

^{13}C Nuclear Magnetic Resonance Spectra of Some π -Allylic-palladium(II) Complexes

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Summary The ^{13}C n.m.r. spectra of a number of π -allylic-palladium complexes are reported and the chemical shifts discussed in terms of the nature of the allyl-palladium bonding.

ALTHOUGH ^{13}C n.m.r. spectroscopy has been widely applied to organic chemistry, and it is often possible to predict ^{13}C chemical shifts within a few p.p.m.,¹ its applications to organometallic chemistry have so far been very limited.²

† No reprints available.

We have now examined a number of π -allylic-palladium complexes by ^{13}C n.m.r. spectroscopy, and the results are given in the Table. The ^{13}C chemical shifts can be conveniently interpreted using a VB treatment for the allylic-palladium bonding. It would be expected that the canonical forms (Ia) and (Ib) would predominate. This is supported by an MO treatment of diallylpalladium³ in which it is found that the Pd-C-1 bond overlap population is $2\frac{1}{2}$ times the palladium-C-2 bond overlap population, and the charge on the allyl group is only -0.151 , implying that canonical forms (Ia) and (Ib) are more important than (Ic) or (Id).

One might expect therefore, that the ^{13}C chemical shift for C-1 (or C-3) of a π -allylic group would be approximately halfway between the values for $=\text{CH}_2$ and $-\text{CH}_2\text{-Pd}$ groups.

The ^{13}C chemical shift of the $=\text{CH}_2$ group can be estimated as *ca.* 110 p.p.m.† from the ^{13}C chemical shifts in $\text{C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ (114.3 p.p.m.)¹ or $[\text{IrCl}_2(\text{CH}_2\text{CMe}=\text{CH}_2)\text{-}(\text{CO})(\text{AsMe}_2\text{Ph})_2]$ (107.9 p.p.m.)⁴. The ^{13}C chemical shift of a $-\text{CH}_2\text{-Pd}$ carbon has not been reported but we estimate it to be about +10 p.p.m. as found for the $-\text{CH}_2\text{-Ir}$ of $[\text{IrCl}_2(\text{CH}_2\text{CMe}=\text{CH}_2)(\text{CO})(\text{AsMe}_2\text{Ph})_2]$ (+10.6 p.p.m.)⁴ and as estimated for $-\text{CH}_2\text{-Pt}$ [for a series of methylplatinum(II) complexes the shifts for $^{13}\text{Me-Pt}$ are +8.1 to -13.4 p.p.m.,^{2,5} *i.e.* averaging *ca.* 0 p.p.m., and the ^{13}C shifts for CH_2 groups are generally *ca.* +10 p.p.m. to higher frequency than for Me groups in similar environments].⁶

Thus, as expected on the VB picture, the values of the ^{13}C chemical shifts for the C-1 and C-3 atoms of the symmetrically bonded allylic ligands (45.8–65.2 p.p.m.) (see Table) lie approximately halfway between the values for $=\text{CH}_2$ and $-\text{CH}_2\text{-Pd}$ carbon atoms. The ^{13}C shifts of C-2 (95.0–129.2 p.p.m.) are closer to those of $=\text{CH}_2$ or $=\text{CHMe-}$ groups¹ but moved to lower frequency by *ca.* 20 p.p.m., presumably by contributions from the canonical forms (Ic) and/or (Id). [The shift of $=\text{CHMe-}$ in $[\text{IrCl}_2(\text{CH}_2\text{CMe}=\text{CH}_2)(\text{CO})(\text{AsMe}_2\text{Ph})_2]$ is at +145.2 p.p.m.]

The ^{13}C n.m.r. data for $[\text{PdCl}(2\text{-methylallyl})(\text{PPh}_3)]$ are also given in the Table. The asymmetry in bonding of the 2-methylallyl group to palladium was first shown by ^1H n.m.r. spectroscopy^{7,8} and represented by the structure (II) in which the dashed line indicates that two carbon atoms are joined by a bond of higher order than the other two (joined by a dotted line). The X-ray structure of $[\text{PdCl}(2\text{-methylallyl})(\text{PPh}_3)]$ ⁹ and of $[\text{PdCl}(\text{allyl})(\text{PPh}_3)]$ ¹⁰ show that the asymmetry in the allylic-palladium bonding is in the sense summarised by structure (II). In the ^{13}C n.m.r. spectrum (Table) two CH_2 groups were detected: a singlet at 62.6 p.p.m. due presumably to the CH_2 *trans* to chlorine and a doublet $^2J(\text{P-C})$ 31 Hz shifted *ca.* 17 p.p.m. to higher frequency and presumably due to the CH_2 *trans* to the triphenylphosphine. This shift to higher frequency is consistent with an increased olefin character as suggested by the ^1H n.m.r. spectrum and X-ray results.

† The chemical shifts are quoted with respect to $(\text{CH}_3)_3\text{Si}^{13}\text{CH}_3$ and increasing frequency is taken as positive.

¹ E. F. Mooney and P. H. Winson, *Ann. Rev. N.M.R. Spectroscopy*, 1959, **2**, 153, and references therein.

² A. J. Cheney, B. E. Mann, and B. L. Shaw, *Chem. Comm.*, 1971, 431 and references therein.

³ I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, 1969, **47**, 27.

⁴ B. E. Mann, B. L. Shaw, and R. E. Stainbank, unpublished results.

⁵ A. J. Cheney, B. E. Mann, and B. L. Shaw, unpublished results.

⁶ D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.

⁷ J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Comm.*, 1965, 78.

⁸ J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1967, 1839.

⁹ R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.

¹⁰ A. E. Smith, *Acta Cryst.*, 1969, **25A** [3S], 161.

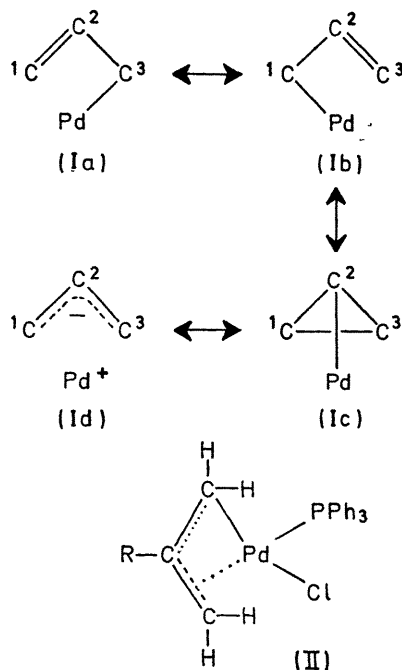
As can be seen from the Table in both the allyl and 2-methylallyl series the ^{13}C shifts for C-1 and C-3 decrease

^{13}C N.m.r. chemical shifts^a for some π -allylic-palladium complexes.

	C-1, C-3	C-2	Me
$[\text{PdCl}(\text{allyl})]_2$	63.2	111.9	—
$[\text{PdBr}(\text{allyl})]_2$	65.2	111.3	—
$[\text{Pd}(\text{C}_6\text{H}_5)(\text{allyl})]$	45.8	95.0	—
$[\text{Pd}(\text{acac})(\text{C}_6\text{H}_5)]$	55.8	113.5	—
$[\text{PdCl}(2\text{-methylallyl})]_2$	61.7	127.9	23.1
$[\text{PdBr}(2\text{-methylallyl})]_2$	64.4	127.2	23.3
$[\text{Pd}(\text{C}_6\text{H}_5)(2\text{-methylallyl})]$	47.0	112.2	23.6
$[\text{Pd}(\text{acac})(2\text{-methylallyl})]$	54.8	129.2	23.4
$[\text{PdCl}(2\text{-methylallyl})(\text{PPh}_3)]^b$	62.6;	— ^c	24.1
	78.1		

^a The chemical shifts were measured in CH_2Cl_2 solution at *ca.* 40 °C and are accurate to ± 0.1 p.p.m. The spectra were measured at 22.62 MHz with random noise decoupling of the protons. C_6F_6 was used as an internal ^{19}F field/frequency lock.

in the order of *trans*-ligands $\mu\text{-Br} > \mu\text{-Cl} > \text{acetylacetonate} (\text{acac}) > \pi\text{-C}_5\text{H}_5$ and for C-2 in the order $\text{acac} \sim \mu\text{-Cl} \sim \mu\text{-Br} > \pi\text{-C}_5\text{H}_5$.



This preliminary investigation suggests that ^{13}C n.m.r. spectroscopy will be useful in studying allylic-metal complexes.

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