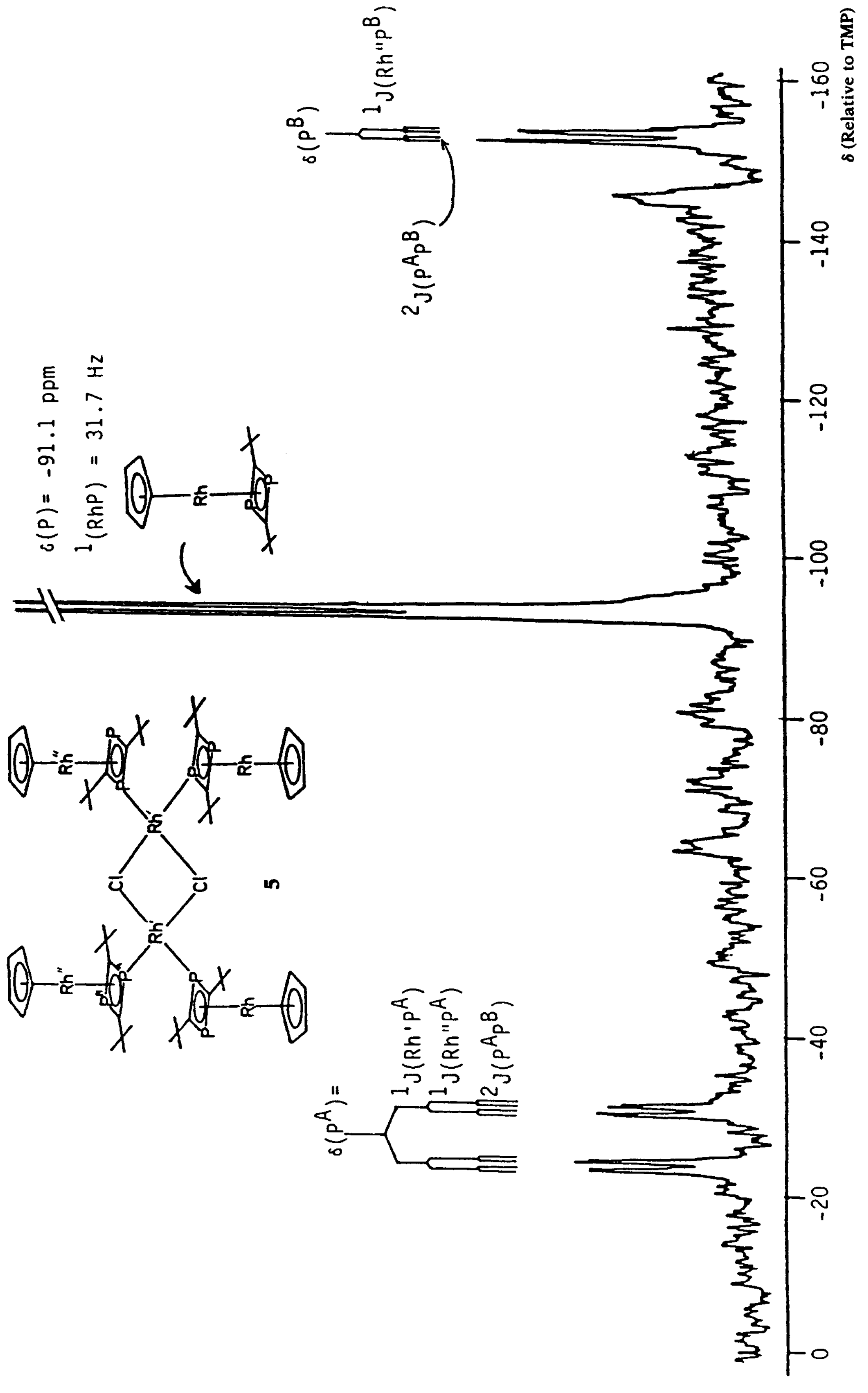

FIGURE 1 $^{31}P\{^1H\}$ NMR Spectrum of 5

Description of the Structure of $[Rh_2Cl_2\{Rh(Cp)(P_2C_2Bu^t_2)\}_4]$ **5**

The molecular structure of **5** · $5CHCl_3$ is shown in Figure 2 together with selected bond lengths and bond angles. There are a number of $CHCl_3$ solvent molecules incorporated in the structure, and their presence made accurate refinement of data very difficult, leading to a larger than normally acceptable R-factor (R = 0.116, R′ = 0.147); however, the structural features of the hexarhodium complex are clearly defined. (See also Tables 2 and 3.)

The molecular structure of **5** shows that the four units of the η^4-1,3-diphosphacyclobutadiene rhodium complexes are linked to the two chloro-bridged rhodium atoms Rh(2) and Rh(2′) through one of the phosphorus atoms of the four-membered ring (P(1), P(1′), P(3), and P(3′)).

It is interesting to note that the two rhodium atoms (Rh(2) and Rh(2′)), the two chlorine atoms (Cl(1) and Cl(1′)), and all eight phosphorus atoms in the molecule (P(1), P(2), P(3), P(4), P(1′), P(2′), P(3′), and P(4′)) lie in the same plane. However, the four η^4-1,3-diphosphacyclobutadiene rings that are still planar, even after coordination to Rh(2) and Rh(2′), are inclined at about 53–55° to the former plane. The arrangement of the four [Rh(Cp)] groups is in a fashion that minimizes the steric repulsion;

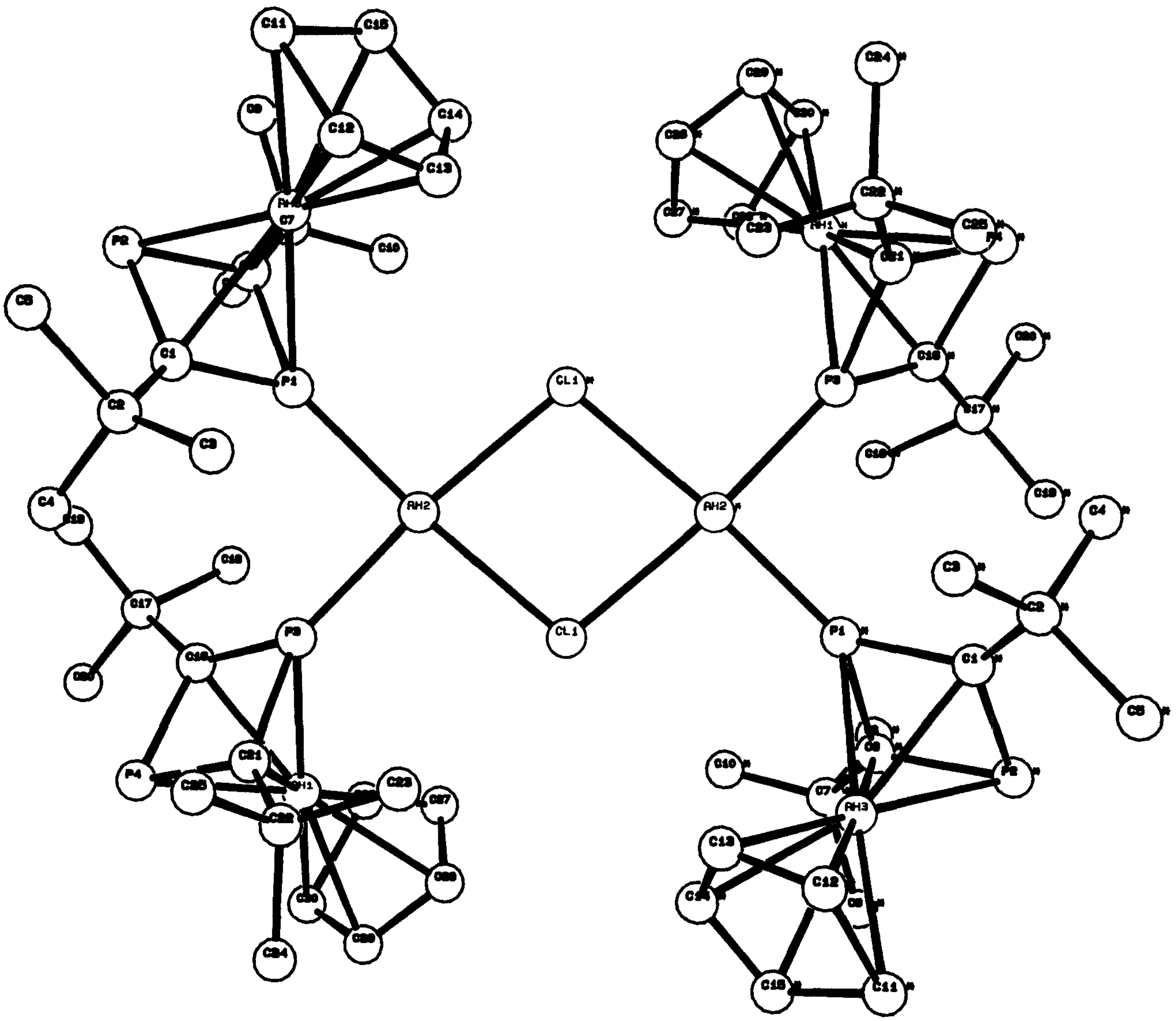

FIGURE 2 The Molecular Structure of 5·$5CHCl_3$. Important dimensions: Rh(1)–P(3) 2.317(7) Å, Rh(1)–P(4) 2.333(9) Å, Rh(2)–P(1) 2.174(8) Å, Rh(2)–P(3) 2.178(7) Å, Rh(3)–P(1) 2.339(7) Å, Rh(3)–P(2) 2.351(9) Å, P(1)–C(6) 1.84(3) Å, P(1)–C(1) 1.79(3) Å, P(2)–C(1) 1.84(3) Å, P(2)–C(6) 1.83(3) Å

TABLE 2 Intramolecular Distances (Å) and Angles (°) for **5** with Estimated Standard Deviations in Parentheses

Bonds				*Angles*			
Rh(1)–P(3)	2.317(7)	Rh(1)–P(4)	2.333(9)	Cl(1)–Rh(2)–Cl(1)^a	80.3(2)	Cl(1)–Rh(2)–P(1)	174.5(3)
Rh(1)–C(16)	2.13(3)	Rh(1)–C(21)	2.19(3)	Cl(1)–Rh(2)–P(3)	93.7(3)	Cl(1)^a–Rh(2)–P(1)	95.3(3)
Rh(1)–C(26)	2.27(4)	Rh(1)–C(27)	2.21(4)	Cl(1)–Rh(2)–P(3)	173.2(3)	P(1)–Rh(2)–P(3)	90.9(3)
Rh(1)–C(28)	2.20(4)	Rh(1)–C(29)	2.22(4)	Rh(2)–Cl(1)–Rh(2)^a	99.7(2)	Rh(2)–P(1)–C(1)	136(1)
Rh(1)–C(30)	2.24(4)	Rh(3)–P(1)	2.339(7)	Rh(2)–P(1)–C(6)	139(1)	C(1)–P(1)–C(6)	85(1)
Rh(3)–P(2)	2.351(9)	Rh(3)–C(1)	2.25(3)	C(1)–P(2)–C(6)	84(1)	Rh(2)–P(3)–C(16)	136(1)
Rh(3)–C(6)	2.16(3)	Rh(3)–C(11)	2.34(4)	Rh(2)–P(3)–C(21)	140(1)	C(16)–P(3)–C(21)	84(1)
Rh(3)–C(12)	2.25(4)	Rh(3)–C(13)	2.30(4)	C(16)–P(4)–C(21)	80(1)	P(1)–C(1)–P(2)	97(2)
Rh(3)–C(14)	2.18(4)	Rh(3)–C(15)	2.34(4)	P(1)–C(1)–C(2)	132(2)	P(2)–C(1)–C(2)	131(2)
Rh(2)–Cl(1)	2.411(8)	Rh(2)–Cl(1)^a	2.404(6)	C(1)–C(2)–C(3)	111(3)	C(1)–C(2)–C(4)	98(2)
Rh(2)–P(1)	2.174(8)	Rh(2)–P(3)	2.178(7)	C(1)–C(2)–C(5)	105(2)	C(3)–C(2)–C(4)	116(3)
Cl(2)–C(31)	1.83(6)	Cl(3)–C(31)	1.34(7)	C(3)–C(2)–C(5)	113(3)	C(4)–C(2)–C(5)	111(3)
Cl(4)–C(31)	1.70(6)	Cl(5)–C(32)	1.88(6)	P(1)–C(6)–P(2)	95(1)	P(1)–C(6)–C(7)	134(3)
Cl(5)–C(32)	1.49(7)	Cl(6)–C(32)	1.56(7)	P(2)–C(6)–C(7)	130(3)	C(6)–C(7)–C(8)	107(2)
Cl(6)–C(32)	1.56(7)	Cl(7)–C(33)	1.37(7)	C(6)–C(7)–C(9)	112(3)	C(6)–C(7)–C(10)	117(3)
Cl(8)–C(33)	1.89(7)	Cl(9)–C(33)	1.75(7)	C(8)–C(7)–C(9)	104(3)	C(8)–C(7)–C(10)	97(3)
P(1)–C(1)	1.79(3)	P(1)–C(6)	1.84(3)	C(9)–C(7)–C(10)	118(3)	C(12)–C(11)–C(15)	91(3)
P(2)–C(1)	1.84(3)	P(2)–C(6)	1.83(3)	C(11)–C(12)–C(13)	113(3)	C(12)–C(13)–C(14)	110(4)
P(3)–C(16)	1.68(3)	P(3)–C(21)	1.80(3)	C(13)–C(14)–C(15)	106(4)	C(11)–C(15)–C(14)	117(3)
P(4)–C(16)	1.86(3)	P(4)–C(21)	1.75(3)	P(3)–C(16)–P(4)	98(1)	P(3)–C(16)–C(17)	140(2)
C(1)–C(2)	1.55(4)	C(2)–C(3)	1.46(5)	P(4)–C(16)–C(17)	120(2)	C(16)–C(17)–C(18)	104(3)
C(2)–C(4)	1.54(4)	C(2)–C(5)	1.68(5)	C(16)–C(17)–C(19)	113(3)	C(16)–C(17)–C(20)	114(2)
C(6)–C(7)	1.47(4)	C(7)–C(8)	1.69(5)	C(18)–C(17)–C(19)	110(3)	C(18)–C(17)–C(20)	107(3)
C(7)–C(9)	1.53(6)	C(7)–C(10)	1.40(6)	C(19)–C(17)–C(20)	110(3)	P(3)–C(21)–P(4)	97(1)
C(11)–C(12)	1.68(6)	C(11)–C(15)	1.53(6)	P(3)–C(21)–C(22)	134(2)	P(4)–C(21)–C(22)	128(2)
C(12)–C(13)	1.32(6)	C(13)–C(14)	1.46(6)	C(21)–C(22)–C(23)	110(3)	C(21)–C(22)–C(24)	108(2)
C(14)–C(15)	1.37(6)	C(16)–C(17)	1.57(4)	C(21)–C(22)–C(25)	109(3)	C(23)–C(22)–C(24)	112(3)
C(17)–C(18)	1.66(5)	C(17)–C(19)	1.47(5)	C(23)–C(22)–C(25)	106(3)	C(24)–C(22)–C(25)	112(2)
C(17)–C(20)	1.51(4)	C(21)–C(22)	1.49(4)	C(27)–C(26)–C(30)	98(3)	C(26)–C(27)–C(28)	119(3)
C(22)–C(23)	1.50(5)	C(22)–C(24)	1.59(5)	C(27)–C(28)–C(29)	105(3)	C(28)–C(29)–C(30)	112(3)
C(22)–C(25)	1.58(5)	C(26)–C(27)	1.33(5)	C(26)–C(30)–C(29)	105(3)	Cl(2)–C(31)–Cl(3)	117(4)
C(26)–C(30)	1.63(5)	C(27)–C(28)	1.37(5)	Cl(2)–C(31)–Cl(4)	101(3)	Cl(3)–C(31)–Cl(4)	124(5)
C(28)–C(29)	1.37(5)	C(29)–C(30)	1.36(6)	Cl(5)–C(32)–Cl(5)^b	101(4)	Cl(5)–C(32)–Cl(6)	106(3)
				Cl(5)–C(32)–Cl(6)	129(5)	Cl(7)–C(33)–Cl(8)	117(4)
				Cl(7)–C(33)–Cl(9)	124(5)	Cl(8)–C(33)–Cl(9)	99(3)

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[a] Symmetry operation: $-x$, y, $0.5 - z$

[b] Symmetry operation: $1 - x$, y, $-0.5 - z$

two [Rh(Cp)] groups are located diagonally above and below the Rh(2)–Rh(2′)–(P(1)–P(2)–P(3)–P(4))–P(1′)–P(2′)–P(3′)–P(4′) plane. The cyclopentadienyl rings and the η^4-1,3-diphosphacyclobutadiene rings are almost parallel to each other.

Reaction of $[Rh(Cp^*)\{\eta^4\text{-}(Bu^tCP)_2\}]$ *with* $[\{RhCl(C_2H_4)_2\}_2]$

In a similar fashion, treatment of $[\mathrm{Rh(Cp^*)\{\eta^4\text{-}(Bu^tCP)_2\}}]$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$), with $[\{\mathrm{RhCl(C_2H_4)_2}\}_2]$ at room temperature afforded the red brown complex, $[\mathrm{Rh_2Cl_2\{Rh(Cp^*)(P_2C_2Bu^t_2)\}_4}]$, **6**.

The product was identified by its $^{31}P\{^1H\}$ NMR spectrum, which is similar to that observed for **5** ($\delta(P^A) = -45.5$ (ddd, $^1J(Rh'P^A) = 233.8$ Hz,

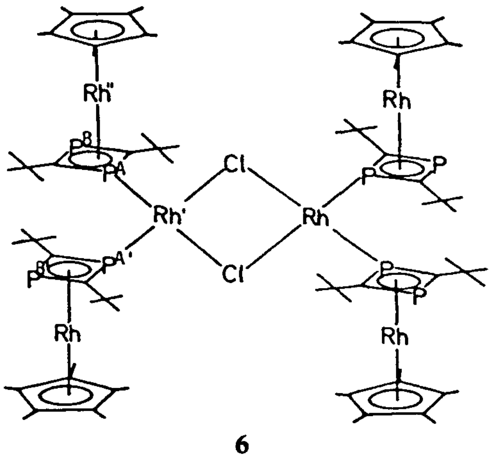

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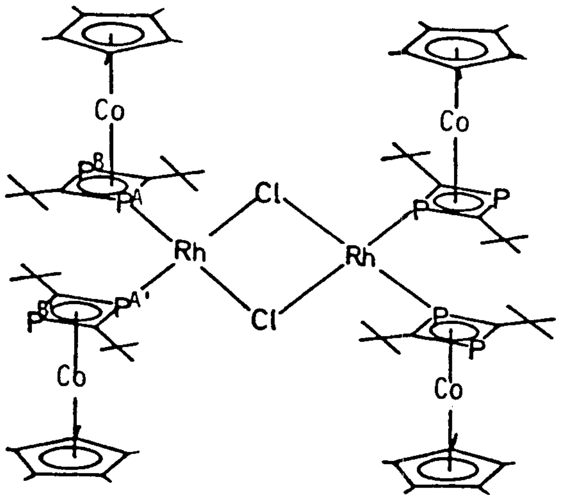
TABLE 3 Fractional Atomic Coordinates for **5** ($\times 10^4$ for Rh, P, Cl; $\times 10^3$ for C) with Estimated Standard Deviations in Parentheses

	x	*y*	*z*
Rh(1)	−1584(1)	1863(2)	947(1)
Rh(2)	65(1)	2611(1)	1872(1)
Rh(3)	1805(1)	3414(2)	1758(1)
Cl(1)	−733(3)	2588(6)	2321(2)
Cl(2)	−3742(9)	1982(13)	1833(8)
Cl(3)	−3878(10)	3448(12)	1348(8)
Cl(4)	−4418(11)	2073(13)	890(8)
Cl(5)	*5493(9)*	−1235(13)	−2130(9)
Cl(6)	5000	273(16)	−2500
Cl(7)	−6496(10)	1947(10)	489(10)
Cl(8)	−6251(11)	3173(15)	1199(9)
Cl(9)	−6695(11)	3602(13)	244(9)
P(1)	838(3)	2708(4)	1522(3)
P(2)	1719(4)	2775(6)	1005(3)
P(3)	−624(3)	2557(4)	1176(3)
P(4)	−1392(4)	2569(5)	288(3)
C(1)	102(1)	336(2)	107(1)
C(2)	72(1)	417(2)	83(1)
C(3)	46(1)	467(2)	116(1)
C(4)	23(1)	377(2)	40(1)
C(5)	129(2)	466(2)	64(1)
C(6)	157(1)	216(2)	150(1)
C(7)	188(2)	140(2)	173(1)
C(8)	158(2)	60(3)	136(1)
C(9)	259(2)	138(3)	175(2)
C(10)	169(2)	111(3)	213(2)
C(11)	271(2)	426(2)	194(1)
C(12)	207(2)	470(2)	206(1)
C(13)	186(2)	431(3)	239(2)
C(14)	223(2)	356(2)	253(1)
C(15)	275(2)	363(3)	235(2)
C(16)	−75(1)	194(2)	68(1)
C(17)	−42(1)	122(2)	47(1)
C(18)	−19(2)	57(2)	92(1)
C(19)	13(1)	151(2)	31(1)
C(20)	−87(2)	76(2)	6(1)
C(21)	−129(1)	313(2)	83(1)
C(22)	−160(1)	393(2)	91(1)
C(23)	−143(2)	415(3)	143(2)
C(24)	−235(2)	383(3)	70(1)
C(25)	−133(2)	466(2)	65(1)
C(26)	−177(2)	55(2)	117(1)
C(27)	−179(2)	109(2)	152(1)
C(28)	−221(2)	173(2)	144(1)
C(29)	−257(2)	160(2)	98(1)
C(30)	−237(2)	93(3)	76(1)
C(31)	−416(3)	271(4)	137(2)
C(32)	503(4)	−64(4)	−267(2)
C(33)	−668(3)	272(4)	60(2)

$^1J(Rh''P^A)$ = 36.8 Hz, $^2J(P^AP^B)$ = 6.9 Hz; $\delta(P^B)$ = −135.0, $^1J(Rh''P^B)$ = 36.8 Hz, $^2J(P^BP^A)$ = 6.9 Hz). The $^{31}P\{^1H\}$ NMR data for **6** are summarized in Table 1, and it is interesting to note that the $^1J(Rh'P^A)$, $^1J(Rh''P^B)$, $^1J(Rh''P^A)$, and $^2J(P^AP^B)$ coupling constants for **5** and **6** are identical.

Reaction of $[Co(Cp^*)\eta^4\text{-}(Bu^tCP)_2]$ *with* $[\{RhCl(C_2H_4)_2\}_2]$

In an analogous way to that described above, the reaction of $[Co(Cp^*)\eta^4\text{-}(Bu^tCP)_2]$ with $[\{RhCl(C_2H_4)_2\}_2]$ gives the greenish brown mixed metal complex $[Rh_2Cl_2\{Co(Cp^*)(P_2C_2Bu^t_2)\}_4]$, **7**. The product was formulated by its $^{31}P\{^1H\}$ NMR and ^1H NMR spectra, and confirmed by elemental analysis.



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The $^{31}P\{^1H\}$ NMR spectrum of **7** shown in Figure 3 is expected to exhibit the $[[AB]_2X]_2$ pattern (A,B = ^{31}P; X = ^{103}Rh) in the $^{31}P\{^1H\}$ NMR spectrum, but the line broadenings caused by the quadrupolar cobalt nuclei makes it impossible to measure $^2J(P^AP^B)$ and other long range couplings between the ^{31}P and ^{103}Rh nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **7** only shows a broad doublet of ($\delta(P^A)$ = −67.9, $^1J(RhP^A)$ = 144.3 Hz) and a broad singlet ($\delta(P^B)$ = −150.6). Table 1 summarizes the NMR data for **7**.

Reaction of $[Co(Cp^*)\eta^4\text{-}(Bu^tCP)_2]$, *with* $[\{Pt(\mu\text{-}Cl)ClPEt_3\}_2]$

A further investigation was made on the utility of the 1,3-diphosphacyclobutadiene metal complexes in the synthesis of mixed metal aggregates by treating $[Co(Cp^*)\eta^4\text{-}(Bu^tCP)_2]$ with the chloro-bridged platinum dimer $[\{Pt(\mu\text{-}Cl)ClPEt_3\}_2]$. The reaction was carried out in an NMR tube and monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

After two days, an orange complex formed and its $^{31}P\{^1H\}$ NMR spectrum exhibits a broad singlet ($\delta(P^A)$ = −95.6 with platinum satellites $^1J(PtP^A)$ = 2278 Hz), a doublet ($\delta(P^B)$ = −120.4, $^1J(PtP^B)$ = 2795 Hz, $^2J(P^AP^B)$ = 7.3 Hz), and an unresolved multiplet ($\delta(P^C)$ = −150.5). The small $^2J(P^APtP^B)$

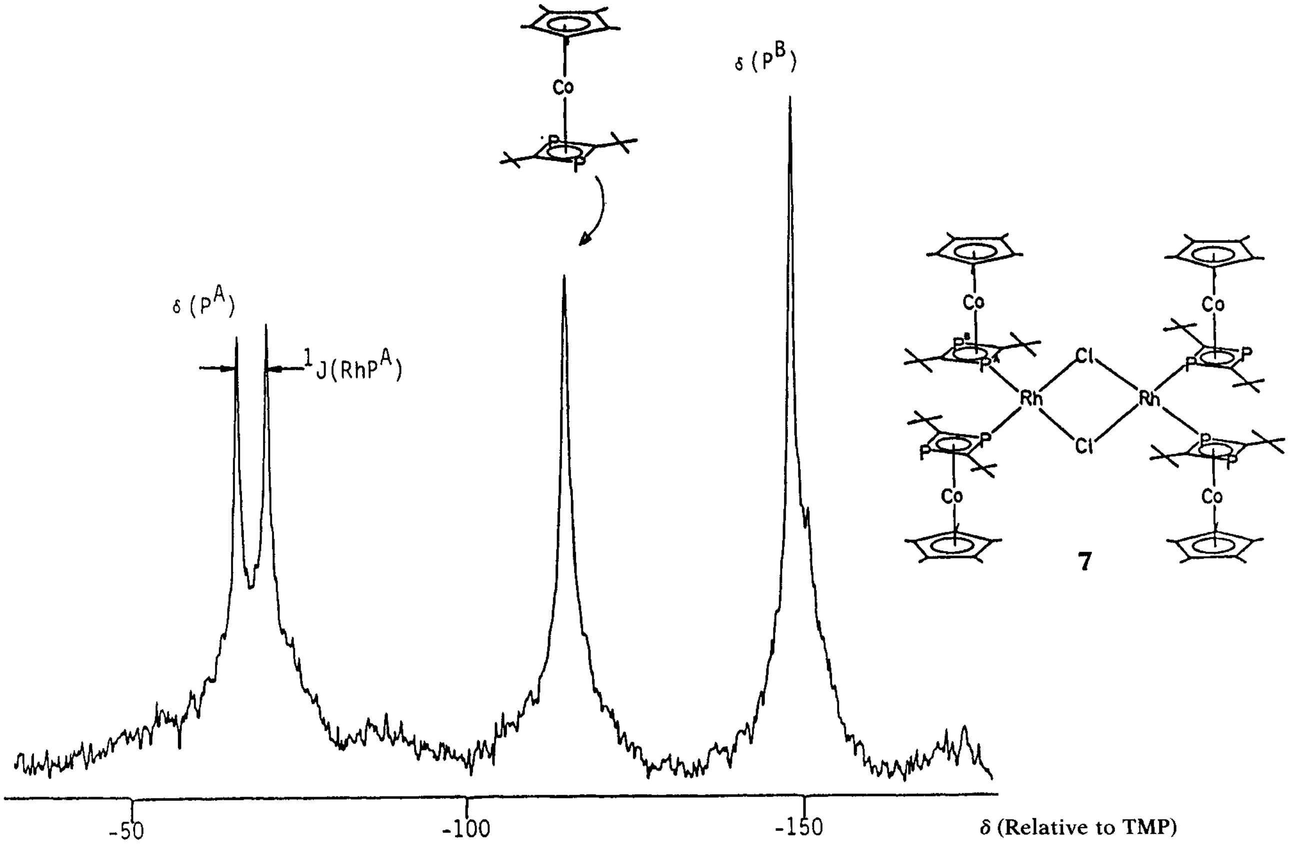

FIGURE 3 $^{31}P\{^1H\}$ NMR Spectrum of $[Rh_2Cl_2\{Co(Cp^*)(P_2C_2Bu^t_2)\}_4]$, **7**

coupling constant (7.3 Hz) indicates that the product might be a *cis*-disubstituted platinum complex; however, after 10 days, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a completely new pattern of resonances in which the small $^2J(PP)$ *cis*-coupling was replaced with a large $^2J(PP)$ coupling constant (>500 Hz), indicating the formation of a *trans*-isomer (see Figure 5). The new complex was identified as trans $[PtCl_2(PEt_3)Co(Cp^*)\eta^4\text{-}(Bu^tCP)_2]$, **8** on the basis of its $^{31}P\{^1H\}$ NMR spectrum (see Table 4).

The $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits two doublets ($\delta(P^A) = -88.8$, $^1J(PtP^A) = 2259$ Hz, $^2J(P^AP^B) = 510$ Hz; $\delta(P^B) = -126.3$, $^1J(PtP^B) = 2814$ Hz, $^2J(P^BP^A) = 510$ Hz) and a broad singlet ($\delta(P^C) = -150.0$).

In addition to the resonances for complex **8**, the $^{31}P\{^1H\}$ NMR spectrum shown in Figure 4 gave evidence for a small amount of a new complex **9** from the observation of two weak sets of doublets, each with platinum satellites ($\delta(P^A) = -112.2$,

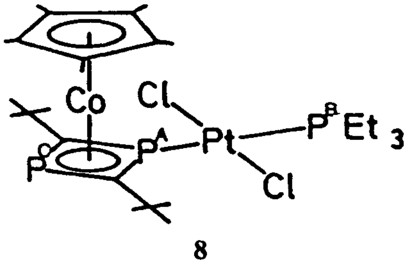

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TABLE 4 $^{31}P\{^1H\}$ NMR data for complexes **8** and **9**

	$\delta(P)^a$			$^1J(PtP)^b$		$^2J(PP')^b$
Complex	P^A	P^B	P^C	$^1J(PtP^A)$	$^1J(PtP^B)$	$^2J(P^AP^B)$
8	−88.8	−126.3	−150.0	2250	2814	510
9	−111.2	−123.5	—	2282	2928	535

[a] Relative to trimethyl phosphite.
[b] In Hz; $^2J(P^AP^C)$ not resolved.

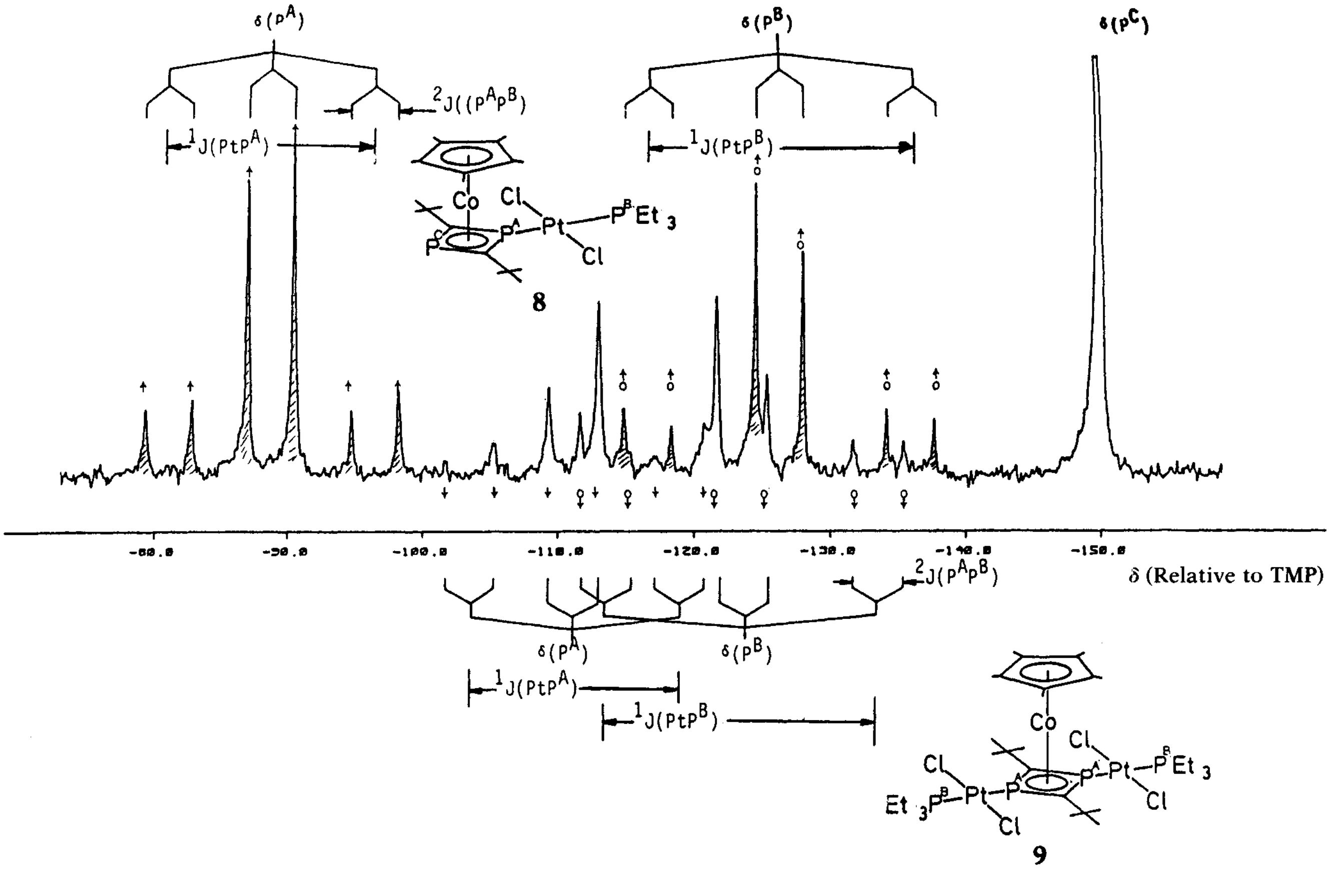
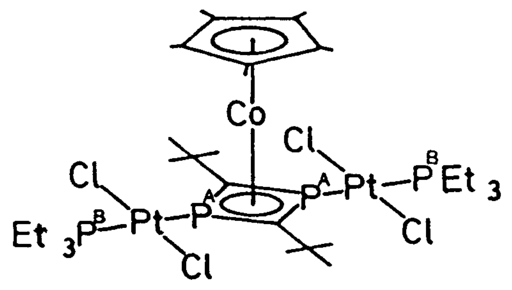


FIGURE 4 $^{31}P\{^1H\}$ NMR spectra of **8** and **9**

$^1J(PtP^A)$ = 2282 Hz, $^2J(P^AP^B)$ = 535 Hz; $\delta(P^B)$ = −123.5, $^1J(PtP^B)$ = 2928 Hz, $^2J(P^AP^B)$ = 535 Hz). The similarity of $^1J(PtP)$ in **9** to that in **8** indicates that it is best formulated as *trans*-[$\{PtCl_2(PEt_3)\}_2Co(Cp^*)\eta^4$-$(Bu^tCP)_2$].



9

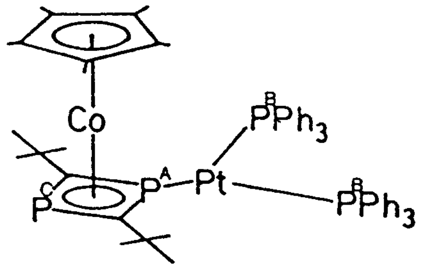
In mixed tertiary phosphine complexes of the type *trans*-[$PtCl_2(PR_3)(P'R_3)$] (R = alkyl, aryl), the values of $^1J(PtP)$ and $^1J(PtP')$ lie in the 2400–2500 Hz region and the value of $^2J(PPtP')$ is ca 470 Hz.

Interestingly, the value of $^1J(PtP_L)$ (P_L = [$Co(Cp^*)\eta^4$-$(Bu^tCP)_2$]) measured in complexes **8** and **9** for the coordinated 'ligand' (L) are unusually small, lying in the range 2250–2282 Hz, and are only slightly larger than the values for $^1J(PtP)$ found for PR_3 trans to Me in complexes of the type *cis*-[$PtMe(PR_3)_2$] [13]. This observation is similar to that also reported by Nixon et al. [14] for phosphaalkyne cluster complexes of the type *trans*-[$PtCl_2(PR_3)$-$\{Mo_2(Bu^tCP)_2(CO)_4(Cp)_2\}$].

The low $^1J(PtP_L)$ values presumably reflect the unusual s-character of the lone pair on phosphorus in the 1,3-diphosphacyclobutadiene ring of **8** and **9**. The C–P–C angles (81.5(5)°) are much smaller than the normal C–P–C angles in PR_3 systems. Similar small angles at the phosphorus have been observed for the related complexes [$Mo_2(CO)_4$-$(Cp)_2(Bu^tCP)$] and [$Mo_2(CO)_4(Cp)_2(Bu^tCP)$-$(W(CO)_5)$] [15].

Reaction of [$Co(Cp^*)(\eta^4$-$(Bu^tCP)_2)$], *with* [$Pt(PPh_3)_2(C_2H_4)$]

Treatment of [$Co(Cp^*)(\eta^4$-$(Bu^tCP)_2)$] with the zero-valent platinum complex [$Pt(PPh_3)_2(C_2H_4)$] in toluene afforded the blood red complex. [$Pt(PPh_3)_2\{Co(Cp^*)(\eta^4$-$(Bu^tCP)_2)\}$], **10**, which was characterized by NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum of **10** shown in Figure 5 exhibits a triplet of doublets ($\delta(P^A)$ = −35.9, $^1J(PtP^A)$ = 4176 Hz, $^2J(P^AP^B)$ = 158 Hz, $^2J(P^AP^C)$ = 9.5 Hz), a doublet ($\delta(P^B)$ = −96.2, $^1J(PtP^B)$ = 4565 Hz, $^2J(P^BP^A)$ = 158 Hz) and a broad singlet ($\delta(P^C)$ = −155.5). The large value of the $^1J(PtP^A)$ coupling constant (4176 Hz) indicates that one of the phosphorus lone pair electrons of the ring is directly bonded to the platinum. This value is of the same order of magnitude as found in η^1-bonded phosphaalkene complexes [Pt(PCy$_3$)$_2$XylP=CPh$_2$)] (Xyl = 2,6-dimethylphenyl) [16] and [Pt(PPh$_3$)$_2${P(mesityl)=CPh$_2$}] [18, 19], and is very much bigger than those of the η^2-bonded phosphaalkyne complexes [PtPPh$_3$)$_2\eta^2$-(Bu^{t}CP)] [17, 20] and [PtPPh$_3$)$_2\eta^2$-(AdCP)] [21]. The $^2J(P^AP^B)$ coupling constant is bigger than that found in η^2-complexes and identical to those of the η^1-complexes.



10

Nixon et al. [18] reported that, in the η^1-phosphaalkene complex, [Pt(PPh$_3$)$_2$P(mesityl)=CPh$_2$], the enhanced s-character of the phosphorus lone pair of the phosphaalkene results in a larger $^1J(PtP^A)$ coupling constant than the $^1J(PtP^C)$ of the PPh$_3$ ligands. However, this is not observed for complex **10** since, although the donor phosphorus atom in the diphosphacyclobutadiene ring is formally sp^2-hybridized, it has a smaller C–P–C bond angle (81.5(5)°) than that in P(mesityl)=CPh$_2$ (107.5°) [16], indicating a higher s-character. A much higher $^1J(PtP^A)$ is expected for **10**, as has been observed in the hexarhodium complexes **5** and **6** ($^1J(RhP^A)$ ca 233 Hz) compared with the corresponding chloro-bridged complex [{Rh(μ-Cl)(PPh$_3$)$_2$}$_2$] (^1J(RhP) = 193 Hz).

EXPERIMENTAL

All manipulations were carried out using Schlenk-tube techniques under an atmosphere of dry argon or dinitrogen gas or in vacuo. All solvents were redistilled and dried before use. ^{31}P and ^{1}H NMR spectra were recorded on a Bruker WP80 or Bruker WM360 FT spectrometer. ^{31}P chemical shifts are relative to P(OME)$_3$. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrometer. Elemental analyses were carried out in the School of Chemistry at Sussex. Bu^{t}C≡P was prepared by published procedures, [22–24] as were the following metal complexes [Co(η^5-C$_5$R$_5$)(C$_2$H$_4$)$_2$] (R = H, Me) [25, 26], [Rh(η^5-C$_5$R$_5$)(C$_2$H$_4$)$_2$] (R = H, Me) [27, 28], [{RhCl(C$_2$H$_4$)$_2$}$_2$] [29], [{Pt(μ-Cl)(Cl)(PEt$_3$)}$_2$] [30], and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] [31].

Reaction of [Rh(Cp)η^4-(Bu^{t}CP)$_2$] with [{RhCl(C$_2$H$_4$)$_2$}$_2$]

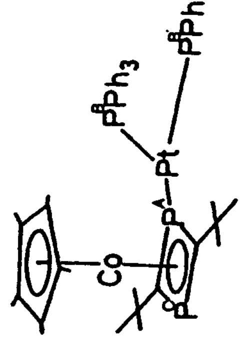
A sealed 8 mm NMR tube containing [Rh(Cp)(η^4-(Bu^{t}CP)$_2$)] (147 mg, 0.40 mmol) and [{RhCl(C$_2$H$_4$)$_2$}$_2$] (38.9 mg, 0.1 mmol) in toluene (1.0 mL) was agitated in an ultrasonic bath for 12 h and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. The red-orange solution changed to reddish brown. The sealed tube was broken open and the solvent removed under reduced pressure, leaving a red brown residue that was redissolved in petroleum ether 30–40°C/CH$_2$Cl$_2$ (9:1) (2 mL) and eluted through an alumina column with the same solvent mixture to afford a red brown solution. Removal of solvent in vacuo gave the red orange product, and further recrystallization from chloroform/hexane afforded red orange crystals of di-μ-chlorotetrakis{η^5-cyclopentadienyl-2,4-di-*t*-butyl-1,3-diphosphacyclobutadiene-rhodium(I)}dirhodium, [Rh$_2$Cl$_2${Rh(Cp)(P$_2$C$_2$Bu$^t_2$)}$_4$] **5** (54 mg, 30%). Found: C, 30.31; H, 4.84: C$_{60}$H$_{92}$Cl$_2$Rh$_6$·5CHCl$_3$ requires C, 33.27; H, 4.16). The ^{31}P{^{1}H} NMR (toluene) spectrum is discussed in the text. ^{1}H NMR ((CDCl)$_3$): δ 0.90 (s, 72H, Bu^t); δ 5.20 (m, 20H, C$_5$H$_5$).

Reaction of [Rh(Cp)(η^4-(Bu^{t}CP)$_2$] with [{RhCl(C$_2$H$_4$)$_2$}$_2$]*

A solution of [Rh(Cp*)(η^4-(Bu^{t}CP)$_2$] (109 mg, 0.25 mmol) in toluene (5 mL) was treated with [{RhCl(C$_2$H$_4$)$_2$}$_2$] (24.4 mg, 0.06 mmol) in toluene (10 mL). The mixture was left to stir at room temperature for 16 h giving a red brown solution. Solvent was removed in vacuo and extraction of the red brown residue and elution through an alumina column with dichloromethane afforded a *red orange* solution. Removal of solvent under reduced pressure gave the red orange complex, di-μ-chlorotetrakis{η^5 - pentamethylcyclopentadienyl-2,4 - di - *t*-butyl - 1,3 - diphosphacyclobutadienerhodium(I)}-dirhodium, [Rh$_2$Cl$_2${Rh(Cp*)(P$_2$C$_2$Bu$^t_2$)}$_4$], **6** (18 mg, 15%). Found: C, 36.27; H, 5.32: C$_{80}$H$_{132}$Rh$_6$Cl$_2$P$_8$·5CHCl$_3$ requires C, 38.86; H, 5.26. The ^{31}P{^{1}H} NMR (d_8-toluene) spectrum is discussed in the text. ^{1}H NMR (d_8-toluene): δ 1.23 (s, 72H, Bu^t); δ 2.15 (s, 60H, C$_5$Me$_5$).

Reaction of [Co(Cp)η^4-(Bu^{t}CP)$_2$] with [{RhCl(C$_2$H$_4$)$_2$}$_2$]*

A solution of [Co(Cp*){η^4-(Bu^{t}CP)$_2$}] (158 mg, 0.4 mmol) and [{RhCl(C$_2$H$_4$)$_2$}$_2$] (38.9 mg, 0.1 mmol) in toluene (20 mL) was stirred at room temperature for 16 h. The dark brown solution later changed to



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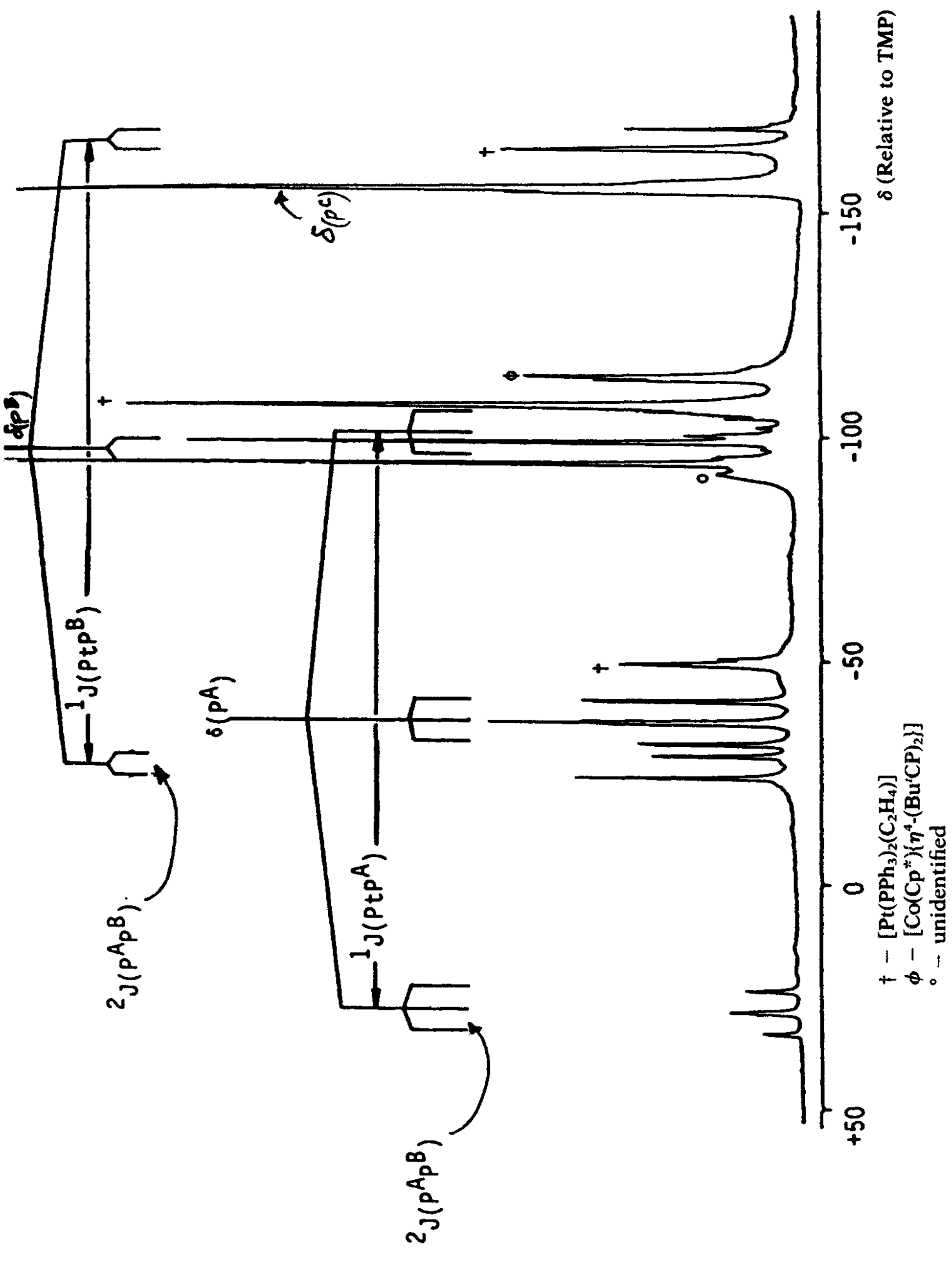

FIGURE 5 $^{31}P\{^1H\}$ NMR spectrum of **10**

greenish brown. Removal of solvent in vacuo afforded a dark brown residue that was redissolved in petroleum ether 30–40°C/CH_2Cl_2 (1 : 1) (5 mL) and eluted through an alumina column. Elution with the same solvent mixture gave a red orange solution that was identified as the starting material, [Co(Cp*){η^4-($Bu^tCP)_2$}] by its $^{31}P\{^1H\}$ and ^1H NMR spectra. Elution with CH_2Cl_2 afforded a green solution that on removal of solvent gave the greenish brown complex, di-μ-chlorotetrakis{η^5-pentamethylcyclopentadienyl-2,4-di-*t*-butyl-1,3-diphosphacyclobutadienecobalt(I)}dirhodium, [Rh_2Cl_2{Co(Cp*)-($P_2C_2Bu^t_2$)}$_4$] **7** (70 mg, 38%). Found: C, 50.88; H, 7.47: $C_{80}H_{132}Co_4Rh_2Cl_2$ requires C, 51.82; H, 7.18. The $^{31}P\{^1H\}$ NMR (d_8-toluene) spectrum is discussed in the text. ^1H NMR (d_8-toluene): δ 1.03 (s, 72H, Bu^t); δ 2.00 (s, 60H, C_5Me_5).

Reaction of [Co(Cp*)η^4-($Bu^tCP)_2$] with [{Pt(μ-Cl)Cl(PEt_3)}$_2$]

Solid [Co(Cp*)η^4-($Bu^tCP)_2$] (11.6 mg, 0.0294 mmol) and [{Pt(μ-Cl)Cl(PEt_3)}$_2$] (11.3 mg, 0.09187 mmol) in a 5 mm NMR tube were dissolved in CD_2Cl_2 (0.5 mL). The solution was left to stand at room temperature and the reaction monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. After 2 days, there was a formation of an orange solution. The product was tentatively identified as *cis*[$PtCl_2(PEt_3)$Co(Cp*)η^4-($Bu^tCP)_2$] (70%). ^1H NMR (CD_2Cl_2): δ 1.07 (s, 18H, Bu^t); δ 1.10–1.50 (m, 9H, CH_3); δ 1.70–2.05 (m, 6H, CH_2) and δ 2.16 (s, 15H, C_5Me_5). The reaction was continued for another 8 days, and two new products were identified by NMR spectroscopy and were assigned as (i) *trans*-dichloro(triethylphosphine)(η^5-pentamethylcyclopentadienyl-2,4-di-*t*-butyl-1,3-diphosphacyclobutadienecobalt (I) platinum (II), trans[Co(Cp*)η^4-($Bu^tCP)_2$($PtCl_2(PEt_3)$)] **8** (60%) and (ii) η^5-pentamethylcyclopentadienyl-2,4-di-*t*-butyl-1,3-bis{dichloro(triethylphosphine)platinum(II)}-phosphacyclobutadienecobalt(I), [Co(Cp*)η^4-$Bu^tCP)_2$-($PtCl_2(PEt_3)_2$], **9** (40%). ^1H NMR ($CDCl_3$), (i) Complex **8**: δ 0.7–0.9 (m, 9H, CH_3); δ 1.0 (s, 18H, Bu^t); δ 1.1–1.4 (m, 6H, CH_2) and δ 2.1 (s, 15H, C_5Me_5); (ii) Complex **9**: δ 1.24 (s, 18H, Bu^t); δ 1.2–1.4 (m, 9H, CH_3), δ 1.98 (s, 15H, C_5Me_5) and δ 1.7–2.0 (m, 6H, CH_2). The $^{31}P\{^1H\}$ NMR spectra for **8** and **9** are discussed in the text.

Reaction of [Co(Cp*)η^4-($Bu^tCP)_2$] with [$Pt(PPh_3)_2(C_2H_4)$]

A solution of [$Pt(PPh_3)_2(C_2H_4)$] (290 mg, 0.389 mmol) in THF (3 mL) was added slowly to a solution of [Co(Cp*)η^4-($Bu^tCP)_2$] (153 mg, 0.389 mmol) in THF (3 mL). The red orange solution immediately turned deep red. The solution was left at room temperature for 16 h and removal of solvent in vacuo afforded blood red crystals of η^5-pentamethylcyclopentadienyl-2,4-di-*t*-butyl-1,3-diphosphacyclobutadienecobalt(I)bis(triphenylphosphine)platinum(O), [Co(Cp*)η^4-($Bu^tCP)_2$ $Pt(PPh_3)_2$], **10** (208 mg, 48%). Found: C, 59.77; H, 5.65: $C_{56}H_{63}P_4CoPt$ requires C, 60.38; H, 5.70. ^1H NMR ($CDCl_3$): δ 1.25 (s, 18H, Bu^t); δ 2.11 (s, 15H, C_5Me_5); δ 7.20–7.80 (m, 30H, Ph).

Crystal Data

$C_{60}H_{92}Cl_2P_8Rh_6 \cdot 5CHCl_3$, $FW = 2346.4$, monoclinic, space group $C2/c$, $a = 21.807(13)$ Å, $b = 16.077(5)$ Å, $c = 28.649(14)$ Å, $\beta = 104.51(4)°$, $U = 9723.7$ Å^3, $Z = 4$, $D_c = 1.60$ g cm^{-3}. Graphite monochromated MoKα radiation, $\lambda = 0.71069$ Å, $\mu = 16.2$ cm^{-1}.

Data Collection and Processing

Crystal size ca. 0.5 × 0.3 × 0.3 mm sealed in a capillary, CAD4 diffractometer, θ-2θ mode, $\Delta\theta = (0.8 + 0.35 \tan \theta)°$, maximum scan time 1 minute. 6663 total reflections measured for $2 < \theta < 22°$, $+h + k + l$, 3534 unique reflections with $|F^2| > \sigma(F^2)$ used in the refinement, $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$. No crystal decay. No absorption correction.

Structure Solution and Refinement

The Rh atom positions were located by direct methods (MULTAN), and remaining nonhydrogen atoms found on difference maps. Three independent molecules of chloroform were located, one of which is lying on a twofold rotation axis with the C atom disordered. Refinement was by full matrix least squares with Rh, P, and Cl atoms anisotropic. Hydrogen atoms were omitted. Weighting scheme $w = 1/\sigma^2(F)$. Final residuals R = 0.116, R′ = 0.147. A final difference map had uninterpretable electron density of up to 2.1 e Å^{-3} near $\frac{1}{2}, \frac{1}{2}, \frac{3}{4}$, which is presumably due to further disordered solvent atoms. Programs used were from the Enraf-Nonius SDP-Plus package.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of thermal parameters and observed and calculated structure factors are available from the authors.

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