

Different Structural Features of Half-sandwich Complexes of Rhodium(I) containing the η^5 -1,2,4-Triphosphacyclopentadienyl Ring. Syntheses and ^{31}P N.M.R. Spectra of $[\text{Rh}(\eta^5\text{-C}_2\text{R}_2\text{P}_3)\text{LL}']$ [$\text{R} = \text{Bu}^t$, $\text{L} = \text{L}' = \text{PPh}_3, \text{P}(p\text{-tolyl})_3$; $\text{L} = \text{CO}$, $\text{L}' = \text{PPh}_3$; $\text{LL}' = \text{cyclo-octa-1,5-diene}$; $\text{R} = \text{adamantyl}$, $\text{L} = \text{PMe}_3, \text{PPh}_3$]; Crystal and Molecular Structure of $[\text{Rh}(\eta^5\text{-C}_2\text{Bu}^t_2\text{P}_3)(\eta^4\text{-C}_8\text{H}_{12})]$

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First examples of η^5 -1,2,4-triphosphacyclopentadienyl complexes of rhodium are reported and their structures, elucidated by ^{31}P n.m.r. spectroscopy and X-ray diffraction studies, show interesting differences.

There is considerable current interest in the ligating properties of novel unsaturated ring systems containing two and three phosphorus atoms.¹ The 4-, 5- and 6-membered ring systems (A)—(G) have recently been synthesised in suitable transition metal complexes.^{2–10‡}

The lone pair electrons in (A)—(C) can also undergo further interaction with other transition metal centres.^{3,4,11} The ligating potential of the $\eta^5\text{-C}_2\text{R}_2\text{P}_3$ ring in the development of analogues of metallocenes is currently being developed;¹² however to date there is only one report of a half-sandwich compound containing an $\eta^5\text{-C}_2\text{R}_2\text{P}_3$ ring.⁵ We now describe several rhodium(I) complexes of the type $[\text{Rh}(\eta^5\text{-C}_2\text{R}_2\text{P}_3)\text{LL}']$ ($\text{R} = \text{Bu}^t$, adamantyl), which have interesting n.m.r. and structural features.

Treatment of $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ with $[\text{Li}(\text{dme})_3][\text{C}_2\text{R}_2\text{P}_3]$ ($\text{R} = \text{Bu}^t$; $\text{dme} = 1,2$ -dimethoxyethane), in monoglyme at room temperature gave the yellow crystalline complex $[\text{Rh}(\eta^5\text{-C}_2\text{Bu}^t_2\text{P}_3)(\eta^4\text{-C}_8\text{H}_{12})]$ (1) (10%), whose $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum showed an $[\text{AB}_2]$ pattern [$\delta(\text{P}^{\text{A}}) 126.5$, $\delta(\text{P}^{\text{B}}) 120.3$ p.p.m., $^2J_{\text{PP}} = 39.3$ Hz]. Interestingly no discernible one-bond

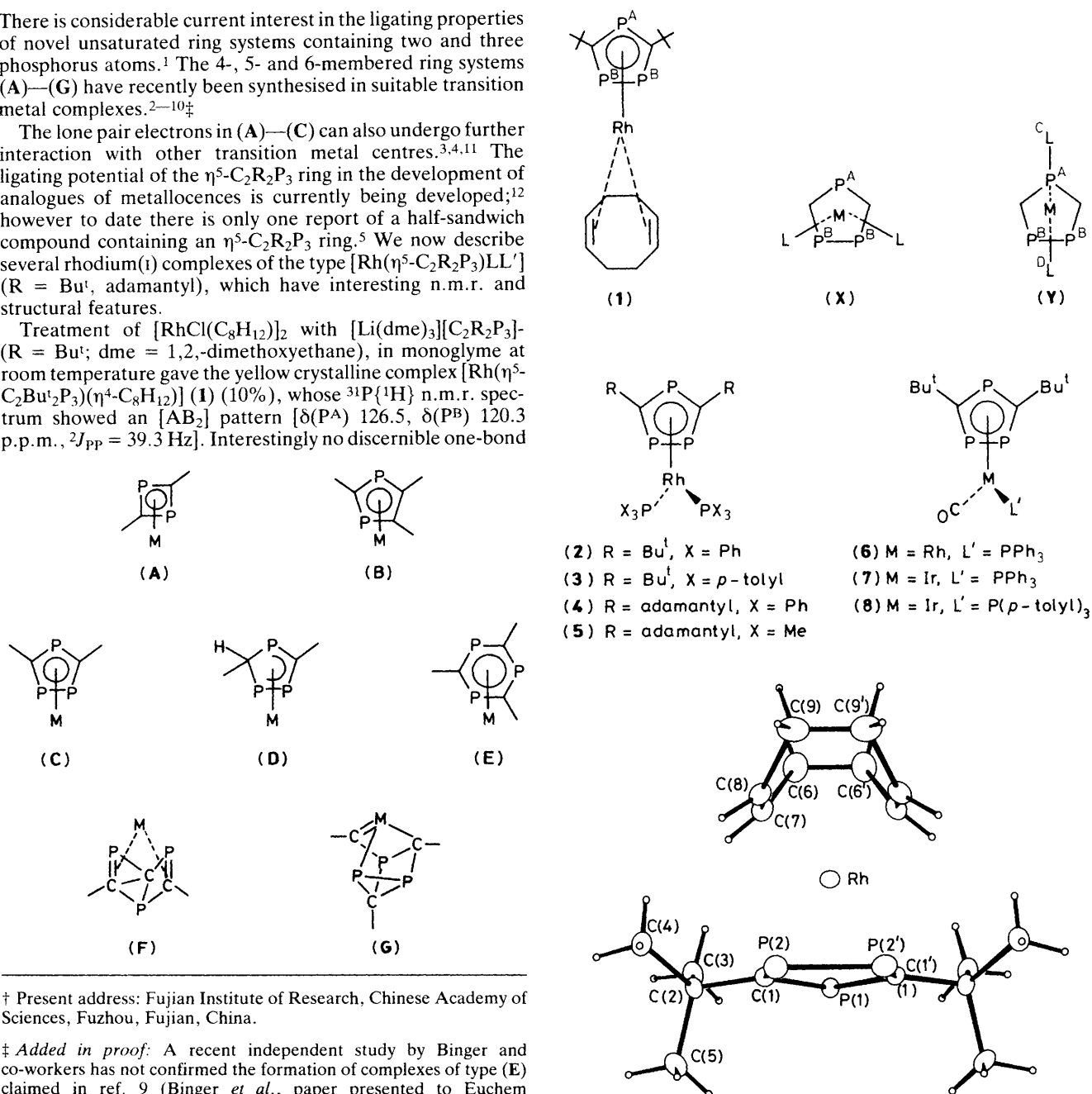


Figure 1. The molecular structure of (1), $[\text{Rh}(\eta^5\text{-C}_2\text{Bu}^t_2\text{P}_3)(\eta^4\text{-C}_8\text{H}_{12})]$.

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‡ Added in proof: A recent independent study by Binger and co-workers has not confirmed the formation of complexes of type (E) claimed in ref. 9 (Binger *et al.*, paper presented to EuChem Conference on phosphorus, silicon, boron, and related elements in low co-ordination states (PSi-BLOCS), Paris-Palaiseau, August 1988).

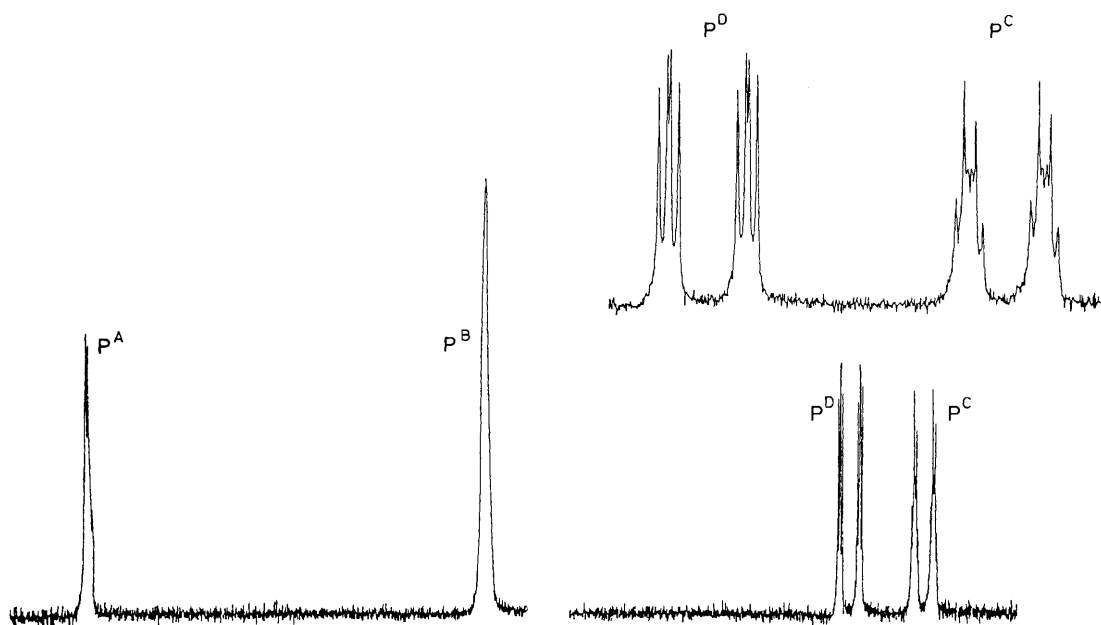


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectrum of compound (2).

coupling to the rhodium-103 nucleus was observed indicating the lower s-character of the $\text{Rh}-(\text{C}_2\text{R}_2\text{P}_3)$ ring bonding compared with the metal-1,3-diphosphacyclobutadiene ring system in $[\text{Rh}(\eta^4\text{-C}_2\text{R}_2\text{P}_2)(\eta^5\text{-C}_5\text{H}_5)]$ ($J_{\text{RhP}} 29.3 \text{ Hz}$).²

The molecular structure of (1) which was confirmed by a single crystal X-ray study is shown in Figure 1 and is clearly of type (X) in which both the C=C double bonds are in equivalent positions with respect to the (P_3C_2) ring.[§]

Similarly treatment of $[\text{RhCl}(\text{PR}_3)_n]$ ($n = 3, \text{R} = \text{Ph}, p\text{-tolyl}; n = 4, \text{R} = \text{Me}$) with $[\text{Li}(\text{dme})_3][\text{C}_2\text{R}_2\text{P}_3]$ gave the red-brown complexes $[\text{Rh}(\eta^5\text{-C}_2\text{R}_2\text{P}_3)\text{L}_2]$ (2)–(5) whereas $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ gave $[\text{Rh}(\eta^5\text{-C}_2\text{R}_2\text{P}_3)(\text{CO})(\text{PPh}_3)]$ (6) [$\nu(\text{C}\equiv\text{O}) 1965 \text{ cm}^{-1}$]. Iridium complexes analogous to (6) have also been prepared: (7), $\nu(\text{C}\equiv\text{O}) 1960 \text{ cm}^{-1}$; (8) $\nu(\text{C}\equiv\text{O}) 1970 \text{ cm}^{-1}$.

Interestingly the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra[¶] of complexes

(2)–(8) clearly establish that they have the alternative structure type (Y) in which the two ligands attached to rhodium are inequivalent. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (2) shown in Figure 2 which is typical of the rhodium complexes (2)–(5) exhibits the expected multiplicity, assignments being based on the expected larger 'trans' coupling of $^2J(\text{P}^{\text{A}}\text{P}^{\text{D}})$ and $^2J(\text{P}^{\text{B}}\text{P}^{\text{C}})$.

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§ Crystal data for $\text{C}_{18}\text{H}_{30}\text{P}_3\text{Rh}$: $M = 442.3$, orthorhombic, space group $Pnma$, $a = 12.580(3)$, $b = 16.568(15)$, $c = 9.295(8) \text{ \AA}$, $U = 1937.3 \text{ \AA}^3$, $Z = 4$, $D_c = 1.52 \text{ g cm}^{-3}$, monochromated Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu = 11.1 \text{ cm}^{-1}$. The structure was solved by routine heavy atom methods and refined by full matrix least squares using 1632 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer. The final residuals were $R = 0.036$. $R' = 0.046$. The molecules lie on crystallographic mirror planes. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ $^{31}\text{P}\{^1\text{H}\}$ N.m.r. data [shifts are in p.p.m. relative to 85% H_3PO_4 ; A–D refer to $\text{P}^{\text{A}}\text{—P}^{\text{D}}$ in structures (X) or (Y)]. (2): $\delta_{\text{A}} 115.25$, $\delta_{\text{B}} 86.8$, $\delta_{\text{C}} 37.9$, $\delta_{\text{D}} 43.2$; $^1J_{\text{Rh,C}} 199$, $^1J_{\text{Rh,D}} 200$, $^2J_{\text{A,D}} 22$, $^2J_{\text{B,C}} 20$, $^2J_{\text{C,D}} 30 \text{ Hz}$. (3): $\delta_{\text{A}} 117.1$, $\delta_{\text{B}} 89.6$, $\delta_{\text{C}} 35.7$, $\delta_{\text{D}} 39.5$; $^1J_{\text{Rh,C}} 205$, $^1J_{\text{Rh,D}} 204$, $^2J_{\text{A,B}} 30$, $^2J_{\text{A,D}} 24$, $^2J_{\text{A,C}} 6$, $^2J_{\text{B,C}} 19$, $^2J_{\text{B,D}} 7$, $^2J_{\text{C,D}} 30 \text{ Hz}$. (4): $\delta_{\text{A}} 112.7$, $\delta_{\text{B}} 85.5$, $\delta_{\text{C}} 43.5$, $\delta_{\text{D}} 38.3 \text{ p.p.m.}$; $^1J_{\text{Rh,C}} 170$, $^1J_{\text{Rh,D}} 170$, $^2J_{\text{A,B}} 24$, $^2J_{\text{A,D}} 26$, $^2J_{\text{B,C}} 20$, $^2J_{\text{C,D}} 29 \text{ Hz}$. (5): $\delta_{\text{A}} 125.75$, $\delta_{\text{B}} 71$, $\delta_{\text{C}} -9.6$, $\delta_{\text{D}} -13.0$; $^1J_{\text{Rh,C}} 190$, $^1J_{\text{Rh,D}} 190$, $^2J_{\text{A,B}} 25$, $^2J_{\text{A,D}} 25$, $^2J_{\text{B,C}} 23$, $^2J_{\text{C,D}} 25 \text{ Hz}$. (6): $\delta_{\text{A}} 99.3$, $\delta_{\text{B}} 116.2$, $\delta_{\text{C}} 44.6$; $^2J_{\text{Rh,C}} 183$, $^2J_{\text{A,B}} 36$, $^2J_{\text{A,C}} 23$, $^2J_{\text{B,C}} 0 \text{ Hz}$. (7) $\delta_{\text{A}} 75.0$, $\delta_{\text{B}} 79.0$, $\delta_{\text{C}} 11.0$; $^2J_{\text{A,B}} 36$, $^2J_{\text{A,C}} 15$, $^2J_{\text{B,C}} 5 \text{ Hz}$. (8): $\delta_{\text{A}} 74.4$, $\delta_{\text{B}} 78.5$, $\delta_{\text{C}} 8.1$; $^2J_{\text{A,B}} 42$, $^2J_{\text{A,C}} 15$, $^2J_{\text{B,C}} 5 \text{ Hz}$.