

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 $P(\text{mesityl})=CPh_2$, *e.g.* in $Pt(\text{triphos})\{P(\text{mesityl})=CPh_2\}$, [triphos = $(PPh_2CH_2)_3CMe$], the phospha-alkene is η^2 -bonded to the metal whereas in $Pt\{P(\text{mesityl})=CPh_2\}_3$ and $Pt\{P(\text{mesityl})=CPh_2\}_2(P\equiv CBu^t)$ 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 $RP=CR^2$, and phospha-alkynes, $RC\equiv P$, 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 $RC\equiv P$ molecules^{5,6} indicate that the HOMO is also of the π -type and the $\pi-\sigma$ separation is much greater than that found in the analogous $RC\equiv N$ 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 $P(\text{mesityl})=CPh_2$ in single crystal *X*-ray studies on *cis*- $PtCl_2\{P(\text{mesityl})=CPh_2\}_2$,⁷ $Cr(CO)_5\{P(\text{mesityl})=CPh_2\}_2$,⁸ and $Pt(PPh_3)_2\{P(\text{mesityl})=CPh_2\}$.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 com-

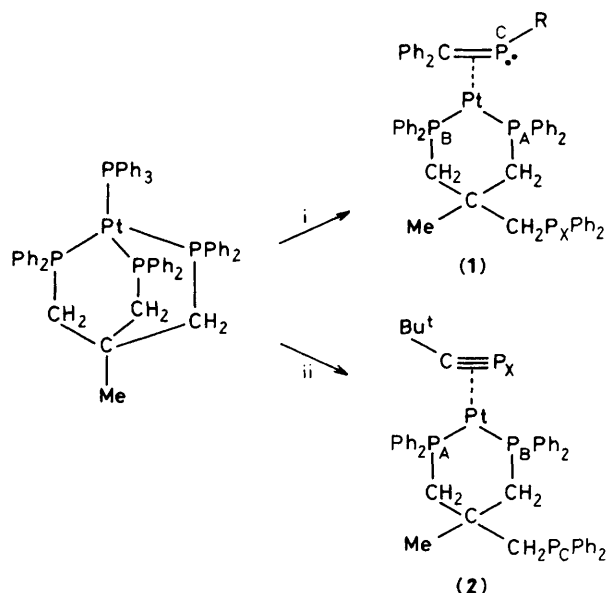
plex $Pt(\text{triphos})\{P(\text{mesityl})=CPh_2\}$ (1), [triphos = $(PPh_2CH_2)_3CMe$] formed unexpectedly in the displacement reaction of PPh_3 from $Pt(PPh_3)(\text{triphos})$ (see Scheme 1). The η^2 -phospha-alkyne complex $Pt(\text{triphos})(P\equiv CBu^t)$ (2) was formed in a similar way.

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.

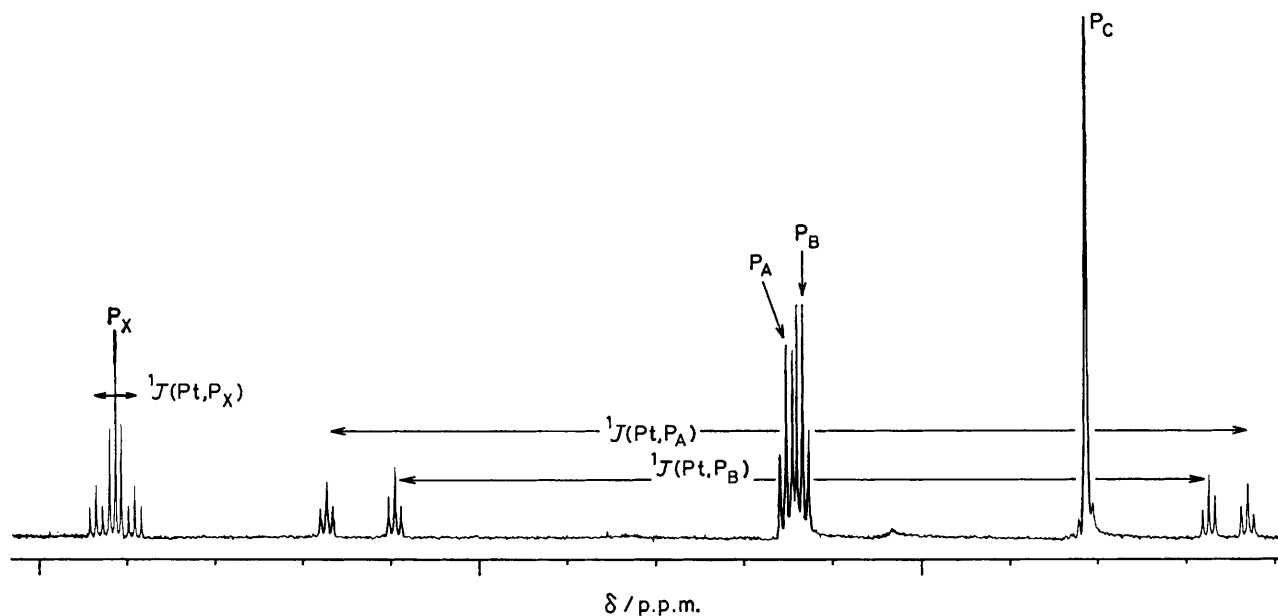
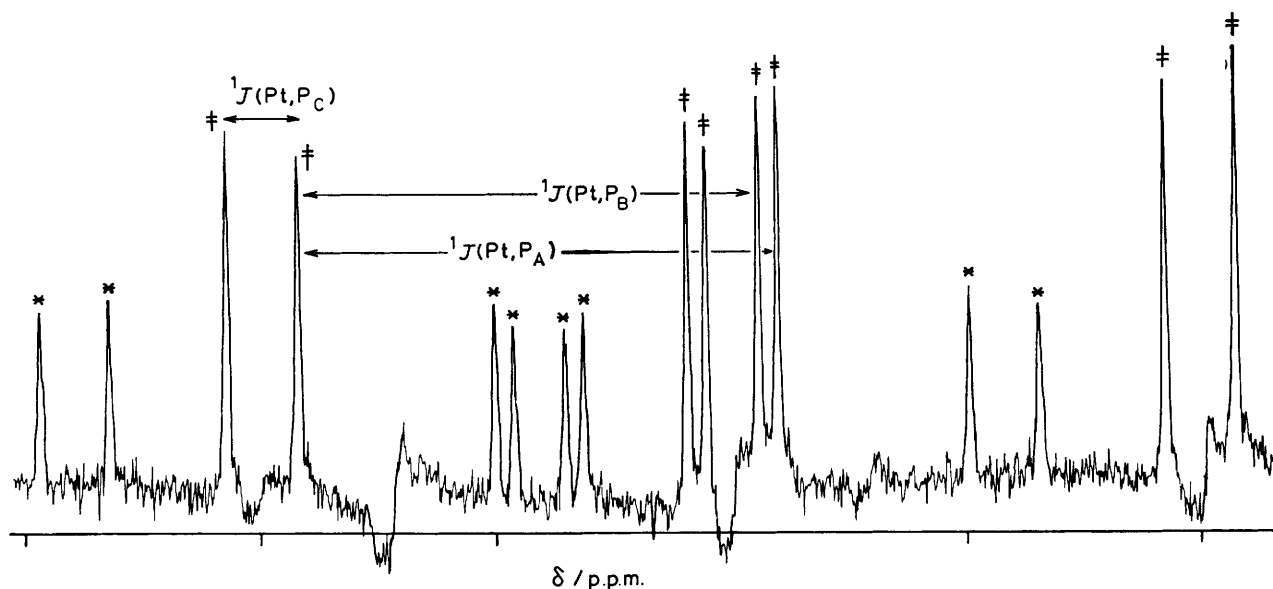
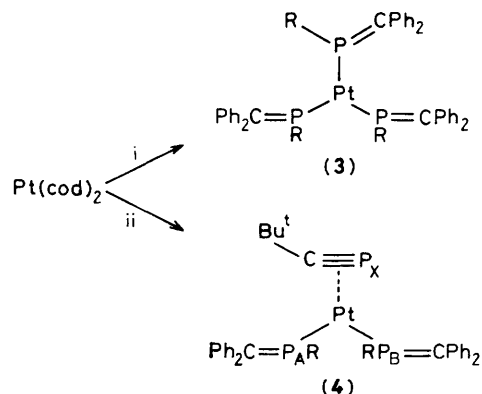
The η^2 -mode of co-ordination of both (1) and (2) is unambiguously established by the unusually small values of $^1J(Pt,P)$ for the co-ordinated phospha-alkene and phospha-alkyne (467, 455; and 144 Hz, respectively). The very low values reflect the large *s*-character of the phosphorus lone pair of 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 us¹⁰ in the η^2 - $Pt(PPh_3)(P\equiv CBu^t)$ complex.

In contrast to the above, treatment of $Pt(cod)_2$ (*cod* = 1,5-cyclo-octadiene), with $P(\text{mesityl})=CPh_2$ gave the η^1 -complex $Pt\{P(\text{mesityl})=CPh_2\}_3$ (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 $P(\text{mesityl})=CPh_2$ and $P\equiv CBu^t$ reacted with $Pt(cod)_2$ the product was $Pt\{P(\text{mesityl})=CPh_2\}_2(P\equiv CBu^t)$ (4) which is an interesting example of a complex containing only ligated



Scheme 1. i, $P(\text{mesityl})=CPh_2$; ii, $P\equiv CBu^t$; R = mesityl.

[†] 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_O); $^2J(P_A,P_B)$ 20, $^2J(P_B,P_O)$ 12, $^2J(P_A,P_O)$ 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_O); $^1J(Pt,P_A)$ 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. $^{31}\text{P}\{^1\text{H}\}$ 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, $\text{P}(\text{mesityl})=\text{CPh}_2$; ii, $\text{P}(\text{mesityl})=\text{CPh}_2$: $\text{P}=\text{CBu}^t$ 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 $^1J(\text{Pt}, \text{P})$ for the η^2 -co-ordinated $\text{P}=\text{CBu}^t$ in $\text{Pt}(\text{PPh}_3)_2(\text{P}=\text{CBu}^t)$ (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 $\text{P}(\text{mesityl})=\text{CPh}_2$ and the very small bite ($\text{P}-\text{Pt}-\text{P}$ 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 $^1J(\text{Pt}, \text{P})$ values found in (2) and (4).

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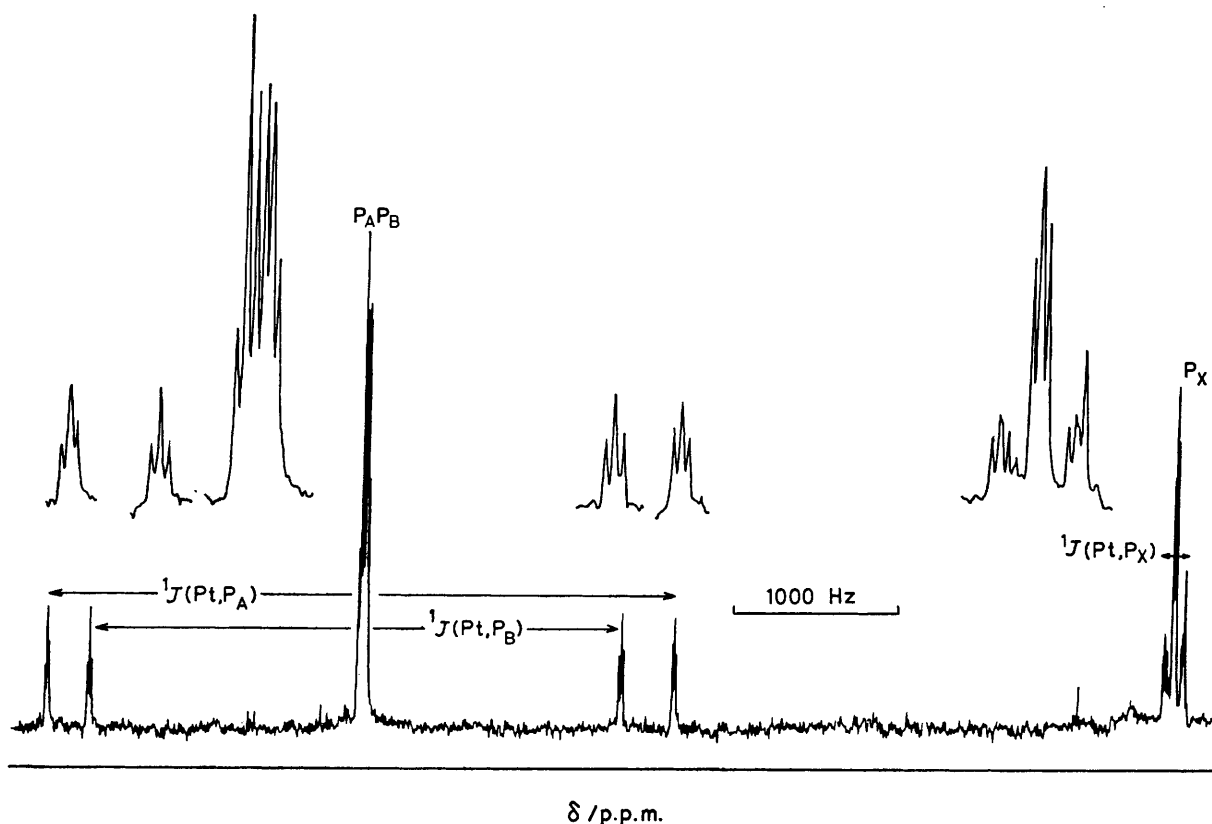


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectrum for compound (4).

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