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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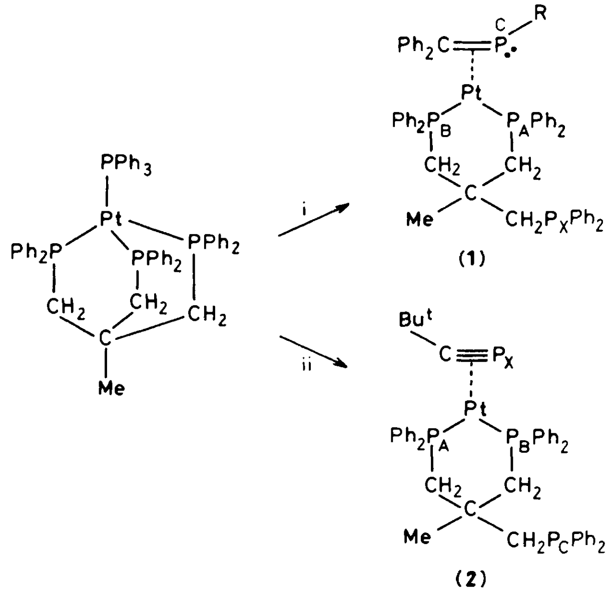
Differing modes of co-ordination are reported for complexes of platinum(0) containing the phospha-alkene P(mesityl)=CPh_2, *e.g.* in Pt(triphos){P(mesityl)=CPh_2}, [triphos = $(PPh_2CH_2)_3CMe$], the phospha-alkene is η^2-bonded to the metal whereas in Pt{P(mesityl)=CPh_2}$_3$ and Pt{P(mesityl)=CPh_2}$_2$(P≡CBu^t) 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 = $(PPh_2CH_2)_3CMe$] 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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**): $^{31}P\{^1H\}$ (250 K), δ 85.6 p.p.m. [s with Pt satellites, ^1J(Pt,P) 4951 Hz]; $^{195}Pt\{^1H\}$ (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.)

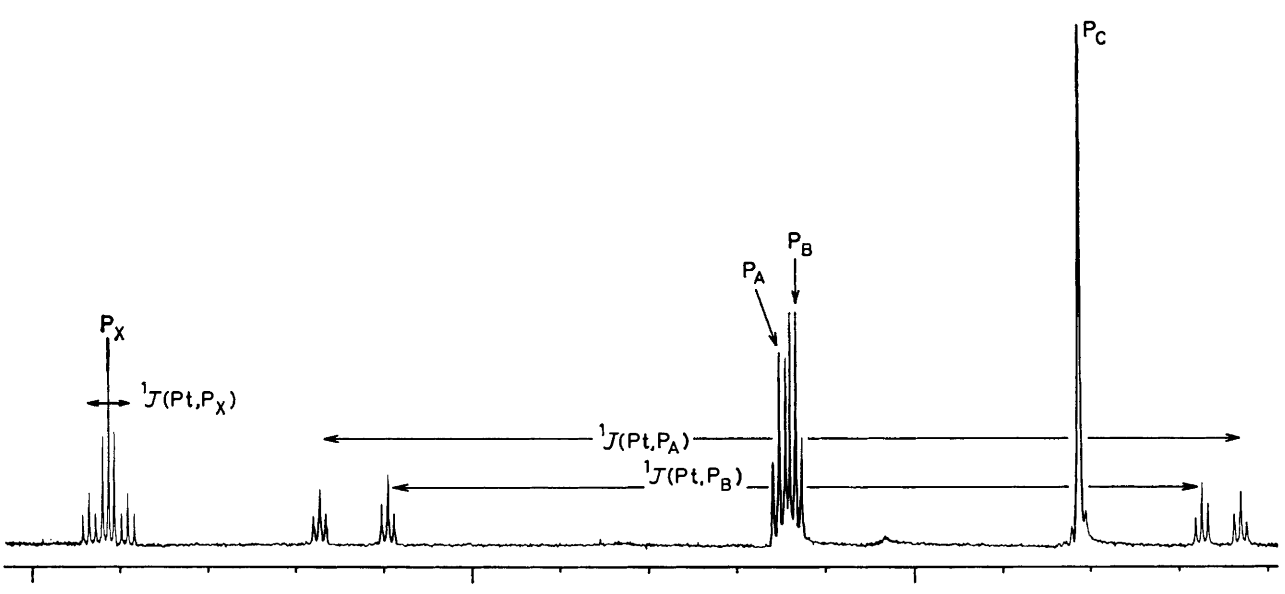


Figure 1. $^{31}P\{^1H\}$ N.m.r. spectrum for compound (**2**).

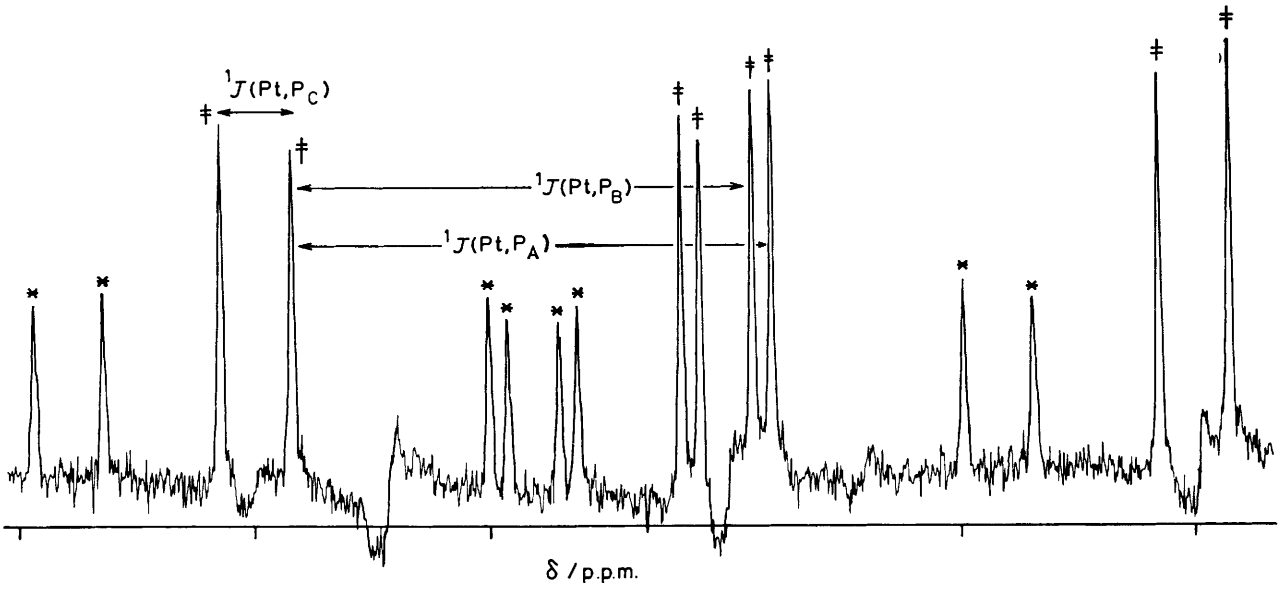
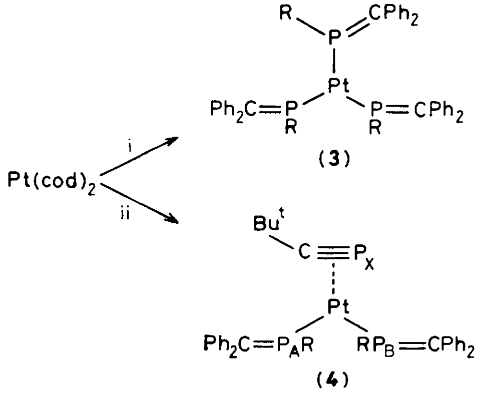


Figure 2. ^{195}Pt N.m.r. spectrum for compound (**1**); * and ‡ indicate isomers (b) and (a) respectively.



Scheme 2. i, P(mesityl)=CPh_2; ii, P(mesityl)=CPh_2: $P{\equiv}CBu^t$ 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 $P{\equiv}CBu^t$ 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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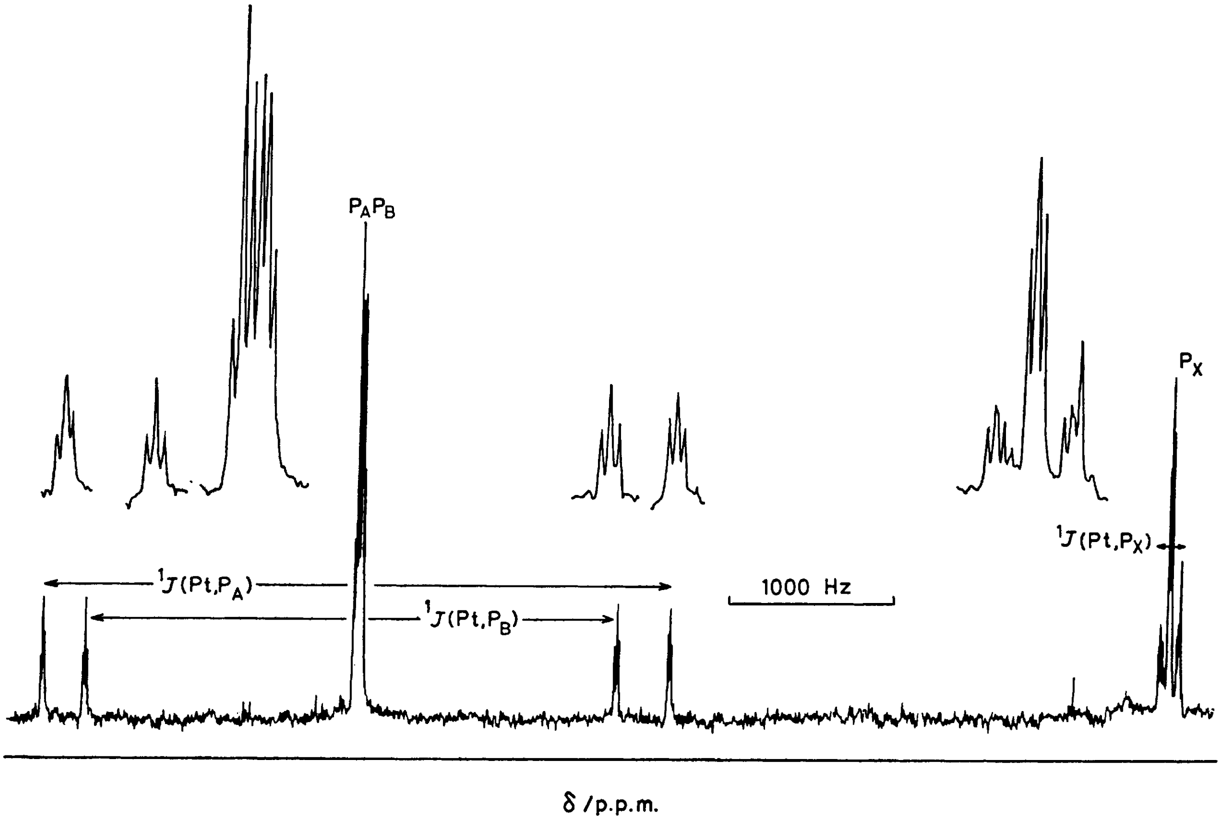

Figure 3. $^{31}P\{^1H\}$ N.m.r. spectrum for compound (**4**).

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