Synthesis and Crystal Structure of New Polynuclear Rhodium Complexes formed by Reaction of Bis(η-ethylene)(η^5-indenyl)rhodium with t-Butylphospha-acetylene†

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Treatment of bis(η-ethylene)(η^5-indenyl)rhodium (**1**) or (cyclo-octa-1,5-diene)(η^5-indenyl)rhodium (**2**) with t-butylphospha-acetylene (**3**) yields [η^4-2,4-di(t-butyl)-1,3-diphosphacyclobutadiene](η^5-indenyl)rhodium (**4**) as the main product together with two other rhodium complexes (**5**) and (**6**) that contain derivatives of the new ligated systems 1,2,4,5-tetraphosphabenzenediyl and 1-rhoda-2,5-diphosphacyclopentenediyl, respectively. Phosphorus-31, ^{1}H, and ^{13}C n.m.r. data are reported and are discussed in relation to the structures, which in the case of (**5**) and (**6**) were established by *X*-ray diffraction analyses. The n.m.r. spectra of (**6**) reveal restricted rotation of one of the indenyl groups.

η^4-1,3-Diphosphacyclobutadiene complexes of cobalt,[1-3] rhodium,[3] and iridium[3] are now readily available from the reaction of compounds of the type [M(η^5-C_5R_5)(C_2H_4)$_2$] (R = H, M = Co or Rh; R = Me, M = Co, Rh, or Ir) or [Co(η^5-C_9H_7)(C_2H_4)$_2$] (C_9H_7 = indenyl) with t-butylphospha-acetylene (3) or isopropylphospha-acetylene.

While the yields of the η^4-1,3-diphosphacyclobutadiene cobalt complexes are good, despite the fact that they are able to form di- and tri-nuclear adducts with the starting material [Co(η^5-C_5H_5)(C_2H_4)$_2$] by interaction with the lone pairs of the two phosphorus atoms of the diphosphacyclobutadiene ring,[1,2] the yields of the corresponding rhodium and iridium complexes are disappointingly low.[3] Di- and tri-nuclear rhodium complexes analogous to those produced by the reaction of (3) with [Co(η^5-C_5H_5)(C_2H_4)$_2$] are obviously not formed, even though such kinds of interaction have been found when [{RhCl(C_2H_4)$_2$}$_2$] is used as the starting material.[4] We therefore undertook a study of the reactions of [Rh(η^5-C_9H_7)(C_2H_4)$_2$] (1) and [Rh(η^5-C_9H_7)(cod)] (2) (cod = cyclo-octa-1,5-diene) with t-butylphospha-acetylene to endeavour to isolate and characterize those rhodium complexes besides [η^4-2,4-di(t-butyl)-1,3-diphosphacyclobutadiene](η^5-indenyl)rhodium (4) that are formed in this reaction. The results of this study are presented herein.

Results and Discussion

The reaction between complex (1) and a two-fold excess of (3) in diethyl ether is complete after 5 h at 0 °C and affords three isolable rhodium complexes (4)—(6) (Scheme 1), in an overall yield of 46%. The red crystalline trinuclear complex (6) is obtained directly in 13% yield by filtration of the reaction mixture while (4) and (5) must be separated chromatographically. On Al_2O_3 and with toluene as eluant, complex (4) is separated first and is obtained as yellow crystals in 30% yield. The second fraction contains the pure complex (5), which is isolated in 3% yield as red crystals. When the rhodium complex (2) is taken as starting material the overall yield is 69% and only the complexes (4) and (6) are obtained (yield 36 and 33%, respectively).

Complex (4) was readily identified as [η^4-2,4-di(t-butyl)-1,3-diphosphacyclobutadiene](η^5-indenyl)rhodium by comparison of its spectroscopic data with those of known 1,3-diphosphacyclobutadiene complexes of cobalt and rhodium.[1-3] Its elemental analysis also agrees with this formulation (see Experimental section). In its ^{31}P n.m.r. spectrum just one signal is observed, a doublet at 45.6 p.p.m. [^1J(RhP) = 31.3 Hz], in agreement with corresponding data for known (1,3-diphosphacyclobutadiene)rhodium complexes.[3] The signal of the 1,3-diphosphacyclobutadiene ring carbon is observed at δ 112.7 [^1J(PC) = 56.0, J(RhC) = 15.1 Hz]. The ^{103}Rh chemical shift is $-10\,216$ p.p.m.[5] {relative to external [Rh(acac)$_3$] (acac = acetylacetonate) Table 5} and thus close to that for [Rh(η^5-C_5H_5)(η^4-C_4H_4)], δ(^{103}Rh) $-10\,415$ p.p.m.[6]

The ^{31}P, ^{103}Rh, and ^{13}C n.m.r. spectra of (6) showed that the compound is pure and is a trinuclear species; at 40 °C some signals were broadened, indicating that dynamic behaviour is present. However, these spectra as well as the ^{31}P n.m.r. spectrum of (5) were too complicated to determine the structures directly because of the large number of magnetically active nuclei that couple with one another. Therefore *X*-ray diffraction studies of the complexes (5) and (6) were carried out.

Perspective views of the molecules (5) and (6) are shown in Figures 1 and 2, respectively; atomic co-ordinates and relevant bond lengths and angles are summarized in Tables 1—4. The most striking feature of (5) is the novel ligated 3,6-t-butyl-1,2,4,5-tetraphosphabenzenediyl heterocyclic ring, which must stem from four t-butyl phospha-acetylenes, with loss of one di-(t-butyl)acetylene; this di(t-butyl)acetylene was detected in the reaction mixture by g.c. analysis. The six-membered ring is located between the two rhodium atoms and consists of two CP_2 subunits, the planes of which are twisted with respect to each other by 49.8°. Each subunit is η^3-co-ordinated to one metal atom and interacts with the other one *via* an additional Rh–P bond. The C–P bond lengths all lie within 1.77—1.81 Å, which is in the range for η^3-1,3-diphospha-allyl metal systems[7] but the bond between P(1) and P(3) [2.445(1) Å] is considerably longer than that between P(2) and P(4) [2.238(1) Å]. However, the observation of J(PP) = 204 Hz between P(1) and P(3) confirms that they must be bonded to one another. In addition each rhodium atom has a η^5-bonded indenyl ligand.

As in (5), each rhodium atom in the trinuclear complex (6) is connected to an indenyl group, but different Rh–C distances suggest that the co-ordination is better described as η^3 bonding. Atom Rh(1) is part of a 1-metalla-2,5-diphosphacyclopent-

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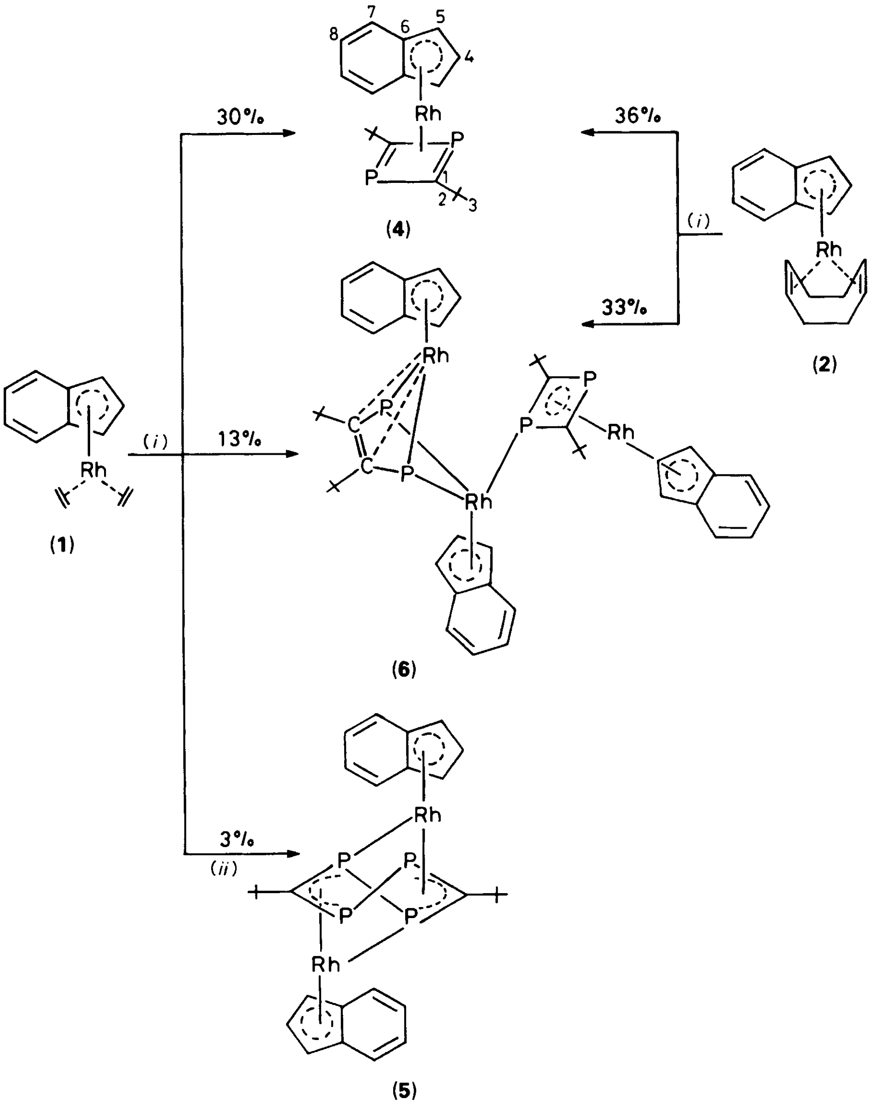
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme 1. (*i*) + P≡CBu^t; (*ii*) − Bu^{t}C≡CBu^t

enediyl ring. It is bent out of the plane defined by the C_2P_2 fragment of the ring by 50.6°. The C_2P_2 fragment of this heterocycle is η^4-co-ordinated to Rh(2) such that Rh(1) and Rh(2) belong to a four-membered Rh_2P_2 ring with an angle of 16.8° between the two RhP_2 planes. The distance of 1.416(6) Å between C(1) and C(6) is typical for a π-bonded C=C double bond, while the distances C(1)–P(1) [1.828(4) Å] and C(6)–P(2) [1.843(4) Å] are somewhat shorter than normal P–C single bonds. No bonding interaction exists between P(1) and P(2) [P(1) ··· P(2); 2.549(2) Å, see discussion of the ^{31}P n.m.r. spectrum]. This part of the molecule is similar to a dirhodium complex, $[Rh_2(\eta^5\text{-}C_5Me_4Et)_2(\eta^4\text{-}P_4)(CO)]$, in which a rhodatetraphosphacyclopentadiene is η^4-bonded to the second rhodium.[8] Atom Rh(3) is part of a fragment similar to the mononuclear [2,4-di(t-butyl)-1,3-diphosphacyclobutadiene]indenylcobalt complex[2] or complex (**4**). This fragment contains an approximately planar 1,3-diphosphacyclobutadiene ring, which is η^4-bonded to Rh(3) and connected to the rest of the molecule *via* a σ-donor–π-acceptor interaction between P(3) and Rh(1).

The n.m.r. spectra of complex (**6**) in solution are consistent with the structure found in the solid. The ^{103}Rh n.m.r. spectrum indicates directly a trinuclear complex. One of the signals (Table 5) is found at −10 392 p.p.m., suggesting that one of the (η^5-indenyl)rhodium moieties is η^4-bonded to a phosphacyclobutadiene ring. Several *J*(RhP) coupling constants were identified, thus simplifying the interpretation of the ^{31}P n.m.r. spectra.

The detailed analysis of the ^{31}P n.m.r. spectrum of complex (**6**) also requires comparison of the spectra recorded at −80 and +40 °C [the couplings to P(1) and P(2) become averaged] (Table 6). At −80 °C four signals are observed at δ 3.1 [P(4)], 88.4 [P(3)], 83.1 and 115.7 p.p.m. [P(1) and P(2)]. Examination of the spectra shows that two of the phosphorus atoms do not undergo exchange. Their data are consistent with P(3) and P(4) (numbering in Figure 2) in the 1,3-diphosphacyclobutadiene ring; P(3) is identified by the large coupling to the σ-bonded rhodium atom Rh(1) (228 Hz). The phosphorus atoms resonating at 115.7 and 83.1 p.p.m. undergo exchange with one another, such that at 40 °C a very broad signal ($\Delta\nu_{\frac{1}{2}}$ *ca.* 1 000 Hz) is observed at 91 p.p.m. At −80 °C the coupling constant *J*[P(1), P(2)] is unresolved and must be less than 5 Hz, confirming that P(1) is not bonded to P(2). Interestingly, the coupling constants between P(1), P(2), and Rh(1) (48 and 42 Hz) are only slightly greater than those to Rh(2).

In the ^{13}C n.m.r. spectrum at −80 °C *all* the carbon atoms (except the methyl carbons of the t-butyl groups) are inequivalent. At 40 °C the signals have coalesced pairwise with the exception of those from the 2 position of the indenyl groups. Atoms C(11) and C(16) in the 1,3-diphosphacyclobutadiene ring (−80 °C, 108.7 and 107.5: 40 °C, 109.1 p.p.m.) are easily identified by the similarity of their chemical shifts and coupling constants with those of related systems[2] {^1J[P(4) C] = 60, ^1J[P(3) C] = 15 Hz [the lone pair of P(3) is donated to a further atom]}. Atoms C(1) and C(6) (−80 °C, 122.1 and 121.7; 40 °C, 121.5 p.p.m.) are distinguished from the remaining signals from quaternary carbons by the large coupling constants to the directly bonded phosphorus atoms (*ca.* 80 Hz).

Dynamic N.M.R. Spectroscopy.—The observed exchange phenomena in compound (**6**) can be explained by restricted rotation of the indenyl ligands. The *X*-ray structure reveals that the long axes of all three indenyl groups lie approximately perpendicular to the plane containing P(3), P(4), and the three rhodium atoms Rh(1), Rh(2), and Rh(3). If all three ligands rotate rapidly about the metal–ligand axes then both sides of this plane will be equivalent. Thus P(1) and P(2) would give one signal, as would C(1) and C(6) and also C(11) and C(16). In the indenyl groups themselves, the pairs of atoms on either side of the long axes [*e.g.* in the case of the indenyl group attached to Rh(1), C(27) and C(28) or C(26) and C(29)] are equivalent under the same conditions.

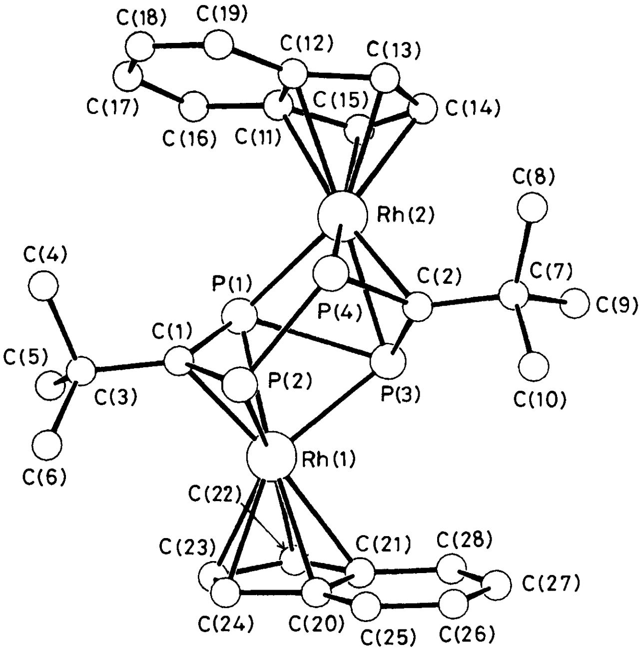


Figure 1. Molecular structure of compound (**5**)

However, if just one of the indenyl rings rotates about the metal–ligand bond slowly on the n.m.r. time-scale this is sufficient to remove the time-averaged symmetry of the molecule about the plane P(3)–P(4)–Rh(1)–Rh(2)–Rh(3), so that P(1) and P(2) and similar pairs of atoms above and below this plane are then no longer symmetrically equivalent. Furthermore, not only are the pairs of atoms either side of the long axis of the indenyl ligand that rotates slowly then inequivalent, all the carbon atoms in both the other indenyl ligands also become different because the molecule is then chiral and these pairs of atoms are diastereotopic. This corresponds exactly to the behaviour observed in the spectra.

Only one indenyl group is strongly hindered. Should two or more indenyl ligands experience restricted rotation then different rotamers would be formed, which would have caused further splitting of all signals.

In order to confirm this interpretation and to attempt to establish which of the indenyl groups experiences the highest barrier to rotation, it was necessary to assign the indenyl signals in more detail. This was achieved by recording a two-dimensional ^{13}C–^{1}H chemical shift-correlated n.m.r. spectrum using long-range couplings. Since only the carbon nuclei and protons within the same indenyl group couple with one another, the cross-peaks fall in three groups (see Table 7), one from each indenyl ligand.

The ^{13}C chemical shifts of one of the indenyl ligands are very similar to those of complex (**4**) and they were accordingly assigned to the ligand on Rh(3). In the other two indenyl groups, the shifts of the ring-junction atoms are 114.0 and 115.0 in one case and 118.4 and 123.1 p.p.m. in the other. Because the ring-junction carbon atoms in the indenyl group attached to Rh(1) are further away from the metal than those of the other ligand from Rh(2), the shifts 118.4 and 123.1 p.p.m. were assigned to C(21)/C(25) in the indenyl ligand bonded to Rh(1). Inspection of the data shows that the differences between the chemical

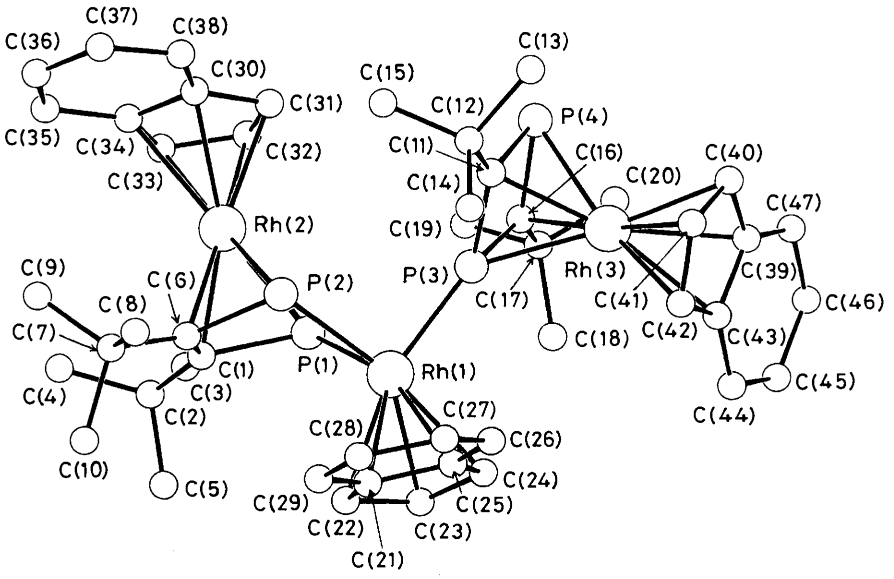


Figure 2. Molecular structure of compound (**6**)

Table 1. Atomic fractional co-ordinates with standard deviations in parentheses for complex (**5**)

Atom	*x*	*y*	*z*
Rh(1)	0.272 4(1)	0.052 2(1)	0.219 0(1)
Rh(2)	0.221 4(1)	0.245 4(1)	0.249 5(1)
P(1)	0.131 9(1)	0.142 3(1)	0.179 2(1)
P(2)	0.266 5(1)	0.082 8(1)	0.398 8(1)
P(3)	0.337 4(1)	0.162 1(1)	0.188 9(1)
P(4)	0.314 3(1)	0.193 1(1)	0.419 9(1)
C(1)	0.135 0(2)	0.083 7(1)	0.290 5(2)
C(2)	0.393 9(2)	0.204 9(1)	0.320 1(2)
C(3)	0.026 5(3)	0.041 6(2)	0.291 1(3)
C(4)	−0.044 1(3)	0.085 8(2)	0.351 6(4)
C(5)	−0.049 6(4)	0.026 2(3)	0.174 8(3)
C(6)	0.058 6(4)	−0.025 6(2)	0.353 7(4)
C(7)	0.508 4(3)	0.246 0(2)	0.343 2(3)
C(8)	0.505 5(4)	0.310 2(2)	0.411 7(4)
C(9)	0.539 7(4)	0.266 4(3)	0.236 9(4)
C(10)	0.603 7(3)	0.198 7(3)	0.411 0(5)
C(11)	0.046 6(3)	0.303 9(2)	0.172 9(3)
C(12)	0.091 7(3)	0.325 7(2)	0.284 6(3)
C(13)	0.204 8(4)	0.354 8(2)	0.291 5(4)
C(14)	0.222 1(4)	0.352 3(2)	0.183 8(4)
C(15)	0.130 6(3)	0.318 7(2)	0.112 7(3)
C(16)	−0.065 8(3)	0.274 9(2)	0.138 0(4)
C(17)	−0.130 5(4)	0.269 3(3)	0.210 0(5)
C(18)	−0.088 8(4)	0.289 4(2)	0.318 6(4)
C(19)	0.018 0(4)	0.316 1(2)	0.359 2(3)
C(20)	0.417 1(3)	−0.029 1(1)	0.244 3(3)
C(21)	0.413 2(3)	0.005 0(1)	0.141 7(3)
C(22)	0.298 5(3)	−0.005 4(2)	0.068 7(3)
C(23)	0.235 8(3)	−0.048 3(2)	0.122 9(3)
C(24)	0.305 5(3)	−0.060 5(2)	0.231 4(3)
C(25)	0.520 7(3)	−0.026 3(2)	0.332 3(3)
C(26)	0.614 7(3)	0.007 0(2)	0.316 5(4)
C(27)	0.610 9(3)	0.040 4(2)	0.216 0(4)
C(28)	0.512 8(3)	0.040 5(2)	0.130 0(3)

Table 2. Selected distances (Å) and angles (°) for complex (**5**)

Rh(1)–P(1)	2.393(1)	Rh(2)–C(11)	2.343(3)
Rh(1)–P(2)	2.352(1)	Rh(2)–C(12)	2.329(3)
Rh(1)–P(3)	2.356(1)	Rh(2)–C(13)	2.233(4)
Rh(1)–C(1)	2.154(3)	Rh(2)–C(14)	2.257(4)
Rh(1)–C(20)	2.307(3)	Rh(2)–C(15)	2.278(4)
Rh(1)–C(21)	2.339(3)	P(1)–P(3)	2.445(1)
Rh(1)–C(22)	2.290(4)	P(1)–C(1)	1.803(3)
Rh(1)–C(23)	2.291(3)	P(2)–P(4)	2.238(1)
Rh(1)–C(24)	2.247(3)	P(2)–C(1)	1.775(3)
Rh(2)–P(1)	2.346(1)	P(3)–C(2)	1.809(3)
Rh(2)–P(3)	2.391(1)	P(4)–C(2)	1.774(3)
Rh(2)–P(4)	2.361(1)	C(1)–C(3)	1.534(4)
Rh(2)–C(2)	2.158(3)	C(2)–C(7)	1.542(4)
C(1)–Rh(1)–P(3)	97.0(1)	C(2)–P(3)–P(1)	104.0(1)
C(1)–Rh(1)–P(2)	46.1(1)	C(2)–P(3)–Rh(2)	59.9(1)
C(1)–Rh(1)–P(1)	46.4(1)	C(2)–P(3)–Rh(1)	109.8(1)
P(3)–Rh(1)–P(2)	90.9(1)	P(1)–P(3)–Rh(2)	58.0(1)
P(3)–Rh(1)–P(1)	62.0(1)	P(1)–P(3)–Rh(1)	59.7(1)
P(2)–Rh(1)–P(1)	79.2(1)	Rh(2)–P(3)–Rh(1)	109.5(1)
C(2)–Rh(2)–P(4)	46.0(1)	C(2)–P(4)–P(2)	102.1(1)
C(2)–Rh(2)–P(3)	46.5(1)	C(2)–P(4)–Rh(2)	61.0(1)
C(2)–Rh(2)–P(1)	97.0(1)	P(2)–P(4)–Rh(2)	105.7(1)
P(4)–Rh(2)–P(3)	79.6(1)	C(3)–C(1)–P(2)	124.1(2)
P(4)–Rh(2)–P(1)	91.2(1)	C(3)–C(1)–P(1)	120.3(2)
P(3)–Rh(2)–P(1)	62.1(1)	C(3)–C(1)–Rh(1)	125.5(2)
C(1)–P(1)–P(3)	104.4(1)	P(2)–C(1)–P(1)	115.5(1)
C(1)–P(1)–Rh(2)	110.3(1)	P(2)–C(1)–Rh(1)	72.8(1)
C(1)–P(1)–Rh(1)	59.8(1)	P(1)–C(1)–Rh(1)	73.8(1)
P(3)–P(1)–Rh(2)	59.8(1)	C(7)–C(2)–P(4)	123.1(2)
P(3)–P(1)–Rh(1)	58.3(1)	C(7)–C(2)–P(3)	120.6(2)
Rh(2)–P(1)–Rh(1)	109.8(1)	C(7)–C(2)–Rh(2)	125.4(2)
C(1)–P(2)–P(4)	103.0(1)	P(4)–C(2)–P(3)	116.2(2)
C(1)–P(2)–Rh(1)	61.0(1)	P(4)–C(2)–Rh(2)	73.1(1)
P(4)–P(2)–Rh(1)	106.8(1)	P(3)–C(2)–Rh(2)	73.6(1)

shifts of C(22)/C(24), C(21)/C(25), and C(26)/C(29) are much greater than for the other indenyl groups and therefore we conclude that this must be the ligand for which the rotation is restricted. According to the chemical shifts of C(21) and C(25), this ligand shows the greatest tendency towards η^3 co-ordination (when the indenyl group is η^3 bonded the ring-junction carbon signal is found at *ca.* 142 p.p.m.[9]) and also appears to be in the most crowded environment.

Conclusion

This study reveals that the reactions of a λ^3-phospha-alkyne with rhodium(I) compounds are more complex than with the corresponding cobalt(I) compounds.[1–3] To form the rhodium complex (**5**) it is necessary to cleave P/C bonds of (**3**). The detection of di(t-butyl)acetylene in the reaction mixture shows that this process does indeed occur, although it is unknown at what stage of the reaction sequence it takes place.

The most interesting feature of complex (**6**) is the existence of a 1-rhoda-2,5-diphosphacyclopentenediyl unit, which must have been formed by a C–C coupling of two phospha-alkyne molecules. However, in all other dimerization reactions of (**3**) hitherto known coupling takes place with P–C bond formation, in accordance with the charge distribution in the free phospha-alkynes.[10] One possible explanation for this difference in behaviour is the reaction sequence for the formation of (**6**) outlined in Scheme 2.

It is assumed that complex (**4**) is formed initially and then reacts with a second molecule of (**1**) by interaction of the metal with the lone pair of one of the phosphorus atoms of the diphosphacyclobutadiene ring.[2] We postulate that for steric reasons ethylene in adduct (**I**) can be displaced by (**3**) only when the latter is 'end-on' co-ordinated. This would also cause a change in the charge distribution in the phospha-alkyne ligand allowing oxidative coupling of this 'end-on' bonded (**3**) with a free phospha-alkyne to take place with formation of a C–C bond. If this is true, the regiochemistry of the oxidative coupling of two phospha-alkynes in the co-ordination sphere of a metal should be influenced by the steric bulk of the other ligands attached to the metal. Experiments to verify this hypothesis are in progress.

Experimental

All reactions were carried out under oxygen-free argon using Schlenk-tube techniques. Solvents were dried rigorously before use. The n.m.r. spectra were measured with Bruker WP 80 FT (^{1}H, 80; ^{31}P, 32.4 MHz), WM 300 FT (^{13}C, 75.4; ^{31}P, 121.4 MHz), and AM 200 FT (^{1}H, 200 MHz) instruments with $SiMe_4$ as internal standard for ^{1}H and ^{13}C and H_3PO_4 as external standard for ^{31}P. The ^{103}Rh n.m.r. spectra (12.59 MHz) were measured by indirect two-dimensional n.m.r. (161.9 MHz) using ^{31}P detection on a Bruker WH-400 instrument. The mass spectra are recorded with a Varian MAT 311 A DF spectrometer at 70 eV (1.12×10^{-17} J). Elemental analyses were performed by the microanalytical laboratory Dornis and Kolbe, Mülheim a. d. Ruhr.

The compounds $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ (**1**),[11] $[Rh(\eta^5$-

Table 3. Atomic fractional co-ordinates with standard deviations in parentheses for complex (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	0.181 9(1)	0.339 9(1)	0.221 6(1)	C(21)	0.160 3(3)	0.471 9(3)	0.058 5(3)
Rh(2)	0.210 6(1)	0.039 2(1)	0.255 1(1)	C(22)	0.062 6(4)	0.455 0(4)	0.119 3(4)
Rh(3)	0.385 2(1)	0.330 2(1)	0.423 5(1)	C(23)	0.040 9(4)	0.496 7(4)	0.208 0(4)
P(1)	0.103 3(1)	0.208 3(1)	0.292 8(1)	C(24)	0.129 9(5)	0.521 5(4)	0.213 5(4)
P(2)	0.264 1(1)	0.183 5(1)	0.151 5(1)	C(25)	0.204 4(4)	0.510 7(3)	0.118 4(4)
P(3)	0.292 9(1)	0.271 7(1)	0.339 7(1)	C(26)	0.301 4(5)	0.530 0(4)	0.081 8(5)
P(4)	0.415 3(1)	0.144 5(1)	0.485 7(1)	C(27)	0.352 3(5)	0.511 4(5)	−0.014 2(5)
C(1)	0.070 0(3)	0.164 3(3)	0.194 4(3)	C(28)	0.309 9(5)	0.473 0(5)	−0.072 4(4)
C(2)	−0.043 4(3)	0.153 9(4)	0.212 1(4)	C(29)	0.215 9(4)	0.451 9(4)	−0.037 8(4)
C(3)	−0.084 0(4)	0.125 1(5)	0.329 2(4)	C(30)	0.355 1(4)	−0.127 0(4)	0.277 5(4)
C(4)	−0.046 9(4)	0.063 2(5)	0.170 5(4)	C(31)	0.324 6(4)	−0.072 0(4)	0.360 5(4)
C(5)	−0.122 3(4)	0.263 3(5)	0.174 2(5)	C(32)	0.222 0(5)	−0.072 4(4)	0.406 6(4)
C(6)	0.158 2(3)	0.153 3(3)	0.114 8(3)	C(33)	0.183 0(4)	−0.118 6(4)	0.349 9(4)
C(7)	0.176 1(4)	0.128 0(4)	0.007 5(3)	C(34)	0.266 9(4)	−0.156 1(4)	0.271 0(4)
C(8)	0.274 4(5)	0.148 1(5)	−0.055 2(4)	C(35)	0.279 9(5)	−0.216 7(4)	0.194 5(5)
C(9)	0.185 3(5)	0.014 1(5)	0.006 6(4)	C(36)	0.375 5(7)	−0.242 7(5)	0.133 0(5)
C(10)	0.078 8(5)	0.211 6(5)	−0.048 9(4)	C(37)	0.460 0(6)	−0.213 8(5)	0.139 8(6)
C(11)	0.431 5(3)	0.194 1(3)	0.348 4(3)	C(38)	0.453 6(5)	−0.156 9(5)	0.208 4(6)
C(12)	0.530 0(3)	0.163 9(3)	0.269 1(3)	C(39)	0.396 1(4)	0.434 0(4)	0.526 1(4)
C(13)	0.633 4(3)	0.135 0(4)	0.316 5(4)	C(40)	0.499 4(5)	0.373 8(5)	0.482 6(6)
C(14)	0.523 9(4)	0.254 8(4)	0.175 6(4)	C(41)	0.508 0(5)	0.410 2(5)	0.378 0(6)
C(15)	0.536 3(3)	0.061 1(4)	0.238 3(4)	C(42)	0.412 0(6)	0.487 3(5)	0.351 7(4)
C(16)	0.277 6(3)	0.231 6(3)	0.475 1(3)	C(43)	0.338 4(4)	0.506 8(4)	0.444 8(4)
C(17)	0.180 6(3)	0.251 1(3)	0.557 1(3)	C(44)	0.234 1(6)	0.583 8(5)	0.466 5(6)
C(18)	0.096 1(4)	0.363 2(4)	0.525 2(4)	C(45)	0.193 4(5)	0.583 0(6)	0.570 2(8)
C(19)	0.132 0(4)	0.161 8(4)	0.573 0(3)	C(46)	0.251 9(7)	0.511 1(7)	0.646 8(6)
C(20)	0.215 1(4)	0.245 1(4)	0.657 5(3)	C(47)	0.349 4(6)	0.436 9(5)	0.628 9(5)

C_9H_7)(η^4-cod)] (**2**),[11] and P≡CBu^t (**3**)[12] were prepared by methods described previously.

Reaction of [Rh(η^5-C_9H_7)(C_2H_4)$_2$] (**1**) *with* P≡CBu^t (**3**).—A solution of complex (**1**) (1.46 g, 5.33 mmol) in Et_2O (50 cm^3) was treated with (**3**) (2.42 g, 24.20 mmol). After stirring for *ca.* 6 h red crystals of (**6**) (0.25 g, 13.3%) precipitated which were isolated by removing the solution by a glass capillary, washing with pentane (5 cm^3), and drying *in vacuo*. Crystals suitable for *X*-ray analysis were obtained by recrystallization from a mixture of tetrahydrofuran, Et_2O, and pentane in the ratio 1:2:2; m.p. 247 °C (decomp.). The solvent was removed from the remaining reaction solution *in vacuo*. In the −78 °C condensate di(t-butyl)acetylene was detected by g.c. analysis (identified by comparison of its retention time with that of an authentic sample). The residue was dissolved in toluene (400 cm^3) and chromatographed (3 × 60 cm column, Al_2O_3). Elution with this solvent gave a yellow eluate (120 cm^3) and, after an intermediate eluate (20 cm^3), a red eluate (150 cm^3). The solvent was removed from the yellow eluate *in vacuo* and the residue was dissolved in pentane (10 cm^3), filtered on Celite, and cooled to −20 °C. Yellow needles of (**4**) (0.66 g, 30%) were obtained which were isolated by filtration and drying *in vacuo*; m.p. 119 °C. Complex (**5**) was obtained in the same manner as red crystals from the red eluate (50 mg, 2.6%) after removing toluene, dissolving in Et_2O (10 cm^3), and cooling to −78 °C; m.p. 148 °C (decomp.).

Complex (**4**). m/z = 418 (62, M^+ for ^{103}Rh), 280 (100, [$C_9H_7P_2Rh$]$^+$), 218 (59, [C_9H_7Rh]$^+$), and 115 (17%, [C_9H_7]$^+$) (Found: C, 54.35; H, 6.50; Rh, 24.40. Calc. for $C_{19}H_{25}P_2Rh$: C, 54.55; H, 6.00; Rh, 24.60%). N.m.r.: ^{31}P (C_6D_6, 32 MHz), δ 45.6 p.p.m. [d, *J*(RhP) = 31.3]; ^{1}H (C_6D_6, 200 MHz; numbering scheme as in Scheme 1), δ 0.71 {d, *J*[H(3)P] = 0.8, H(3)}, 5.14 {m, *J*[H(4)H(5)] = 2.7, *J*[H(4)Rh] = 1.4, H(4)}, 6.09 {dd, *J*[H(5)Rh] = 0.7, H(5)}, 6.77 [m, H(8)], and 7.29 [m, H(7)]; ^{13}C ([$^2H_8$]toluene, 75 MHz), δ 124.7 [d, *J*(CH) = 160 Hz, C(7) or C(8)], 123.8 [d, *J*(CH) = 165, C(8) or C(7)], 112.7 [s, *J*(PC) = 56, *J*(RhC) = 15.1, C(1)], 108.3 [s, *J*(RhC) = 4.2, C(6)], 87.6 [d, *J*(CH) = 176, *J*(RhC) = 6.1, C(4)], 77.3 [d, *J*(CH) = 176, *J*(RhC) = 5.3, C(5)], 34.5 [s, *J*(PC) = 6.6, C(2)], and 30.2 p.p.m. [q, *J*(CH) = 126, *J*(PC) = 4.9, C(3)].

Complex (**5**). m/z = 698 (100, M^+ for ^{103}Rh), 641 (2, [$M - C_4H_9$]$^+$), 598 (17, [$M - Me_3CCP$]$^+$), 583 (48, [$M - C_9H_7$]$^+$), and 115 (29%, [C_9H_7]$^+$). N.m.r.: ^{31}P ([$^2H_8$]tetrahydrofuran, 121.4 MHz; numbering scheme as in Figure 1), AA′MM′XX′ spin system [AA′ = P(1), P(3); MM′ = P(2), P(4); XX′ = Rh(1), Rh(2)], δ 86.2 [m, P(1), P(3)] 55.2 [m, P(2), P(4)], *J*[P(1)P(3)] = 204.3, *J*[P(1)P(2)] = *J*[P(3)P(4)] = 0.7, *J*[P(1)P(4)] = *J*[P(2)P(3)] = 6.7, *J*[P(2)P(4)] = 221.2, *J*[Rh(1)P(1)] = *J*[Rh(2)P(3)] = 37.3, *J*[Rh(2)P(1)] = *J*[Rh(1)P(3)] = 21.0, *J*[Rh(1)P(2)] = *J*[Rh(2)P(4)] = 35.1, *J*[Rh(2)P(2)] = *J*[Rh(1)P(4)] = 2.8 Hz; ^{1}H ([$^2H_8$]tetrahydrofuran, 200 MHz), δ 0.94 (s, t-C_4H_9), 5.90, 5.95, 6.17, 7.07, 7.20, and 7.44 (m, indenyl H).

Complex (**6**). m/z = 1 054 (<1, M^+), 939 (1, [$M - C_9H_7$]$^+$), 639 {2, [(RhC_9H_7)$_2$(Me_3CCP)$_2$]$^+$}, 418 {44, [Rh(C_9H_7)(Me_3CCP)$_2$]$^+$}, 280 {85, [Rh(C_9H_7)P_2]$^+$}, and 115 (100%, [C_9H_7]$^+$) (Found: C, 52.90; H, 5.50; P, 11.80; Rh, 29.70. Calc. for $C_{47}H_{57}P_4Rh_3$: C, 53.55; H, 5.45; P, 11.75; Rh, 29.25%). ^{1}H N.m.r. ([$^2H_8$]toluene, 400 MHz), δ 0.87 (s, 18 H, t-C_4H_9), 1.26 (s, 18 H, t-C_4H_9); 5.45—5.68 (m, 3 H), 5.41—6.21 (m, 6 H), 6.86—7.10 (m, 6 H), and 7.18—7.39 (m, 6 H) (indenyl H).

Reaction of [Rh(η^5-C_9H_7)(η^4-cod)] (**2**) *with* P≡CBu^t (**3**).—Compound (**3**) (1.13 g, 11.3 mmol) was added dropwise to a solution of (**2**) (1.13 g, 3.47 mmol) in toluene (30 cm^3) at 0 °C. After 0.5 h the solution was warmed to 20 °C, stirred for another 3 h at this temperature, and filtered on Al_2O_3. The solution was evaporated to dryness *in vacuo* (10^{-2} mbar, 1 Pa) and treated with pentane (20 cm^3). Complex (**6**), which is insoluble in pentane, was filtered off (D-3 frit) and dried *in vacuo* to obtain a red powder (0.4 g, 33%).

Complex (**4**) was obtained from the filtrate as a yellow

Table 4. Selected distances (Å) and angles (°) for complex (**6**)

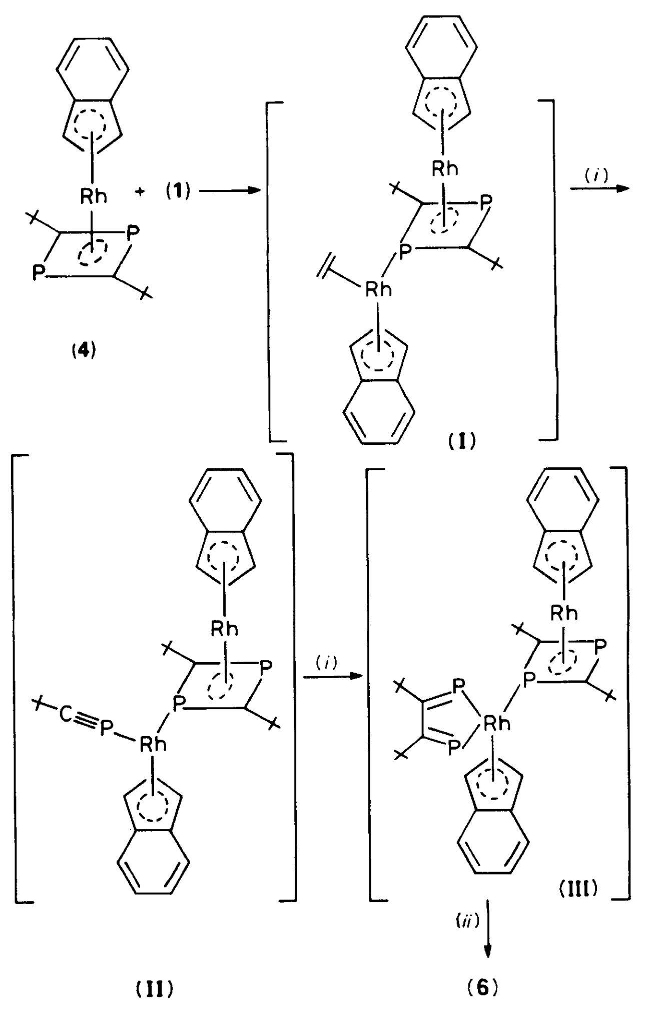
Rh(1)–P(1)	2.310(1)	Rh(3)–C(11)	2.178(4)
Rh(1)–P(2)	2.346(1)	Rh(3)–C(16)	2.224(4)
Rh(1)–P(3)	2.241(1)	Rh(3)–C(39)	2.316(5)
Rh(1)–C(21)	2.460(5)	Rh(3)–C(40)	2.230(6)
Rh(1)–C(22)	2.225(5)	Rh(3)–C(41)	2.214(7)
Rh(1)–C(23)	2.246(5)	Rh(3)–C(42)	2.227(6)
Rh(1)–C(24)	2.271(5)	Rh(3)–C(43)	2.320(5)
Rh(1)–C(25)	2.460(5)	P(1) ··· P(2)	2.549(2)
Rh(2)–P(1)	2.325(1)	P(1)–C(1)	1.828(4)
Rh(2)–P(2)	2.347(1)	P(2)–C(6)	1.843(4)
Rh(2)–C(1)	2.167(4)	P(3)–C(11)	1.781(4)
Rh(2)–C(6)	2.191(4)	P(3)–C(16)	1.782(4)
Rh(2)–C(30)	2.352(5)	P(4)–C(11)	1.819(4)
Rh(2)–C(31)	2.198(6)	P(4)–C(16)	1.802(4)
Rh(2)–C(32)	2.219(5)	C(1)–C(2)	1.557(6)
Rh(2)–C(33)	2.306(6)	C(1)–C(6)	1.416(6)
Rh(2)–C(34)	2.426(5)	C(6)–C(7)	1.553(6)
Rh(3)–P(3)	2.340(1)	C(11)–C(12)	1.515(6)
Rh(3)–P(4)	2.339(1)	C(16)–C(17)	1.512(6)
P(3)–Rh(1)–P(2)	91.9(1)	C(16)–P(4)–C(11)	82.1(2)
P(3)–Rh(1)–P(1)	91.2(1)	C(16)–P(4)–Rh(3)	63.4(1)
P(2)–Rh(1)–P(1)	66.4(1)	C(11)–P(4)–Rh(3)	61.7(1)
C(6)–Rh(2)–C(1)	37.9(2)	C(6)–C(1)–C(2)	135.6(4)
C(6)–Rh(2)–P(2)	47.8(1)	C(6)–C(1)–P(1)	107.1(3)
C(6)–Rh(2)–P(1)	70.9(1)	C(6)–C(1)–Rh(2)	72.0(2)
C(1)–Rh(2)–P(2)	72.1(1)	C(2)–C(1)–P(1)	117.2(3)
C(1)–Rh(2)–P(1)	47.9(1)	C(2)–C(1)–Rh(2)	124.7(3)
P(2)–Rh(2)–P(1)	66.1(1)	P(1)–C(1)–Rh(2)	70.6(1)
C(16)–Rh(3)–C(11)	65.4(1)	C(7)–C(6)–C(1)	132.5(4)
C(16)–Rh(3)–P(4)	46.4(1)	C(7)–C(6)–P(2)	118.6(3)
C(16)–Rh(3)–P(3)	45.9(1)	C(7)–C(6)–Rh(2)	127.7(3)
C(11)–Rh(3)–P(4)	47.3(1)	C(1)–C(6)–P(2)	108.8(3)
C(11)–Rh(3)–P(3)	46.2(1)	C(1)–C(6)–Rh(2)	70.1(2)
P(4)–Rh(3)–P(3)	70.2(1)	P(2)–C(6)–Rh(2)	70.6(1)
C(1)–P(1)–Rh(2)	61.5(1)	C(12)–C(11)–P(4)	129.9(3)
C(1)–P(1)–Rh(1)	111.0(1)	C(12)–C(11)–P(3)	133.0(3)
Rh(2)–P(1)–Rh(1)	112.9(1)	C(12)–C(11)–Rh(3)	124.5(3)
C(6)–P(2)–Rh(2)	61.7(1)	P(4)–C(11)–P(3)	96.7(2)
C(6)–P(2)–Rh(1)	108.3(1)	P(4)–C(11)–Rh(3)	71.0(1)
Rh(2)–P(2)–Rh(1)	110.9(1)	P(3)–C(11)–Rh(3)	71.7(1)
C(16)–P(3)–C(11)	83.7(2)	C(17)–C(16)–P(4)	129.4(3)
C(16)–P(3)–Rh(3)	63.6(1)	C(17)–C(16)–P(3)	133.0(3)
C(16)–P(3)–Rh(1)	135.5(1)	C(17)–C(16)–Rh(3)	125.3(3)
C(11)–P(3)–Rh(3)	62.1(1)	P(4)–C(16)–P(3)	97.3(2)
C(11)–P(3)–Rh(1)	138.2(1)	P(4)–C(16)–Rh(3)	70.1(1)
Rh(3)–P(3)–Rh(1)	139.4(1)	P(3)–C(16)–Rh(3)	70.5(1)

Table 5. ^{103}Rh N.m.r. data for compounds (**4**) and (**6**) (measured by indirect two-dimensional n.m.r. spectroscopy using ^{31}P detection)

Compound		$\delta(^{103}\text{Rh})$[a]	$J(^{103}\text{Rh}^{31}\text{P})$[b]/Hz
(**4**)[c]		−10 216	31.3
(**6**)[d]	Rh(1)	−8 859	J[Rh(1)P(3)] 228
			J[Rh(1)P(1)] 48
			J[Rh(1)P(2)] 42
	Rh(2)	−9 936	J[Rh(2)P(2)] 38
			J[Rh(2)P(1)] 42
	Rh(3)	−10 392	J[Rh(3)P(3)] 42
			J[Rh(3)P(4)] 38

[a] In p.p.m. relative to external [Rh(acac)$_3$]. [b] The assignments of P(1)/P(2) may be reversed. [c] At 300 K. [d] At 193 K.

powder (0.52 g, 36%) after evaporation of the solvent to half volume, cooling to −78 °C, and filtration.



Scheme 2. (*i*) P≡CBu^t; (*ii*) complex (**1**)

Crystal Structure Determinations.—Both data sets were collected on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo-K_α X-radiation (λ = 0.710 69 Å) by a θ—2θ scan technique. The intensities of three standard reflections, remeasured every 100 reflections, showed no significant variation during data collection. The data sets were corrected for Lorentz and polarization effects and data for complex (**5**) were also corrected for absorption; $\sigma(F)$ was calculated from $[\sigma(I)^2 + (Ik)]^2/2F$, where $k = 0.02$. Equivalent reflections were averaged. Only intensities that satisfied the criterion $I > 2.0\sigma(I)$ were used in the solution and refinement of the structure.

The structures were solved by the heavy-atom method. Refinement was by full-matrix least-squares methods, where the function minimized was $\Sigma w(\Delta F)^2$ with $w = 1/\sigma(F)^2$ and $\Delta F = |F_o| - |F_c|$. The H atoms of (**5**) were located in a difference Fourier synthesis and included isotropically in the refinement with fixed isotropic thermal parameters; those of (**6**) were inserted at calculated positions with fixed isotropic thermal parameters (0.08 Å^2) and not refined. Atomic scattering curves were taken from ref. 13.

Crystal data for complex (**5**). $C_{28}H_{32}P_4Rh_2$, M = 698.3, dark red, crystal dimensions 0.29 × 0.36 × 0.22 mm, monoclinic, space group $P2_1/c$, a = 11.890(2), b = 19.631(3), c = 12.535(1) Å, β = 105.51(1)°, U = 2 819.3 Å^3, Z = 4, D_c = 1.64 g cm^{-3}, μ = 13.92 cm^{-1}, $F(000)$ = 1 400.

6 845 Reflections were collected in the range 1.04 < θ < 27.33. Empirical absorption correction: minimum 0.824, maximum 1.174. 5 338 Observed reflections, R = 0.026, R' = 0.031.

Crystal data for complex (**6**). $C_{47}H_{57}P_4Rh_3$, M = 1 054.6, dark red, crystal dimensions 0.07 × 0.50 × 0.14 mm, triclinic,

Table 6. Phosphorus-31 n.m.r. spectra of complex (**6**) (in [$^2H_8$]tetrahydrofuran, 121.4 MHz, numbering scheme as in Figure 2)

T/°C	Atom	$\delta(^{31}P)$/p.p.m.	Multiplicity	$J(^{103}Rh^{31}P)$/Hz	$J(^{31}P^{31}P)$/Hz
40	P(1), P(2)	≈91[a]	($\Delta\nu_{\frac{1}{2}} \approx$ 1 000 Hz)[b]		
	P(3)	91.7	m	J[Rh(1)P(3)] 230	J[P(1)P(3)] = J[P(2)P(3)] = 60
				J[Rh(2)P(3)] 8	
				J[Rh(3)P(3)] 37	
−80	P(4)	10.2	m	J[Rh(3)P(4)] 38	
	P(1)[c]	83.1	m	J[Rh(1)P(1)] ≈44	J[P(1)P(2)] < 5[d]
				J[Rh(2)P(1)] ≈44	J[P(1)P(3)] ≈ 69
	P(2)[c]	115.7	m	J[Rh(1)P(2)] ≈47	J[P(2)P(3)] ≈ 40
				J[Rh(2)P(2)] ≈40	
	P(3)	88.4	m	J[Rh(1)P(3)] 228	
				J[Rh(3)P(3)] ≈42	
	P(4)	3.1	m	J[Rh(3)P(4)] 38	

[a] Exchange, average value. [b] $\Delta\nu_{\frac{1}{2}}$ = linewidth at half-height. [c] Assignments of P(1)/P(2) may be reversed. [d] Unresolved.

Table 7. ^{13}C N.m.r. data for complex (**6**); J(PC)/Hz in parentheses

	δ/p.p.m.	
Atom	40 °C	−80 °C
C(1)	121.5 (76)	122.1 (80)
C(6)		121.7 (76)
C(2)	38.2	39.2
C(7)		38.4
C(3)	33.4	33.4
C(8)		33.2
1,3-Diphosphacyclobutadiene ring		
C(11)[a]	109.1 (61,15)	108.7 (60,15)
C(16)[a]		107.5
C(12)	35.0 (6.7)	35.4
C(17)		34.2
C(13)	30.9	30.6
C(18)		30.6
Indenyl on Rh(1)		
C(23)	100.3	100.4
C(22)	81.3	85.7[b]
C(24)		76.4
C(21)	122.0	123.1
C(25)		118.4
C(26)	119.3	121.2
C(29)		117.5
C(27)	124.3	124.6[c]
C(28)		125.0[c]

	δ/p.p.m.	
Atom	40 °C	−80 °C
Indenyl on Rh(2)		
C(32)	86.9	86.4[b]
C(31)	76.9	76.9
C(33)		76.1
C(30)	114.4	115.0
C(34)		114.0
C(35)	122.9	123.4
C(38)		122.6
C(37)	123.7	123.6[c]
C(36)		123.7[c]
Indenyl on Rh(3)		
C(41)	89.0	89.0
C(40)	79.3	80.3
C(42)		79.8
C(39)	110.1	109.6
C(43)		109.4
C(44)	124.5	123.9[c]
C(47)		124.6[c]
C(45)	125.8	125.9
C(46)		125.8

[a] J[Rh(3)C(11)] and J[Rh(3)C(16)] = 15 Hz. [b] Assignments of C(22) and C(32) may be interchanged. [c] Assignments of C(27)/C(28), C(37)/C(36), and C(44)/C(47) may be interchanged.

space group $P\bar{1}$, a = 13.573(2), b = 13.604(1), c = 13.781(3) Å, α = 74.14(1), β = 76.62(1), γ = 67.31(1)°, U = 2 235.3 Å^3, Z = 2, D_c = 1.57 g cm^{-3}, μ = 12.50 cm^{-1}, F(000) = 1 068, 10 127 reflections were collected in the range 1.56 < θ < 27.34, 7 426 observed, R = 0.033, R' = 0.036.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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