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Phosphaalkyne cyclodimerization at a rhodium(I) centre. Syntheses of a cationic η^4-1,3-diphosphacyclobutadiene rhodium complex and of its platinum(II) or tungsten(0) adducts

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Treatment of [RhCl(triphos)] [triphos = $PPh(CH_2CH_2PPh_2)_2$] in thf with P≡CBu^t, in the presence of $TlBF_4$, gave the η^4-1,3-diphosphacyclobutadiene complex [Rh(triphos){η^4-$(PCBu^t)_2$}][BF_4] **1a** which formed the diadducts [Rh(triphos){$\eta^4:\eta^1:\eta^1$-[$W(CO)_5$]$_2$$(PCBu^t)_2$}][$BF_4$] **2** or [Rh(triphos){$\eta^4:\eta^1:\eta^1$-[$PtCl_2(PEt_3)$]$_2$$(PCBu^t)_2$}][$BF_4$] **3** on reaction with [$W(CO)_5$(thf)] or [$Pt_2Cl_4(PEt_3)_2$], respectively. These adducts dissociated in solution, the former in the presence of Na[BPh_4] to give [Rh(triphos){η^4-$(PCBu^t)_2$}][BPh_4] **1b**, and the latter to the mono-η^1-adduct [Rh(triphos){$\eta^4:\eta^1$-[$PtCl_2(PEt_3)$]$(PCBu^t)_2$}][BF_4] **4**. Reactions of [RhCl(triphos)] in thf with the 1-alkynes HC≡CR (R = CO_2Me or CO_2Et) in the presence of Tl[BF_4] afforded the corresponding benzene derivative complexes [Rh(triphos){η^4-$(HCCR)_3$}][BF_4] **5a** or **5b**.

Introduction

Phosphaalkynes are known to undergo a variety of cycloaddition reactions at transition metal centres to generate novel P-containing rings,[1,2] and in particular η^4-1,3-diphosphacyclobutadiene complexes of Group 9 metals[3–12] have been prepared in such a way. However, in contrast to Co, the yields of the η^4-1,3-diphosphacyclobutadiene compounds of Rh are commonly low and a variety of other products can be formed involving *e.g.* the co-ordination of the phosphorus lone pair to another metal centre, the formation of a metallacycle or the occurrence of P–P coupling, namely in the reactions of a phosphaalkyne with η^5-indenyl or η^5-cyclopentadienyl complexes such as [Rh(η^5-L)(η^2-CH_2=CH_2)] (L = C_9H_7, C_5H_5 or C_5Me_5).[3–6]

We have selected a rhodium centre, [RhCl(triphos)] [triphos = $PPh(CH_2CH_2PPh_2)_2$], presenting a tridentate ligand with different steric and electronic properties to those of η^5-indenyl or η^5-cyclopentadienyl and now report its reaction with P≡CBu^t, which leads to the selective formation, in high yield, of the η^4-1,3-diphosphacyclobutadiene complex [Rh(triphos){η^4-$(P{\equiv}CBu^t)_2$}][BF_4] **1a**. Moreover in view of our interest in the comparison of the co-ordination chemistries of phosphaalkynes and alkynes,[1,9,13–16] we have also investigated the reactions of HC≡CR (R = CO_2Me or CO_2Et) with the above Rh–triphos starting material and noticed that, in contrast with P≡CBu^t, alkyne cyclodimerization is not the preferred reaction.

Results and discussion

The reaction of P≡CBu^t with [RhCl(triphos)], in thf, in the presence of $TlBF_4$ as a chloride ligand abstractor, results in cyclodimerization of the phosphaalkyne to form the η^4-1,3-diphosphacyclobutadiene complex [Rh(triphos){η^4-$(PCBu^t)_2$}][BF_4] **1a** (reaction 1, Scheme 1) which was isolated in high yield (80%) as a yellow solid and characterized (see Experimental section) by elemental analysis, IR, ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectroscopies and FAB-MS spectrometry.

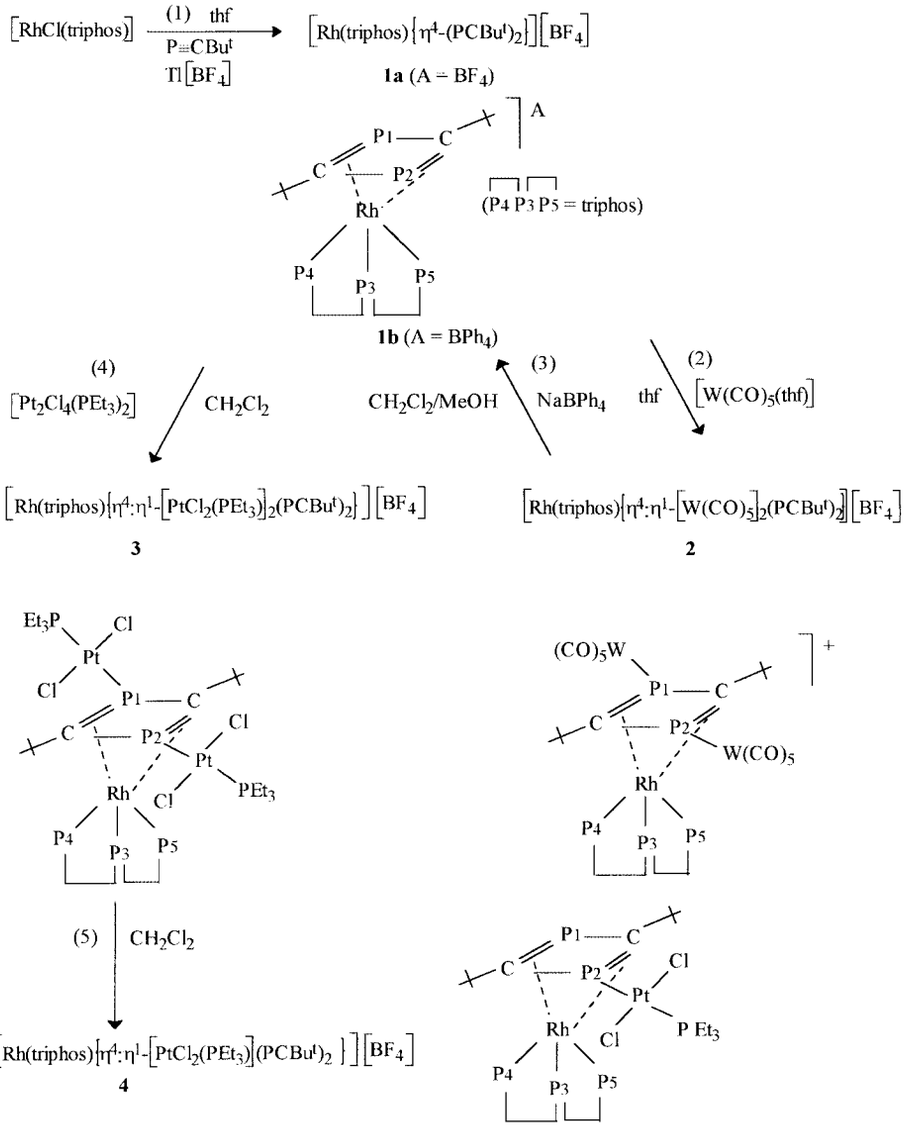
The reported syntheses of the related η^5-cyclopentadienyl-type complexes [M(η^5-C_5R_5){η^4-$(PCBu^t)_2$}] (M = Co, Rh or Ir; R = H or Me)[3,4] and η^5-indenyl compounds [M(η^5-C_9H_7){η^4-$(PCBu^t)_2$}] (M = Co[5] or Rh[6]) occur *via* displacement of the two ethylene ligands from the corresponding diethylene parent complexes, and, in the case of Rh, the yields are low and other types of products are also formed,[6] *e.g.* metallacycles, P–P rings or bridging cyclobutadiene ligands in polynuclear assemblies. Our synthesis is more selective towards a mononuclear η^4-1,3-diphosphacyclobutadiene complex and has a higher yield. The different steric hindrance of triphos compared with the cyclopentadienyl-type ligands, as well as its distinct electronic properties, conceivably constitute favourable factors for the above reaction.

In the ^{13}C-{^{1}H} NMR spectrum of complex **1a** the P=*C*CMe$_3$ signal of the η^4-diphosphacyclobutadiene ligand occurs as a broad resonance at δ 101.0, whereas that of P=C*C*Me$_3$ is observed as a broad singlet at δ 33.30. These chemical shifts are in agreement with those reported[6] for the related (η^4-1,3-diphosphacyclobutadiene)(η^6-indenyl)rhodium complex [Rh(η^5-C_9H_7){η^4-$(PCBu^t)_2$}] (δ 112.7 and 34.5), respectively, although in **1a** the broadness of the resonances precluded the estimate of J(CP) and J(CRh).

The ^{31}P-{^{1}H} NMR spectrum of complex **1a** presents a rather complicated pattern which was successfully analysed (Fig. 1) as an AA′MRR′X spin system (A, A′ = P_1P_2; M = P_3; R, R′ = P_4, P_5; X = Rh, see Scheme 1). In particular, the resonance of the 1,3-diphosphacyclobutadiene ^{31}P nuclei (A, A′) is a complex multiplet centred at δ 83.51 (relative to H_3PO_4) with $^2J(P_1P_2)$ = 17.0 and $J(P_1Rh) = J(P_2Rh)$ = 17.1 Hz. The latter coupling constant is smaller than those observed [$J(P_3Rh)$ = 138.0, $J(P_4Rh) = J(P_5Rh)$ = 129.5 Hz] between the metal and the phosphine ^{31}P nuclei, and is even lower than those reported, *ca.* 30 Hz, for [Rh(η^5-C_5R_5){η^4-$(PCBu^t)_2$}] (R = H or Me)[3] and [Rh(η^5-C_9H_7){η^4-$(PCBu^t)_2$}],[6] thus ruling out[3] the phosphorus metallacycle ring Rh$\overline{P{=}C(Bu^t)C(Bu^t){=}P}$ or possible η^1-P binding mode where a value of J(PRh) of 150–200 Hz would be more typical.

In the FAB-MS spectrum of complex **1a** the molecular ion and the fragment derived from loss of the diphosphacyclobutadiene ring are observed at 839 (M^+) and 638 ([M − 2PCBu^t]$^+$).

Complex **1a**, in thf, reacts with [$W(CO)_5$(thf)], added in a



Scheme 1 Reactions of [RhCl(triphos)] with P≡CBu^t [triphos = $\overline{P_4P_3P_5}$ = PPh(CH$_2$CH$_2$PPh$_2$)$_2$].

2.7 : 1 molar ratio, to form (reaction 2, Scheme 1) the bis-η^1-adduct [Rh(triphos){η^4 : η^1 : η^1-[W(CO)$_5$]$_2$(PCBu^t)$_2$}][BF$_4$] **2**, resulting from ligation of each of the electron lone pairs of the two phosphorus atoms of the diphosphacyclobutadiene ring to a {W(CO)$_5$} centre. The co-ordination of one such P atom to another rhodium site has been recognized previously in other complexes such as [Rh(η^5-C$_5$H$_5$){η^4-(PCBu^t)$_2$}][7] or [Rh(η^5-C$_9$H$_7$){η^4-(PCBu^t)$_2$}],[6] and in the present case the addition reaction proceeded further towards a diadduct involving both P atoms of the ring. Complex **2** was isolated (77% yield) as a greenish orange powder and characterized (see Experimental section) by elemental analysis, IR, ^{1}H and ^{13}P-{^{1}H} NMR spectroscopies and FAB-MS spectrometry.

The ligation of the P atoms (P$_1$ and P$_2$) of the 1,3-diphosphacyclobutadiene ring to the {W(CO)$_5$} centres does not result in a drastic change of the ^{31}P-{^{1}H} NMR spectrum which still exhibits an AA′MRR′X spin system with a slight shift of the complex resonance of such phosphorus nuclei from δ 83.51 (**1a**) to 77.76 (**2**), and a slight increase of J(P$_1$Rh) = J(P$_2$Rh) from 17 (**1a**) to 24 Hz, showing that the identity of the ring has been preserved. The coupling of P$_1$ or P$_2$ to ^{183}W could not be assigned due to the rather complex pattern of the signal.

The adduct **2** undergoes dissociation in CH$_2$Cl$_2$–MeOH, in the presence of Na[BPh$_4$], to regenerate (reaction 3, Scheme 1) the parent complex (isolated in 85% yield) although with [BPh$_4$]$^-$ as the counter ion (**1b**). For this product no IR band which could be assigned to ν(CO) was detected, and its ^{31}P-{^{1}H} NMR spectrum was similar to that of **1a**.

The ability of the ring phosphorus atoms to act as donor sites towards {PtCl$_2$(PEt$_3$)} was also tested and the diadduct [Rh(triphos){η^4 : η^1 : η^1-[PtCl$_2$(PEt$_3$)]$_2$(PCBu^t)$_2$}][BF$_4$] **3** was obtained as an orange solid (reaction 4, Scheme 1). This reaction parallels that observed[8] for [Co(η^5-C$_5$Me$_5$){η^4-(PCBu^t)$_2$}] which adds the same platinum centre to form [Co(η^5-C$_5$Me$_5$){η^4-Pt$_2$Cl$_4$(PEt$_3$)$_2$(PCBu^t)$_2$}] as well as the intermediate mono-adduct.

The molecular ion of the diadduct **3** is observed in its FAB-MS spectrum, as well as the expected fragments derived upon sequential loss of the platinum sites and of the diphosphacyclobutadiene ring, *i.e.* [M − {PtCl$_2$(PEt$_3$)}]$^+$, [M − {PtCl$_2$(PEt$_3$)}$_2$]$^+$ and [M − {PtCl$_2$(PEt$_3$)$_2$}-(PCBu^t)$_2$]$^+$.

Complex **3** in CH$_2$Cl$_2$ solution undergoes a partial discussion to form the monoadduct [Rh(triphos){η^4 : η^1-[PtCl$_2$(PEt$_3$)]-(PCBu^t)$_2$}][BF$_4$] **4** (reaction 5, Scheme 1) which was the product detected by ^{31}P-{^{1}H} NMR. The resonance of the ring-P nucleus (P$_2$) ligated to the PtCl$_2$(PEt$_3$) centre is a doublet [^2J(P$_2$P$_6$) = 493 Hz, P$_6$ = P nucleus at PEt$_3$] of doublets [^2J(P$_2$P$_1$) = 70 Hz] of multiplets, with the expected ^{195}Pt satellites [J(P$_2$Pt) = 1987 Hz]. The high ^2J(P$_2$P$_6$) value is indicative of a *trans* arrangement of the PEt$_3$ and the diphosphacyclobutadiene ligating the Pt as observed[8] for the adduct [Co(η^5-C$_5$Me$_5$){η^4-PtCl$_2$(PEt$_3$)(PCBu^t)$_2$}]. The ^{31}P resonance

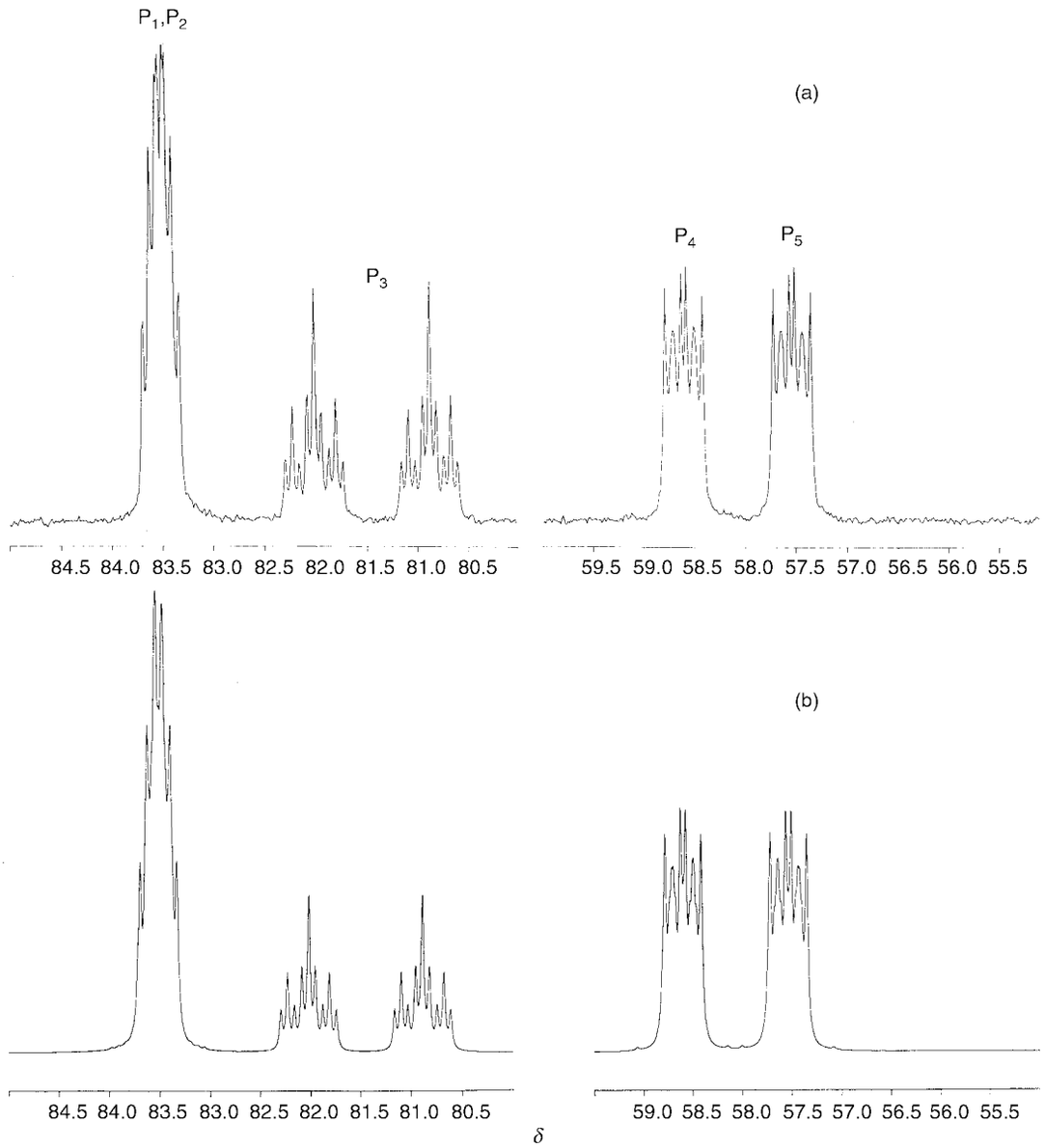


Fig. 1 Experimental (a) and simulated (b) $^{31}P-\{^{1}H\}$ NMR spectra of complex **1a** (CD_2Cl_2) analysed as an AA′MRR′X (A, A′ = P_1,P_2; M = P_3; R,R′ = P_4,P_5; X = Rh) spin system.

associated to the $P_{(6)}Et_3$ ligand is the expected doublet [$^2J(P_6P_2)$ = 493 Hz] at δ 18.55 with ^{195}Pt satellites [$J(P_6Pt)$ = 2901 Hz]. The starting material $[Pt_2Cl_4(PEt_3)_2]$ formed in solution upon dissociation of **3** was also detected by its characteristic singlet at δ 12.08 with ^{195}Pt satellites [J(PPt) = 3827 Hz].

For comparative purposes, we have also investigated the reactions of [RhCl(triphos)], in thf, with the alkynes HC≡CR (R = CO_2Me or CO_2Et) in the presence of $TlBF_4$. They appear to lead to the formation of mixtures of isomers of complexes which we tentatively formulate as the products of alkyne cyclotrimerization [Rh(triphos){η^4-$(HCCR)_3$}][BF_4] (R = CO_2Me **5a** or CO_2Et **5b**) mainly on the basis of elemental analysis, FAB-MS spectrometry and IR spectroscopy (in view of the presence of various isomers, their ^{1}H and $^{31}P-\{^1H\}$ NMR signals could not clearly be identified) which indicate *e.g* the presence of 3 HCCR groups in the molecule. Since the co-ordination of three alkyne molecules would not be expected (one of the P atoms of the strongly co-ordinated triphos should be displaced from the metal co-ordination sphere), a coupling process should occur conceivably involving the cyclotrimerization of the alkynes. In agreement, the FAB-MS spectra of **5a** and **5b** clearly exhibit the corresponding molecular ion signals, as well as those for the fragments derived from the loss of one and three HCCR groups, but not from the loss of two of them. Hence, an alternative formulation with a η^2-cyclobutadiene and a η^2-alkyne ligand would be less favoured, although it cannot be ruled out.

Other examples of the formation of η^4-arene complexes by cyclotrimerization of alkynes are known, namely in the reactions of [Rh(η^5-C_5R_5)$(CO)_2$] (R = H or Me) with R′C≡CR′ (R′ = CF_3[17] or CO_2Me[18]) to yield [Rh(η^5-C_5R_5){η^4-(R′-CCR′)$_3$}]. Only the products derived from alkynes with strongly electron-withdrawing substituents (R′) could be isolated.

There is no evidence that alkynes behave similarly to the phosphaalkyne in our systems and in particular we have not obtained the η^4-ligated cyclobutadiene complexes analogous to the η^4-diphosphacyclobutadiene **1a**. Other cases of preferential formation of the η^4-1,3-diphosphacyclobutadiene ring in comparison with cyclobutadiene are known for Mo[13] or Co.[9]

Experimental

All the manipulations and reactions were carried out in the absence of air using standard inert gas flow and vacuum techniques. Solvents were purified by standard procedures. The compounds [RhCl(triphos)],[19] $[Pt_2Cl_4(PEt_3)_2]$[20] and P≡CBu^t[21] were prepared by published methods, whereas $NaBPh_4$ and the

1-alkynes HC≡CR (R = CO_2Me or CO_2Et) were commercially available (Aldrich).

Infrared measurements (KBr pellets) were carried out on a Perkin-Elmer 683 spectrophotometer, ^1H, ^{31}P and ^{13}C NMR on a Varian Unity 300 spectrometer; δ values are in ppm relative to $SiMe_4$ (^1H and ^{13}C) or to H_3PO_4 (^{31}P). Abbreviations: s = singlet, d = doublet, t = triplet, m = complex multiplet, dd = doublet of doublets, dt = doublets of triplets, dm = doublet of complex multiplets, ddm = doublet of doublets of complex multiplets, dtt = doublet of triplet of triplets, ddt = doublet of doublets of triplets, br = broad. The FAB mass spectrometric measurements were performed on a Trio 2000 spectrometer at the Centro de Química Estrutural. Positive-ion spectra were obtained by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI.

Preparations

[Rh(triphos){η⁴-(PCBu^t)$_2$}][BF_4] 1a. A solution of [RhCl(triphos)] (0.150 g, 0.223 mmol) in thf (10 cm^3) was treated with a 1:1 mixture of P≡CBu^t + $(Me_3Si)_2O$ (0.15 cm^3, 1.0 mmol of P≡CBu^t) followed by addition of solid $TlBF_4$ (0.10 g, 0.34 mmol) and stirred for 15 h. The yellow-orange solution was then filtered and the volatiles were removed *in vacuo.* The residue was extracted in CH_2Cl_2 (10 cm^3), the solution filtered and reduced in volume to *ca.* 1 cm^3. Addition of Et_2O (10 cm^3) precipitated complex **1a** as a yellow solid which was separated by decantation, washed with Et_2O (10 cm^3) and dried *in vacuo* (0.16 g, 80%) (Found: C, 56.8; H, 5.9. $C_{44}H_{51}BF_4P_5Rh$ requires C, 57.1; H, 5.6%). FAB-MS: *m/z* 839 (M^+ for ^{103}Rh) and 638 ([M − 2PCBu^t]$^+$). IR: $\tilde{\nu}$/cm^{-1} 1050s (br) (BF_4^-). NMR (CD_2Cl_2, 25 °C): ^1H, δ 0.017 (s, 9 H, Bu^t), 1.06 (s, 9 H, Bu^t), 2.45–3.04 (m, 8 H, CH_2) and 6.88–7.90 (m, 25 H, Ph); ^{31}P-{^1H}, [AA′MRR′X] spin system (A,A′ = P_1P_2; M = P_3; R,R′ = P_4,P_5; X = Rh), δ 83.51 [M, P_1P_2, $J(P_1P_2)$ = 17.0, $J(P_1Rh) = J(P_2Rh)$ = 17.1], 81.45 [dtt, P_3, $J(P_1P_3) = J(P_2P_3)$ = 8.1, $J(P_3P_4) = J(P_3P_5)$ = 25.5, $J(P_3Rh)$ = 138.0] and 58.06 [ddt, P_4P_5, $J(P_1P_4) = J(P_2P_5)$ = 16.4, $J(P_2P_4) = J(P_1P_5)$ = 2.4, $J(P_4P_5)$ = 25, $J(P_4Rh) = J(P_5Rh)$ = 129.5 Hz); ^{13}C-{^1H}, δ 29.87 [dd, CH_2, $^2J(CP)$ = 11, $^1J(CP)$ = 29], 31.36 [dt, CH_2, $^2J(CP)$ = 8, $^1J(CP)$ = 28 Hz], 32.05 [s, br, C(CH_3)$_3$], 33.30 (s, br, CMe_3) and 101.0 (m, br, P=C).

[Rh(triphos){η⁴-(PCBu^t)$_2$}][BPh_4] 1b. To $NaBPh_4$ (0.025 g, 0.070 mmol) was added a solution of [Rh(triphos){η⁴:η¹:η¹-[$W(CO)_5$]$_2$(PCBu^t)$_2$}][BF_4] **2** (see below) (0.046 g, 0.030 mmol) in CH_2Cl_2 (2.0 cm^3), methanol (15 cm^3) was layered on top and the reaction allowed to proceed without stirring. In 2 d a precipitate of complex **1b** formed as fibrous, orange crystals. The supernatant solution was decanted and the crystals dried *in vacuo* (0.028 g, 85% yield) (Found: C, 70.2; H, 6.2. $C_{68}H_{71}BP_5Rh$ requires C, 70.6; H, 6.2%). FAB-MS; *m/z* 837 (M^+) and 637 ([M − (PCBu^t)$_2$]$^+$). ^1H NMR (CD_2Cl_2, 25 °C): δ 0.013 (s, br, 9 H, Bu^t), 1.02 (s, br, 9 H, Bu^t), 1.96–2.80 (m, 8 H, CH_2) and 6.69–7.78 (m, 45 H, Ph).

[Rh(triphos){η⁴:η¹:η¹-[$W(CO)_5$]$_2$(PCBu^t)$_2$}][BF_2] 2. A solution of [Rh(triphos){η⁴-(PCBu^t)$_2$}][BF_4] **1a** (0.27 g, 0.30 mmol) in thf (15 cm^3) was treated with a solution of [$W(CO)_5$(thf)] (0.80 mmol) in thf (20 cm^3), and stirred in the dark for 3 d to form a clear, dark orange solution. The volatiles were removed *in vacuo* and the residue was extracted in CH_2Cl_2 (30 cm^3), the solution filtered and taken to dryness *in vacuo*. The resulting dark brown sticky solid was washed with Et_2O (10 cm^3) by the freeze–thaw technique and dried *in vacuo* to give a green-orange powder of complex **2** (0.35 g, 77% yield) (Found: C, 43.5; H, 3.7. $C_{54}H_{51}BF_4O_{10}P_5RhW_2$·2thf requires C, 43.4; H, 3.9%). FAB-MS: *m/z* 838 ([M − 2$W(CO)_5$]$^+$) and 637 ([M − 2$W(CO)_5$-2PCBu^t]$^+$). IR: $\tilde{\nu}$/cm^{-1} 1940s (br) [ν(CO)] and 1080s (br) (BF_4^-). NMR (CD_2Cl_2, 25 °C): ^1H, δ 0.007 (s, br, 9 H, Bu^t), 1.04 (s, br, 9 H, Bu^t), 2.15–3.04 (m, 8 H, CH_2) and 6.90–7.94 (m, 25 H, Ph); ^{31}P-{^1H}, δ 77.76 [m, P_1P_2, $J(P_1P_2)$ = 16, $J(P_1Rh) = J(P_2Rh)$ = 24], 75.69 [dtt, P_3, $J(P_1P_3) = J(P_2P_3)$ = 8, $J(P_3Rh)$ = 138, $J(P_3P_4) = J(P_3P_5)$ = 138] and 52.24 [dm, P_4P_5, $J(P_4Rh) = J(P_5Rh)$ = 129, $J(P_1P_4) = J(P_2P_5)$ = 17, $J(P_4P_5)$ = 25 Hz].

[Rh(triphos){η⁴:η¹:η¹-[$PtCl_2$(PEt_3)]$_2$(PCBu^t)$_2$}][BF_4] 3 and [Rh(triphos){η⁴:η¹-[$PtCl_2$(PEt_3)](PCBu^t)$_2$}][BF_4] 4. A solution of [Rh(triphos){η⁴-(PCBu^t)$_2$}][BF_4] **1a** (0.10 g, 0.10 mmol) in CH_2Cl_2 (2 cm^3) was treated with a solution of [$Pt_2Cl_4(PEt_3)$] (0.038 g, 0.050 mmol) in CH_2Cl_2 (2 cm^3) and the mixture stirred for 15 h. The solvent was pumped off and the orange residue washed with Et_2O (2 × 5 cm^3) and dried *in vacuo* to form an orange solid of complex **3**. FAB-MS: *m/z* 1605 (M^+), 1221 ([M − $PtCl_2(PEt_3)$]$^+$), 837 ([M − {$PtCl_2(PEt_3)$}$_2$]$^+$) and 637 ([M − {$PtCl_2(PEt_3)$}$_2$ − (PCBu^t)$_2$]$^+$). IR: $\tilde{\nu}$/cm^{-1} 1080s (br) (BF_4^-).

In solution, the diadduct **3** converts into the corresponding monoadduct **4** identified by ^{31}P-{^1H} NMR of a CD_2Cl_2 solution of **3**: δ 101.59 [ddm, P_2, $J(P_2P_6)$ = 493, $J(P_2P_1)$ 70, $J(P_2Pt)$ = 1987], 84.17 [dm, P_3, $J(P_3Rh)$ = 141.5], 71.94 (dm, br, P_1), 63.73 (m, P_4), 54.62 [dm, P_5, $J(P_5Rh)$ = 146.5], 18.55 [d, P_6 (PEt_3), $J(P_6P_2)$ = 493; $J(P_6Pt)$ = 2901] and 12.08 {s, liberated [$Pt_2Cl_4(PEt_3)$]; J(PPt) = 3827 Hz}.

[Rh(triphos){η⁴-(HCCR)$_3$}][BF_4] (R = CO_2Me 5a or CO_2Et 5b). A solution of [RhCl(triphos)] (0.20 g, 0.30 mmol) in thf (50 cm^3) was treated with the appropriate HC≡CR [1.2 mmol, *i.e.* 0.10 cm^3 (R = CO_2Me) or 0.12 cm^3 (R = CO_2Et)] followed by $TlBF_4$ (0.17 g, 0.58 mmol) and the mixture stirred for 2 d. The solution was then filtered and taken to dryness *in vacuo*. Extraction with CH_2Cl_2 (10 cm^3), filtration of the solution and removal of the solvent *in vacuo* left a residue that was washed with Et_2O (30 cm^3), dried *in vacuo* and recrystallised from CH_2Cl_2–Et_2O to give a dark red (**5a**) or orange (**5b**) solid which was filtered off and dried *in vacuo* (*ca.* 80% yields). Complex **5a** (Found: C, 53.6; H, 4.5. $C_{46}H_{45}BF_4O_6P_3Rh$·CH_2Cl_2 requires C, 53.2; H, 4.5%): FAB-MS *m/z* 888 (M^+), 805 ([M − HCCR]$^+$] and 638 ([M − 3HCCR]$^+$); IR $\tilde{\nu}$/cm^{-1} 1730m and 1680s [ν(CO)], 1070vs (br) (BF_4^-). Complex **5b** (Found: C, 55.6; H, 4.9. $C_{49}H_{51}BF_4O_6P_3Rh$·½CH_2Cl_2 requires C, 56.0; H, 4.9%): FAB-MS *m/z* 931 (M^+), 833 ([M − HCCR]$^+$) and 637 ([M − 3HCCR]$^+$); IR $\tilde{\nu}$/cm^{-1} 1690s [ν(CO)] and 1050vs (br) (BF_4^-).

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References

1 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, New York, 1998, p. 366; J. F. Nixon, *Coord. Chem. Rev.*, 1995, **145**, 201; *Chem. Soc. Rev.*, 1995, 319; *Chem. Ind.*, 1993, 404; *Endeavour*, 1991, **15**, 49; *Chem. Rev.*, 1988, **88**, 1327.

2 M. Regitz, *J. Heterocycl. Chem.*, 1994, **31**, 663; *Proc. 4th Symp. Org. Synth. via Organometallics, Aachen*, 1992, 93; *Chem. Rev.*, 1990, **90**, 191; *Heteroatom Chemistry*, ed. E. Block, VCH, New York, 1990, p. 295; M. Regitz and P. Binger, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, eds. M. Regitz and O. J. Scherer, Georg Thieme, Stuttgart, 1990, ch. 2.

3 P. B. Hitchcock, M. J. Maah and J. F. Nixon, *J. Chem. Soc.*, *Chem Commun.*, 1986, 737.

4 P. Binger, R. Milczarek, R. Mynott, M. Regitz and W. Rosch, *Angew. Chem.*, *Int. Ed. Engl.*, 1986, **25**, 644.

5 P. Binger, R. Milczarek, R. Mynott, C. Kruger, Y. H. Tsay, E. Raabe and M. Regitz, *Chem. Ber.*, 1988, **121**, 637.
6 P. Binger, B. Biedenbach, R. Mynott, R. Benn, A. Rufinska, P. Betz and C. Krüger, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1771.
7 P. B. Hitchcock, M. J. Maah, J. F. Nixon and C. Woodward, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 844.
8 P. B. Hitchcock, M. J. Maah and J. F. Nixon, *Heteroatom Chem.*, 1991, **2**, 253.
9 R. M. Matos, J. F. Nixon and J. Okuda, *Inorg. Chim. Acta*, 1994, **222**, 13.
10 P. Binger, B. Biedenbach, R. Mynott, C. Krüger, P. Betz and M. Regitz, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 1157.
11 H. F. Dare, J. A. K. Howard, M. U. Pilotti, F. G. A. Stone and J. Szameitat, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 2263.
12 R. Gleiter, I. Hyla-Kryspin, P. Binger and M. Regitz, *Organometallics*, 1992, **11**, 177.
13 P. B. Hitchcock, M. J. Maah, M. Green and J. F. Nixon, *J. Organomet. Chem.*, 1994, **466**, 153.
14 P. B. Hitchcock, J. A. Johnson, M. A. N. D. A. Lemos, M. F. Meidine, J. F. Nixon and A. J. L. Pombeiro, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 645.
15 S. S. P. R. Almeida and A. J. L. Pombeiro, *Organometallics*, 1997, **16**, 4469; M. F. N. N. Carvalho, S. S. P. R. Almeida, A. J. L. Pombeiro and R. A. Henderson, *ibid.*, 1997, **16**, 5441.
16 M. F. Meidine, M. A. N. D. A. Lemos, A. J. L. Pombeiro, J. F. Nixon and P. B. Hitchcock, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3319; P. B. Hitchcock, M. A. N. D. A. Lemos, M. F. Meidine, J. F. Nixon and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1991, **402**, C23.
17 R. S. Dickson and G. Wilkinson, *Chem. Ind.*, 1963, 1432; *J. Chem. Soc.*, 1964, 2699; R. S. Dickson and H. P. Hirsch, *Aust. J. Chem.*, 1974, **27**, 61; M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 1963, 365.
18 Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, 1974, **64**, 393.
19 R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1841.
20 F. R. Hartley, *Organomet. Chem. Rev. A*, 1970, **6**, 119.
21 T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis*, 1986, 31.

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