Syntheses of η^1- and η^2-Phospha-alkene–Transition Metal Complexes and the First Examples of Complexes containing only ligated Phospha-alkenes and Phospha-alkynes

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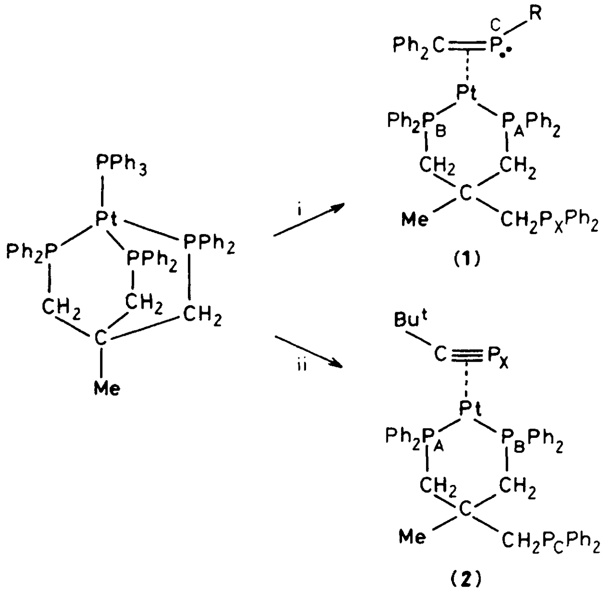
Differing modes of co-ordination are reported for complexes of platinum(0) containing the phospha-alkene P(mesityl)=CPh$_2$, *e.g.* in Pt(triphos){P(mesityl)=CPh$_2$}, [triphos = (PPh$_2$CH$_2$)$_3$CMe], the phospha-alkene is η^2-bonded to the metal whereas in Pt{P(mesityl)=CPh$_2$}$_3$ and Pt{P(mesityl)=CPh$_2$}$_2$(P≡CBu^t) it is η^1-co-ordinated and the last two complexes are the first isolated compounds containing only phospha-alkene or phospha-alkyne ligands.

The chemistry of the novel phospha-alkenes RP=CR$^1_2$, and phospha-alkynes, RC≡P, containing 2p$_\pi$–3p$_\pi$ bonds is of current interest.[1,2] Recent MO calculations,[3,4] suggest that the highest occupied molecular orbital in CH$_2$=PH is of the π-type with the phosphorus lone pair σ-orbital only slightly more stable while the π^* LUMO is relatively low lying. He I photoelectron spectroscopic studies on a variety of RC≡P molecules[5,6] indicate that the HOMO is also of the π-type and the π–σ separation is much greater than that found in the analogous RC≡N systems.

In principle therefore it might be expected that phospha-alkenes are likely to act as both η^1-phosphorus donors and η^2-P=C π-donors towards transition metals whereas phospha-alkynes are likely to behave as η^2-donors. Previously we and others established the η^1-bonding type for the phospha-alkene P(mesityl)=CPh$_2$ in single crystal *X*-ray studies on *cis*-PtCl$_2$(PEt$_3$){P(mesityl)=CPh$_2$},[7] Cr(CO)$_5${P(mesityl)=CPh$_2$},[8] and Pt(PPh$_3$)$_2${P(mesityl)=CPh$_2$}.[9] The latter complex showed a solution n.m.r. spectrum which also supported the possible existence of an η^2-isomer.

We now describe the synthesis of an η^2-phospha-alkene complex Pt(triphos){P(mesityl)=CPh$_2$} (1), [triphos = (PPh$_2$CH$_2$)$_3$CMe] formed unexpectedly in the displacement reaction of PPh$_3$ from Pt(PPh$_3$)(triphos) (see Scheme 1). The η^2-phospha-alkyne complex Pt(triphos)(P≡CBu^t) (2) was formed in a similar way.



Scheme 1. i, P(mesityl)=CPh$_2$; ii, P≡CBu^t; R = mesityl.

Both (1) and (2) show the characteristic ^{31}P{^{1}H} n.m.r. spectrum expected for an [ABM] spin system (A and B represent ^{31}P nuclei of the co-ordinated triphos, M the unique co-ordinated phosphorus of the η^2-phospha-alkene or phospha-alkyne) each line exhibiting the expected satellites due to coupling from the ^{195}Pt nucleus. In addition a singlet is observed for the non-co-ordinated phosphorus of the triphos ligand.†

The ^{31}P{^{1}H} n.m.r. spectrum of (1) is more complex than that of (2) which is shown in Figure 1 because of the existence of two isomers of (1) which arise from the different orientations of the phosphorus lone pair of the phospha-alkene. The ^{195}Pt n.m.r. spectrum of (1) (Figure 2) confirms the presence of the isomeric mixture and consists of two sets of eight lines of equal intensity.

The η^2-mode of co-ordination of both (1) and (2) is unambiguously established by the unusually small values of ^1J(Pt,P) for the co-ordinated phospha-alkene and phospha-alkyne (467, 455; and 144 Hz, respectively). The very low values reflect the large s-character of the phosphorus lone pair of the phospha-alkene and phospha-alkyne which is directed away from the metal atom in (1) and (2) and a similar effect was noted by us[10] in the η^2-Pt(PPh$_3$)(P≡CBu^t) complex.

In contrast to the above, treatment of Pt(cod)$_2$ (cod = 1,5-cyclo-octadiene), with P(mesityl)=CPh$_2$ gave the η^1 -complex Pt{P(mesityl)=CPh$_2$}$_3$ (3), (Scheme 2) as evidence by ^{31}P and ^{195}Pt n.m.r. spectroscopy, the latter showing a widely spaced 1-3-3-1 quartet [^1J(Pt,P) 4946 Hz].† Likewise when a 2:1 mixture of P(mesityl)=CPh$_2$ and P≡CBu^t reacted with Pt(cod)$_2$ the product was Pt{P(mesityl)=CPh$_2$}$_2$(P≡CBu^t) (4) which is an interesting example of a complex containing only ligated

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† N.m.r. data for (1): ^{31}P, δ −137.6 (P$_A$), −139.6 (P$_B$), −184.1 (P$_X$), −168.1 p.p.m. (P$_C$); ^2J(P$_A$,P$_B$) 20, ^2J(P$_B$,P$_C$) 12, ^2J(P$_A$,P$_C$) 57 Hz; ^{195}Pt, δ —460.0 p.p.m. [isomer (a)]; ^1J(Pt,P$_A$) 3141, ^1J(Pt,P$_B$) 3014, ^1J(Pt,P$_X$) 467 Hz; δ −440.7 p.p.m. [isomer (b)]; ^1J(Pt,P$_A$) 3103, ^1J(Pt,P$_B$) 2986, ^1J(Pt,P$_X$) 455 Hz. For (2): ^{31}P, δ −134.8 (P$_A$), −136.6 (P$_B$), −58.7 (P$_X$), −168.7 p.p.m. (P$_C$); ^1J-(Pt,P$_A$) 3381, ^1J(Pt,P$_B$) 2986, ^1J(Pt,P$_X$) 144 Hz; ^2J(P$_A$,P$_B$) = ^2J(P$_B$,P$_X$) = ^2J(P$_A$,P$_X$) = 22 Hz. For (3): ^{31}P{^{1}H} (250 K), δ 85.6 p.p.m. [s with Pt satellites, ^1J(Pt,P) 4951 Hz]; ^{195}Pt{^{1}H} (263 K) δ 521.8, 457.5, 393.2, and 329.1 p.p.m. [1:3:3:1 q, ^1J(Pt,P) 4954 Hz]. For (4): ^{31}P, δ 62.1 (P$_A$), 61.1 (P$_B$), −101.9 (P$_X$); ^1J(Pt,P$_A$) 4048, ^1J(Pt,P$_B$) 3438, ^1J(Pt,P$_X$) 115 Hz; ^2J(P$_A$,P$_B$) = ^2J(P$_A$,P$_X$) = 12, ^2J(P$_B$,P$_X$) 11 Hz. (^{31}P Shifts are relative to trimethyl phosphite, ^{195}Pt shifts relative to the standard in ref. 12.)

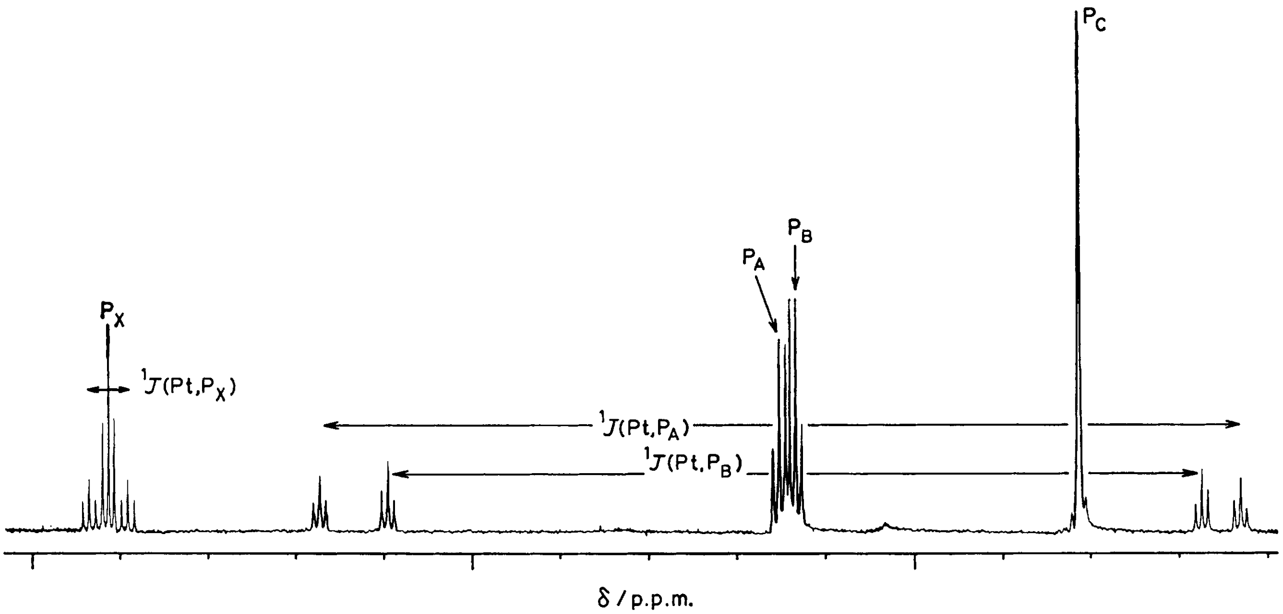


Figure 1. $^{31}P\{^1H\}$ N.m.r. spectrum for compound (**2**).

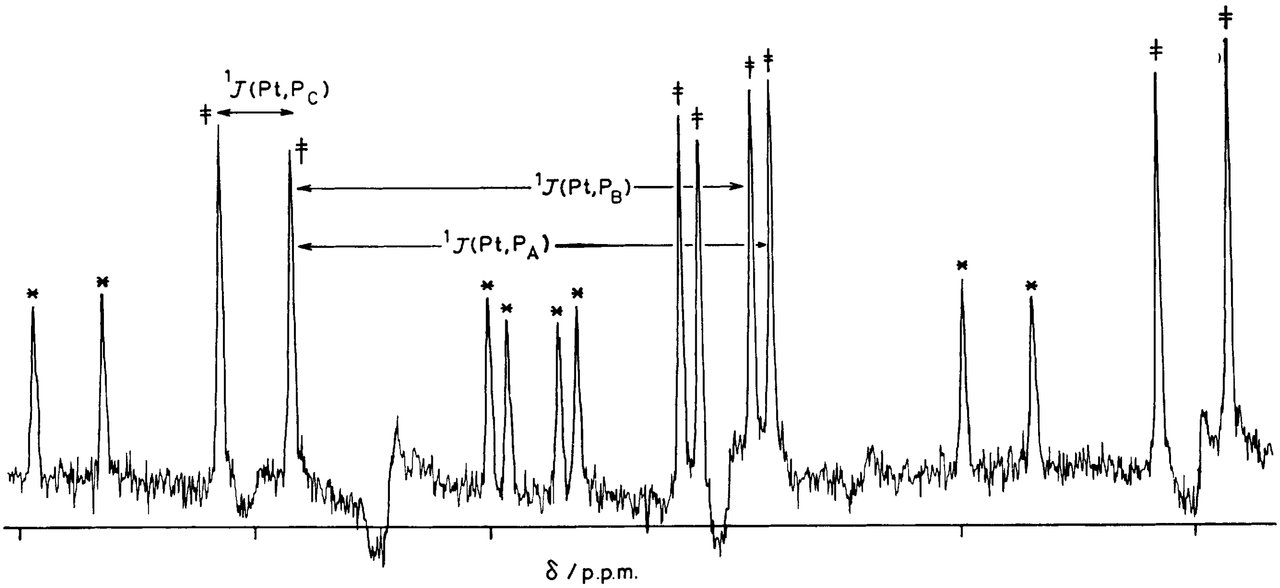
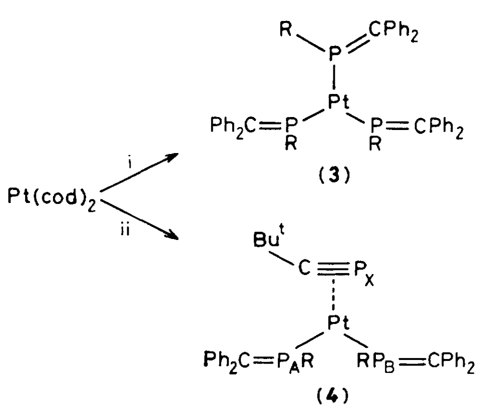


Figure 2. ^{195}Pt N.m.r. spectrum for compound (**1**); * and ‡ indicate isomers (b) and (a) respectively.



Scheme 2. i, P(mesityl)=CPh_2; ii, P(mesityl)=CPh_2: P≡CBu^t 2:1; R = mesityl.

phospha-alkenes (η^1-) and a phospha-alkyne (η^2-) (see Figure 3.)† Clearly a delicate balance of factors can result in either η^1- or η^2-co-ordination of the phospha-alkene.

Finally it is interesting to compare the variation in the magnitude of ^1J(Pt,P) for the η^2-co-ordinated P≡CBu^t in $Pt(PPh_3)_2(P{\equiv}CBu^t)$ (62 Hz),[10] with (**4**) (115 Hz) and (**2**) (144 Hz), since these changes must reflect mainly s-character and electron density differences of the platinum.[11]

The increased s-character of the formally sp^2-hybridised phosphorus in P(mesityl)=CPh_2 and the very small bite (P–Pt–P bond angles typically = *ca.* 94°)[12] of the triphos ligand which diverts more s-character to the platinum hybrid orbital are probably responsible for the larger ^1J(Pt,P) values found in (**2**) and (**4**).

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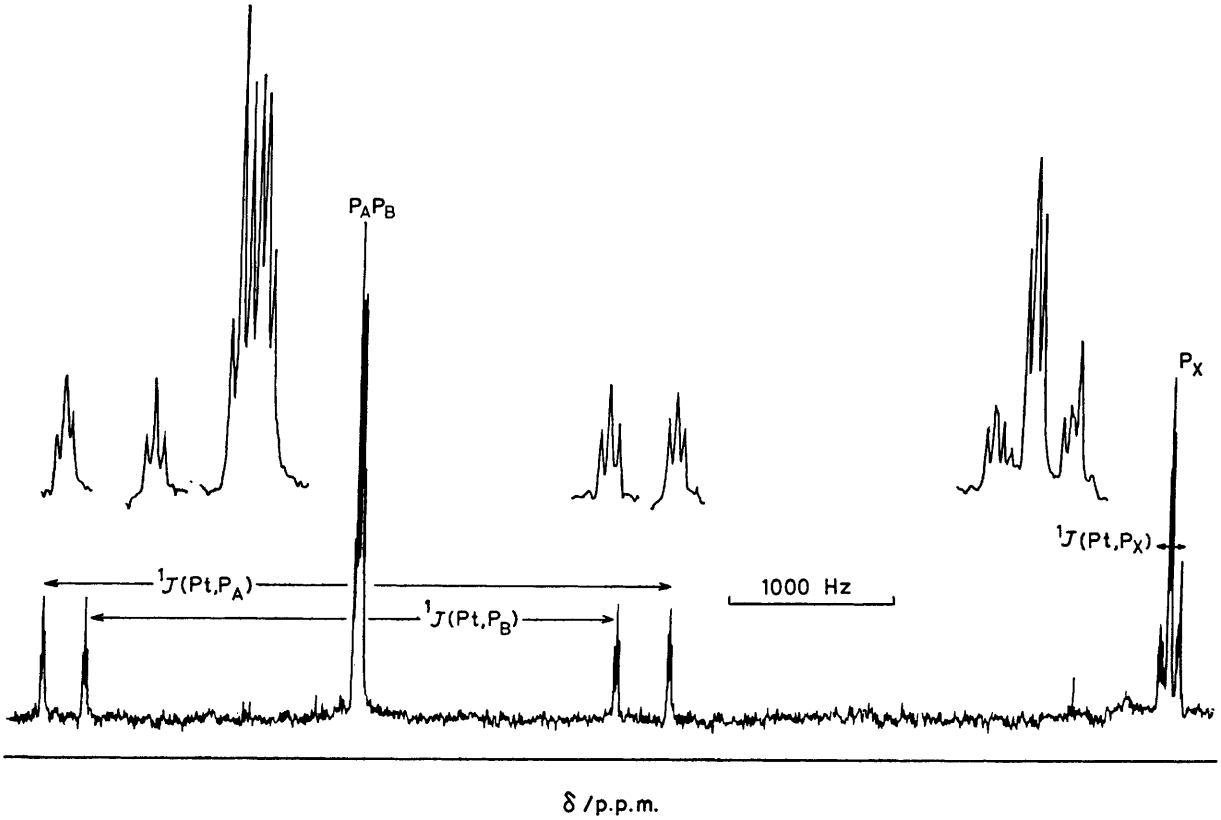

Figure 3. $^{31}P\{^1H\}$ N.m.r. spectrum for compound (**4**).

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