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 $[Rh(\eta^5\text{-}C_2R_2P_3)LL']$ [R = Bu^t, L = L′ = PPh$_3$,P(p-tolyl)$_3$; L = CO, L′ = PPh$_3$; LL′ = cyclo-octa-1,5-diene; R = adamantyl, L = PMe$_3$,PPh$_3$]; Crystal and Molecular Structure of $[Rh(\eta^5\text{-}C_2Bu^t{}_2P_3)(\eta^4\text{-}C_8H_{12})]$

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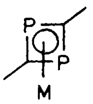
First examples of η^5-1,2,4-triphosphacyclopentadienyl complexes of rhodium are reported and their structures, elucidated by ^{31}P n.m.r. spectroscopy and *X*-ray diffraction studies, show interesting differences.

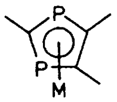
There is considerable current interest in the ligating properties of novel unsaturated ring systems containing two and three phosphorus atoms.[1] The 4-, 5- and 6-membered ring systems (**A**)—(**G**) have recently been synthesised in suitable transition metal complexes.[2—10][‡]

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 η^5-$C_2R_2P_3$ ring in the development of analogues of metallocences is currently being developed;[12] however to date there is only one report of a half-sandwich compound containing an η^5-$C_2R_2P_3$ ring.[5] We now describe several rhodium(I) complexes of the type $[Rh(\eta^5\text{-}C_2R_2P_3)LL']$ (R = Bu^t, adamantyl), which have interesting n.m.r. and structural features.

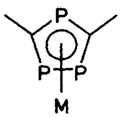
Treatment of $[RhCl(C_8H_{12})]_2$ with $[Li(dme)_3][C_2R_2P_3]$- (R = Bu^t; dme = 1,2,-dimethoxyethane), in monoglyme at room temperature gave the yellow crystalline complex $[Rh(\eta^5\text{-}C_2Bu^t{}_2P_3)(\eta^4\text{-}C_8H_{12})]$ (**1**) (10%), whose $^{31}P\{^1H\}$ n.m.r. spectrum showed an [AB$_2$] pattern [$\delta(P^A)$ 126.5, $\delta(P^B)$ 120.3 p.p.m., $^2J_{PP}$ = 39.3 Hz]. Interestingly no discernible one-bond



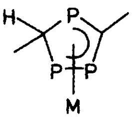
(**A**)



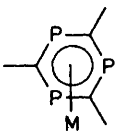
(**B**)



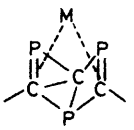
(**C**)



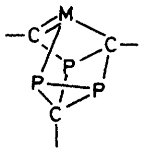
(**D**)



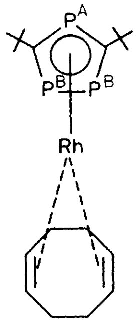
(**E**)



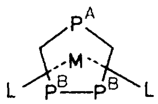
(**F**)



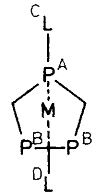
(**G**)



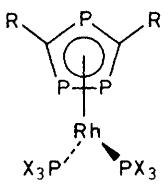
(**1**)



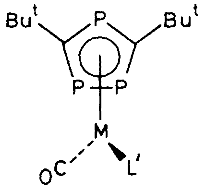
(**X**)



(**Y**)



(**2**) R = Bu^t, X = Ph
(**3**) R = Bu^t, X = *p*-tolyl
(**4**) R = adamantyl, X = Ph
(**5**) R = adamantyl, X = Me



(**6**) M = Rh, L′ = PPh$_3$
(**7**) M = Ir, L′ = PPh$_3$
(**8**) M = Ir, L′ = P(*p*-tolyl)$_3$

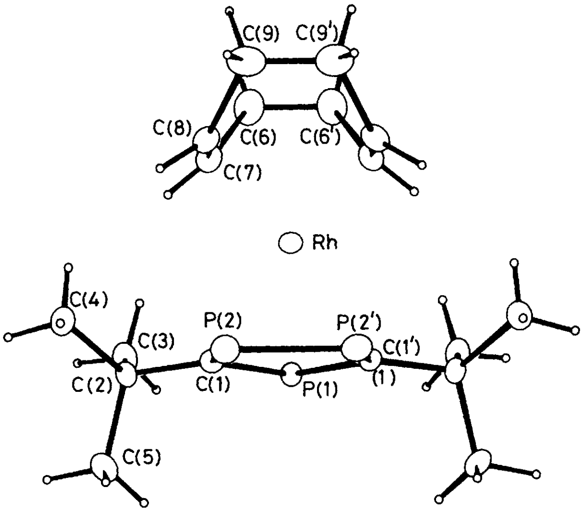


Figure 1. The molecular structure of (**1**), $[Rh(\eta^5\text{-}C_2Bu^t{}_2P_3)(\eta^4\text{-}C_8H_{12})]$.

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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).

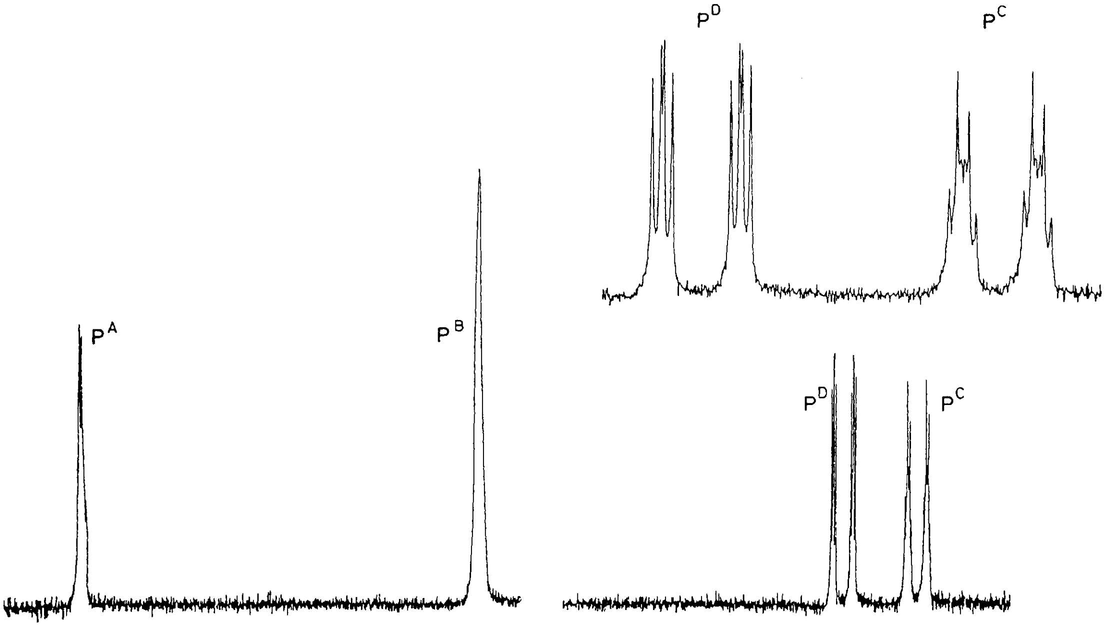

Figure 2. $^{31}P\{^1H\}$ N.m.r. spectrum of compound (**2**).

coupling to the rhodium-103 nucleus was observed indicating the lower s-character of the Rh–($C_2R_2P_3$) ring bonding compared with the metal–1,3-diphosphacyclobutadiene ring system in [Rh(η^4-$C_2R_2P_2$)(η^5-C_5H_5)] (J_{RhP} 29.3 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 [RhCl(PR_3)$_n$] (n = 3, R = Ph, *p*-tolyl; n = 4, R = Me) with [Li(dme)$_3$][$C_2R_2P_3$] gave the red–brown complexes [Rh(η^5-$C_2R_2P_3$)L_2] (**2**)—(**5**) whereas [RhCl(CO)(PPh_3)$_2$] gave [Rh(η^5-$C_2R_2P_3$)(CO)(PPh_3)] (**6**) [ν(C≡O) 1965 cm^{-1}]. Iridium complexes analogous to (**6**) have also been prepared: (**7**), ν(C≡O) 1960 cm^{-1}; (**8**) ν(C≡O) 1970 cm^{-1}.

Interestingly the $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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 $^2J(P^AP^D)$ and $^2J(P^BP^C)$.

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12 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, unpublished results.

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§ *Crystal data* for $C_{18}H_{30}P_3Rh$: M = 442.3, orthorhombic, space group *Pnma*, a = 12.580(3), b = 16.568(15), c = 9.295(8) Å, U = 1937.3 Å^3 Z = 4, D_c = 1.52 g cm^{-3}, monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 11.1 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 co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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