

## PRELIMINARY COMMUNICATION

## BIS(TRIPHENYLPHOSPHINE)ALLENEPLATINUM(0) COMPLEXES

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The nature of phosphorus-metal bonds in low-valent post-transition metal phosphine or phosphite complexes is now well understood in terms of  $\sigma$ -donation from the ligand reinforced with a synergic  $\pi$ -back donation from the metal. In only a few cases, however, information such as the bond length or force constant is available to support the  $\pi$ -bond character. We found that phosphine(allene)platinum(0) complexes, Pt(allene)-(PR<sub>3</sub>)<sub>2</sub>, are a particularly relevant system for the NMR spectroscopic studies to obtain further insight into the nature of the Pt-P bond as well as of the Pt-allene bonding.

Bis(triphenylphosphine) (allene)platinum(0), [Pt(C<sub>3</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (I), was obtained as colorless, thermally stable needles, m.p. 152–154° (dec.), when *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] was reduced with hydrazine hydrate in the presence of allene at 70–80°, in an autoclave using 95% ethanol as a solvent. Similarly, bis(triphenylphosphine)(1,3-diphenylallene)platinum(0), [Pt(PhCH=C=CHPh)(PPh<sub>3</sub>)<sub>2</sub>] (II), was obtained as bright yellow cubic crystals m.p. 170–182° (dec.). Molecular weight measurements and elemental analyses for these two complexes agree well with calculated values.

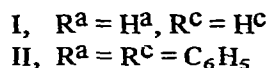
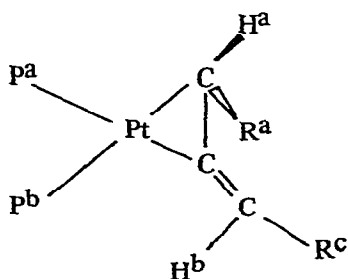
TABLE 1  
100 Mc NMR SPECTRA<sup>a</sup> OF Pt(allene)(PPh<sub>3</sub>)<sub>2</sub> IN CDCl<sub>3</sub> AT 22.5°

Compound	Chem. shift $\tau$ (multiplicity)	Coupling constant (cps)
CH <sub>2</sub> =C=CH <sub>2</sub> (free)	5.30 (singlet)	
I	H <sup>a</sup> 7.98 (triplet) <sup>b</sup>	$J(\text{Pt}-\text{H}^a) = 65$
	H <sup>b</sup> 5.46 (doublet) <sup>c</sup>	$J(\text{P}^a-\text{H}^b) = 12.5$
	H <sup>c</sup> 4.00 (doublet) <sup>c</sup>	$J(\text{P}^a-\text{H}^c) = 22.5$
PhCH=C=CHPh (free)	3.44 (singlet)	
II	H <sup>a</sup> 6.25 (triplet) <sup>b,d</sup>	$J(\text{Pt}-\text{H}^a) = 65$ $J(\text{P}^a-\text{H}^a) = 5.5$ $J(\text{P}^b-\text{H}^a) = 9.5$ $J(\text{H}^a-\text{H}^b) = 3.0$
	H <sup>b</sup> 4.18 (doublet) <sup>c</sup>	$J(\text{P}^a-\text{H}^b) = 12.5$

<sup>a</sup> Measured with a Jeol JNM 4H-100 instrument using TMS as the internal standard. Resonances for phenyl protons are omitted. <sup>b</sup> It consists of a main broad peak and two satellite peaks due to coupling with <sup>195</sup>Pt(33.8% abundance). <sup>c</sup> Each peak in the doublet is fairly broad. Couplings with <sup>195</sup>Pt are not observable owing to the small S/N ratio. <sup>d</sup> Each peak splits into a septet.

The IR spectrum of I (nujol mull) shows a weak band at  $1680\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{C}=\text{C})$  of coordinated allene, and a strong one at  $855\text{ cm}^{-1}$  assignable to  $\delta(=\text{CH}_2)$ . These bands are absent in II (The similar IR spectral characteristic is found in the related  $\text{Rh}^{\text{I}}(-)\text{allene complexes}^1$ ).

The NMR spectra for I and II summarized in Table I are best explained by a square planar structure depicted below. It should be noted that the uncoordinated olefinic carbon atom with  $\text{H}^{\text{b}}$  and  $\text{R}^{\text{c}}$  also lies in the same plane.



The highest field resonance for I occurs at  $\tau$  7.98 showing a large  $^{195}\text{Pt}-^1\text{H}$  coupling constant (62.5 cps) comparable to values for the  $\text{Pt}-\text{CH}_3$  coupling constant as found in methylplatinum complexes<sup>2,4</sup>. The large up-field shift from free allene ( $\Delta\tau = 2.7$ ) as well as the large spin-spin coupling with  $^{195}\text{Pt}$  are consistent with the idea of enhanced  $\sigma$ -bonding between Pt and the two carbons of allene. The signals at  $\tau$  5.46 and  $\tau$  4.00 assigned to  $\text{H}^{\text{b}}$  and  $\text{H}^{\text{c}}$ , respectively, are both split into doublets by coupling with  $^{31}\text{P}$  ( $S = 1/2$ ). The doublet splitting affords support for the square planar structure but not for a tetrahedral structure. The latter structure involving two equivalent phosphorus nuclei requires triplet splitting for the  $\text{H}^{\text{b}}$  and  $\text{H}^{\text{c}}$  resonances.

The surprisingly large coupling constant (22.5 cps) for the long-range interaction between  $\text{P}^{\text{a}}$  and  $\text{H}^{\text{c}}$  in I renders the  $\sigma$ -interaction mechanism unlikely for such an extended system. It appears that a  $\sigma$ - $\pi$ -interaction facilitated through a conjugated  $\pi$ -bond system,  $\text{P}^{\text{a}}=\text{Pt}-\text{C}=\text{C}-\text{H}$ , will rationalize the large long-range coupling. This may be the first reported example for a  $\pi(3d-5d)-\pi(2p-2p)$  conjugation that is effective for a nuclear spin interaction. The long-range coupling constant is smaller in  $J(\text{P}^{\text{a}}-\text{H}^{\text{b}})$  than in  $J(\text{P}^{\text{a}}-\text{H}^{\text{c}})$ . It is to be noted that the *trans*  $\text{P}^{\text{a}}$  couples with the two protons more effectively than does the *cis*  $\text{P}^{\text{b}}$ . This is in accord with the previous observations in many octahedral or square planar complexes<sup>5</sup>, specifically in a structurally related complex,  $\text{Pt}(\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_3)(\text{PPh}_3)_2$ <sup>4</sup>.

In the 1,3-diphenylallene complex II, the phenyl group at the uncoordinated carbon will occupy the  $\text{R}^{\text{c}}$  site for steric reason (The two sites at  $\text{C}^1$  are equivalent). The proposed structure is consistent with the observed chemical shift ( $\tau$  4.18) of the lower field absorption that is assigned to  $\text{H}^{\text{b}}$ ; if the phenyl group occupies the  $\text{H}^{\text{b}}$  site a resonance for the proton at the  $\text{R}^{\text{c}}$  site would appear at a lower field than that for the free ligand ( $\tau$  3.44) as in I. The structure receives further support from coupling schemes of the  $\text{H}^{\text{b}}$  proton shown in Table 1.

The substitution of two protons in I with phenyl groups simplifies the spectrum and the septets at  $\tau$  6.25 arise from overlap of the splittings due to coupling of  $\text{H}^{\text{a}}$  with  $\text{H}^{\text{b}}$ ,  $\text{P}^{\text{a}}$ , and  $\text{P}^{\text{b}}$ . Here again, the long-range coupling between  $\text{H}^{\text{b}}$  and  $\text{P}^{\text{a}}$  (12.5 cps) is greater than the coupling of  $\text{H}^{\text{a}}$  with the two phosphorus atoms. If the proposed structure is correct, as

it seems to be, the Pt atom may be regarded formally as a  $5d^8$  ion assuming a rigid planar tetra-coordinated configuration. This view explains the thermal stability observed for I and II.

Studies on the effect of nature of phosphorus-containing ligands upon these spin-spin interactions in this type of complexes are now in progress.

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