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η^1- AND η^2-COORDINATION IN PHOSPHAALKENEPLATINUM(0) COMPLEXES. HIGH RESOLUTION SOLID STATE ^{31}P NMR SPECTRUM OF MESITYL(DIPHENYLMETHYLENE)PHOSPHINEBIS-(TRIPHENYLPHOSPHINE)PLATINUM(0)

HAROLD W. KROTO, STANLEI I. KLEIN *, MOHAMED F. MEIDINE, JOHN F. NIXON*,
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex (Great Britain)

ROBIN K. HARRIS*, KENNETH J. PACKER and PATRICK REAMS
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ (Great Britain)

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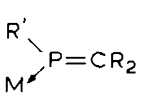
Summary

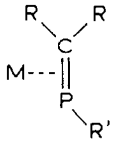
The high resolution solid state ^{31}P NMR spectrum of $Pt(PPh_3)_2(P(mesityl){=}CPh_2)$ shows the expected features for an η^1-coordinated phosphaalkene ligand and is completely different from that of the η^2-complex which exists in solution.

Introduction

There is considerable current interest in the coordination chemistry of phosphaalkenes $R_2C{=}PR'$ and phosphaalkynes $RC{\equiv}P$ [1,2]. In principle, in mononuclear complexes both types of ligand can act as either η^1-phosphorus donors (**a**) and (**c**) or η^2-P=C (or η^2-P≡C) π-donors (**b**) and (**d**) towards transition metals.



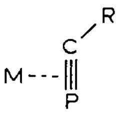
(a)



(b)

$M \leftarrow P{\equiv}CR$

(c)



(d)

Examples of types **a**, **b** and **d** are now well known [3–10] whereas the lone pair on phosphorus in RC≡P seems only to interact with a single transition metal after the P≡C π unit has been previously coordinated, e.g. to a dinuclear metallic centre as in the complexes $Co_2(CO)_6(^tBuCP)W(CO)_5$ [11], $Mo_2(C_5H_5)_2(CO)_4(^tBuCP)W(CO)_5$

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* Present address: Grupo de Ciencias des Materials, Universidade de Brasilia, CxP 153047, Brazilia, Brazil CEP 70.919.

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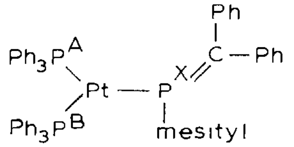
[11] and $Mo_2(C_5H_5)_2(CO)_4(^tBuCP)M_3(CO)_{11}$ (M = Ru, Os) [12].

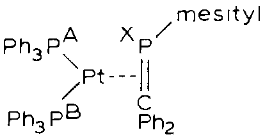
The η^2-coordination preference of the phosphaalkyne ligand reflects our previous observations that the HOMO of a number of RC≡P molecules (R = F, Me, Ph, ^{t}Bu) [13] is of the π-type as evidenced by He(I) photoelectron spectroscopic studies, with the phosphorus lone pair σ-orbital lying lower in energy. The π–σ separation is known to be much greater than that found in the analogous RC≡N systems. The ordering of the orbital energies in the phosphaalkene ligands is however less clear cut, since whereas MO calculations by Thomson [14] and Schoeller and Niecke [15] on CH_2=PH suggested that the HOMO is of the π-type with the phosphorus lone pair orbital only slightly (0.8 eV) more stable, a more recent calculation [16], which is sensitive to the HCP bond angle, inverted the ordering. It confirmed that in view of their closeness in energy both could be important as frontier orbitals in interactions with reaction partners *. We have recently obtained [17] the He(I) photoelectron spectra of several simple phosphaalkenes CH_2=PX (X = H, F, Cl) and confirm that for X = H the σ and π orbitals are almost degenerate.

The delicate balance of factors in determining η^1- or η^2-phosphaalkene bonding is well evidenced by our recent report of several Pt^0 complexes in which the bonding mode differed e.g. η^1- in PtL_3; $PtL_2(^tBuCP)$ but η^2- in PtL(triphos) (L = P(mesityl)=CPh_2)) [6]. We also find that $\eta^1 \rightarrow \eta^2$ bonding can be observed in the formation of η^2-Pt(Bu^{t}NC)$_2$ (mesityl P=CPh_2), (^1J(PtP) 608 Hz), from η^1-Pt(mesityl)P=CPh_2)$_3$, (^1J(PtP) 4946 Hz), by treatment with Bu^{t}NC. The former complex can also be obtained from $Pt_3(^tBuNC)_6$ and P(mesityl)=CPh_2 [18].

Of special interest in this $\eta^1 \rightarrow \eta^2$ interconversion is the report by Bickelhaupt et al. [7] of the complex $Pt(PPh_3)_2$(P(mesityl)=CPh_2) (I) in which the phosphaalkene was shown to be η^1-bonded, (structure Ia), by a single crystal X-ray diffraction study, whereas the ^{31}P NMR spectrum at −55°C in solution showed an ABX pattern and an unusually low value for ^1J(PtP) (505 Hz) for the coordinated phosphaalkene, normally diagnostic [2,6] of η^2-coordination (structure Ib). Since the solution NMR data and the solid state X-ray structural information were at variance we undertook a study of the high resolution solid state ^{31}P NMR spectrum of I.



(Ia)



(Ib)

Experimental

The red complex I was obtained as previously described [7] by displacement of ethylene from $Pt(PPh_3)_2(C_2H_4)$ by treatment with P(mesityl)=CPh_2. Its toluene solution ^{31}P NMR spectrum recorded at 32.4 MHz using a Bruker WP 80 Fourier transform spectrometer at −50°C was in good agreement with that previously reported and the chemical shift and coupling constant data are listed in Table 1. Chemical shifts were measured relative to TMP and corrected to the 85% H_3PO_4 scale using known shift differences.

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* We thank Prof. F. Bickelhaupt for a copy of this manuscript prior to publication

TABLE 1

^{31}P NMR DATA FOR Ib IN TOLUENE SOLUTION AT −50°C [a]

	δ [b]	^1J(PtP) [c]	^2J(PPtP) [c]
P_A	24.2 (22.2)	3398 (3392)	9 8 (11.1)
P_B	22.8 (21.9)	3368 (3359)	29.3 (29.6)
P_X	−30.9 (−33.5)	498 (505)	53.7 (56.4)

[a] Values in parentheses from Ref 7. [b] In ppm rel. H_3PO_4 (measured rel. TMP and corrected using chemical shift difference of TMP and H_3PO_4 = 141 ppm). [c] In Hz.

The high resolution solid state ^{31}P NMR spectra were recorded at ambient temperature using the CXP 200 NMR spectrometer at UEA operating at 81.013 MHz using cross polarisation and magic angle spinning techniques. The powdered sample was contained in a Delrin rotor which was rotated at ca. 3 kHz. ^{31}P Chemical shifts were initially referenced to $[Ph_2Me_2P]I$ and calculated relative to 85% H_3PO_4 using known chemical shift data. The solid state ^{13}C NMR spectrum of I was also recorded as well as the non-quaternary suppression ^{13}C NMR spectrum. The data are listed below:

^{13}C (ppm rel.TMS) spectrum. 21.7, 23.7, 123.7, 127.4, 129.4, 130.6, 133.4, 135.9, 138.2, 139.6, 140.9, 142.5, 143.9, 153.1, 154.0. ^{13}C (non quaternary suppression) 21.7, 23.4, 130.3, 131.6, 135.7, 137.4, 140.8, 142.4, 144.0, 153.0 ppm. The resonances ca. 21.7 and 23.5 ppm can be readily assigned to the two types of methyl group of the mesityl group and resonances lying between 123–154 ppm to aromatic carbons but it was not possible to unambiguously assign the P=C carbon resonance. In the free phosphaalkene the ^{13}C NMR data are as follows (in $CDCl_3$ solution) 21.0, 72.1 (^3J(PC) 9 Hz) 125.5–144.9 (aryl C) 193.4 (P=C) (^1J(PC) 43.5 Hz).

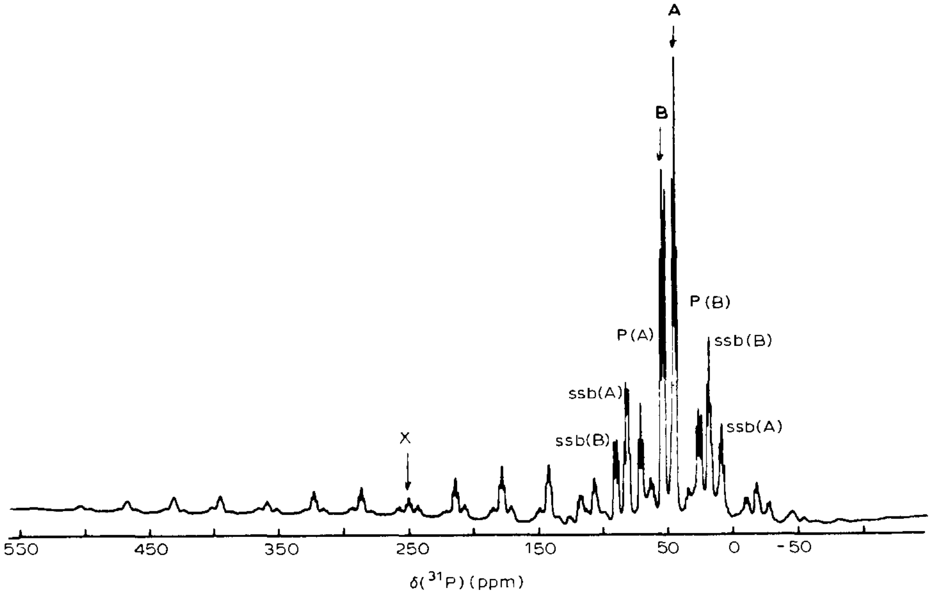

Fig. 1 81.013 MHz ^{31}P NMR spectrum using cross polarisation and magic angle rotation of $Pt(PPh_3)_2(P(mesityl)=CPh_2)$ in the solid state. (Spinning speed 2940 Hz; No of scans = 4000; Recycle time 10 s; Contact time 1 ms).

Results and discussion

The solid state ^{31}P NMR spectrum of $Pt(PPh_3)_2(P(mesityl)=CPh_2)$ (I) is completely in agreement with that expected on the basis of the single crystal X-ray diffraction study and confirms the η^1-structure.

The two centre bands (Fig. 1) labelled **A** and **B** are due to the two phosphorus atoms P_A and P_B of the PPh_3 ligands. The band marked **B** is split into four lines

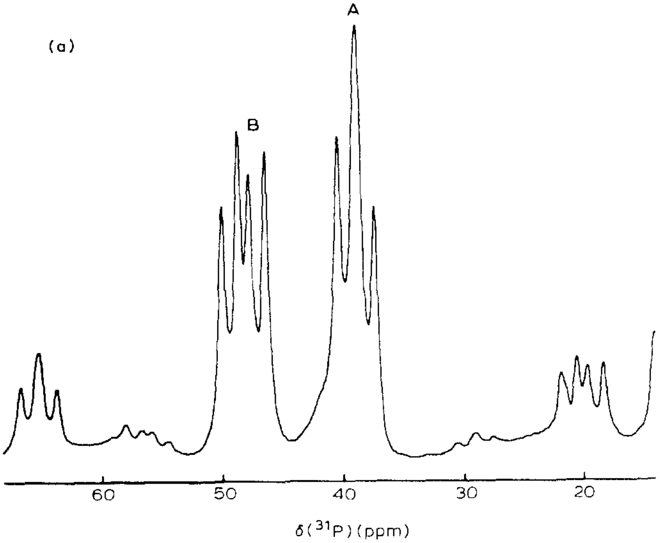

Fig. 1a. Expansion of Fig 1 in P_A and P_B region.

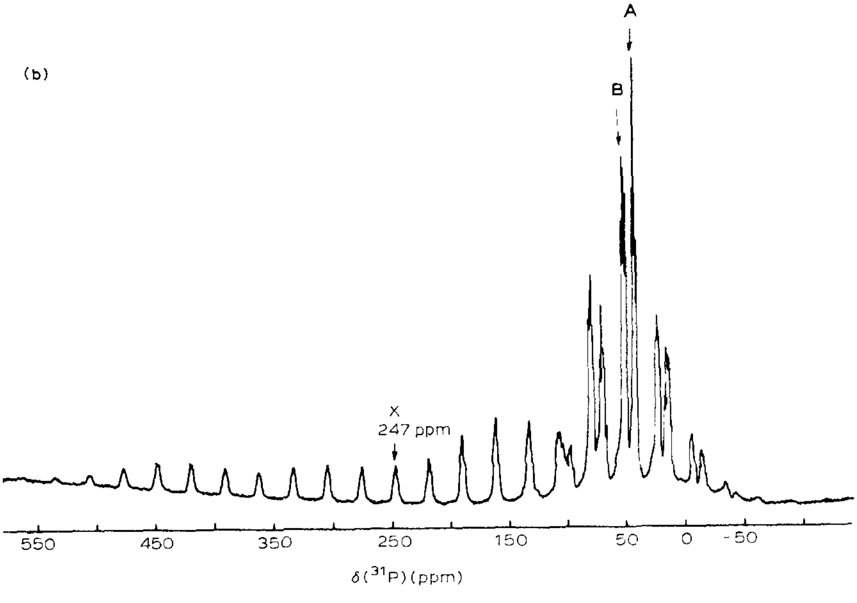

Fig. 1b. Same conditions as Fig. 1 except spinning speed = 2345 Hz

whereas **A** is apparently split into three lines, (Fig. 1a), however with resolution enhancement (Fig. 2) it can be seen clearly to consist of 4 lines. This part of the spectrum is the *AB* part of an *ABX* spin system and exhibits further satellite splitting due to spin-coupling with the ^{195}Pt nucleus and the $^1J(PtP_A)$ and $^1J(PtP_B)$ (4250 and 4550 Hz) values are larger than those normally found in complexes of zerovalent platinum. The non-equivalence of the PPh_3 ligands is a result of the unsymmetrical conformation of the complex in the crystal, the angle between the σ-plane of the phosphaalkene and the plane of PtP_AP_B being 67°.

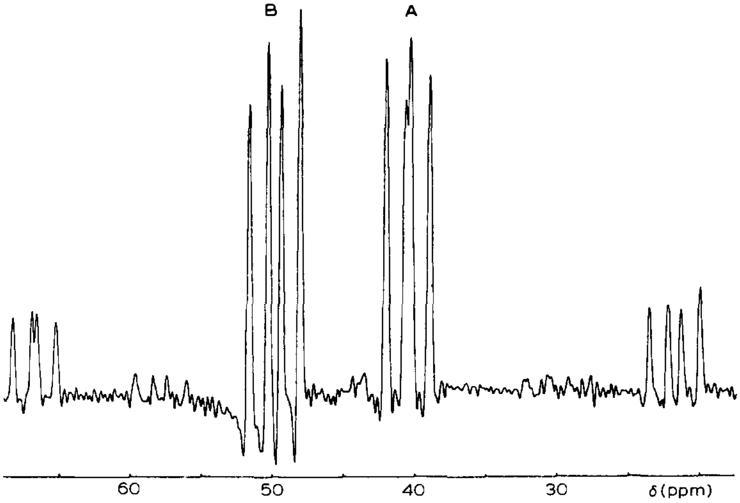

Fig. 2 Expanded and resolution enhanced spectrum of P_A and P_B from Fig. 1. (No. of scans = 5000).

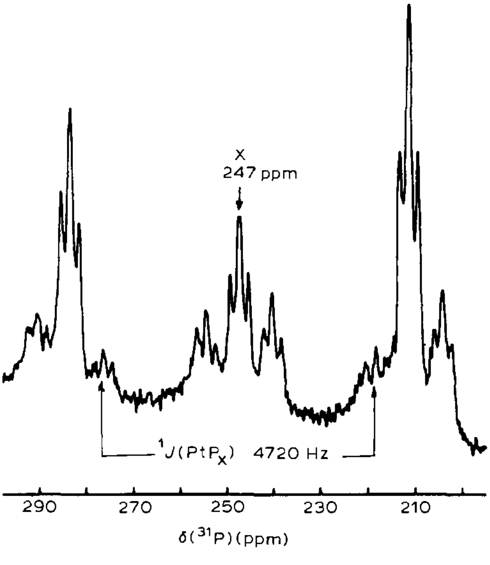

Fig. 3. Expansion of the P_X part of spectrum in Fig. 1 showing ^{195}Pt satellites.

TABLE 2

^{31}P NMR DATA FOR Ib IN THE SOLID STATE

	δ ^{a}	^1J(PtP) ^{b}	^2J(PPtP) ^{b}
P_A	40.5	4250	109 (P_AP_B)
P_B	49.8	4550	183 (P_BP_X)
P_X	247	4720	135 (P_XP_A)

^{a} In ppm rel H_3PO_4 (see text) ^{b} In Hz

The resonance of the P_X phosphorus of the coordinated phosphaalkene was more difficult to locate because of its lower intensity (Fig. 1) arising from a much larger chemical shift anisotropy as shown by the number of spinning side bands (ssb) marked on the spectrum. The signal due to P_X is assigned at 247 ppm which is close to that of the free ligand and very different from that of the side-bonded η^2-ligand observed in solution.

Confirmation of the position of the P_X centre band which is determined by the isotropic chemical shift was established by varying the spinning speed of the sample (Fig. 1b). The observation of platinum satellites of P_X (Fig. 3) leads to a large value of $^1J(PtP_X)$ (4720 Hz) for the η^1-coordinated phosphaalkene ligand consistent with the phosphorus lone pair interacting directly with the metal. Interestingly $^1J(PtP_X)$ for the phosphaalkene is bigger than $^1J(PtP_A)$ or $^1J(PtP_B)$ for the PPh_3 ligands which no doubt reflects the greater *s*-character of the former in which the phosphorus is formally sp^2 hybridised. The solid state ^{31}P chemical shift and spin–spin coupling data are listed in Table 2.

Our solid state NMR spectroscopic results establish the dual η^1- and η^2-coordination behaviour of P(mesityl)=CPh_2 in Pt$(PPh_3)_2$(P(mesityl)=CPh_2) and are in good agreement with a study by Bickelhaupt et al. [16] carried out independently. These authors have also investigated solution dynamic behaviour and undertaken a theoretical analysis of the electronic and steric factors governing the coordination behaviour of phosphaalkenes.

Acknowledgements

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