Deceptive ^{13}C Nuclear Magnetic Resonance Spectra in Bis-phosphine Metal Derivatives

By David E. Axelson and Clive E. Holloway*

[*Chemistry Department, York University, Downsview* (*Toronto*) M3J 1P3, *Canada*]

Summary The proposal that ^{13}C n.m.r. should be more widely applicable than ^{1}H n.m.r. for determining the stereochemistry of bis-phosphine metal complexes is shown to be invalid.

The use of ^{1}H n.m.r. spectroscopy for the determination of stereochemistry in bis-phosphine metal complexes has been well documented.[1] There are some exceptions to the general rule that only *trans* complexes exhibit characteristic triplet resonances due to virtual coupling between the phosphorus atoms.[2] It has recently been suggested that ^{13}C n.m.r. should be a more applicable technique in this respect.[3] We question this proposal, because $^{2}J_{PH}$ and $^{1}J_{PC}$ are often quite comparable, and also because the ^{1}H and ^{13}C n.m.r. spectra are of different types. The ^{1}H spectra are typically of the $AA'X_nX'_n$ type ($A = {}^{31}P$, $X = {}^{1}H$), whereas the ^{13}C spectra are of the $AA'X$ type ($X = {}^{13}C$). This is because in natural abundance ^{13}C n.m.r. spectroscopy the average substituted molecule contains only one ^{13}C nucleus. The behaviour of $AA'X_nX'_n$ and $AA'X$ spectra, although similar in some respects, differ drastically under the conditions often encountered in bis-phosphine metal complexes. The $^{13}C(X)$ part of a PP' ^{13}C ($AA'X$) spectrum is *normally* a triplet[4] except when $J_{PP'}$ is very much less than $J_{CP} - J_{P'C}$. This means that for relatively similar J_{PH} and J_{PC} values, the triplet will occur in the ^{13}C spectrum at much smaller values of $J_{PP'}$ than it would have in the ^{1}H spectrum (where $J_{PP'}$ has to *exceed* $J_{PH} - J_{P'H}$ by an appreciable amount). Thus in cases where the proton spectrum of a phosphine group is too complex to use, the much simpler ^{13}C n.m.r. spectrum could be more ambiguous, especially in the borderline cases. When $J_{PP'}$ approaches zero a doublet will be observed in the ^{13}C spectrum provided that $J_{PC} >> J_{P'C}$, otherwise two doublets will occur.[4]

We have examined a series of cationic π-allyl palladium complexes by ^{13}C n.m.r. Related bis-phenyl phosphine derivatives have been shown[5] to give ^{1}H n.m.r. spectra typical of the "intermediate $J_{PP'}$ type", and similar ^{1}H spectra were obtained in the present series. By contrast, the ^{13}C n.m.r. spectra showed clean triplets for every carbon to which phosphorus coupling was observable (Figure).

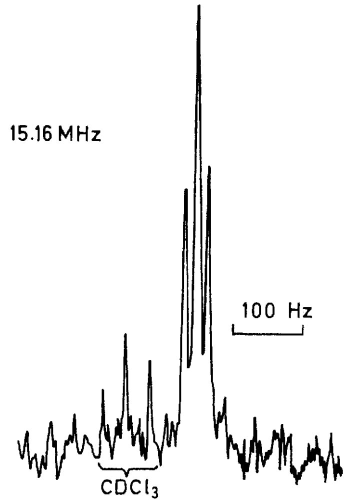

FIGURE. ^{13}C *n.m.r. spectra of allyl* - CH_2 *for* [Pd(2-*methallyl*)(PEt_2Ph)$_2$]$^+BF_4^-$.

Here then are examples of undeniably *cis* phosphine complexes with $^{2}J_{PP'}$ values not excessively large in which triplet ^{13}C resonances are seen. Clearly, unless analysed in the context of an $AA'X$ system, the conclusions drawn

TABLE. ^{13}C *n.m.r. data*

	^{13}C Chemical shifts[a] (p.p.m.)						
Derivative (BF$_4^-$ salt)	Allyl			Phenyl[b]			
	C_1 and C_3	C_2	CH_3	*ortho*	*meta*	*para*	Other
AllylPd$(PPh_3)_2^+$	78·9	127·3	—	133·5	128·0	130·0	—
	t(15·0)[c]	t(8)		t(6·5)[c]	t(5·1)		—
AllylPd$(PEt_2Ph)_2^+$	71·6	122·6	—	131·0	128·8	130·5	Et: CH_2 18·3 CH_3 8·2
	t(15·0)	t(7)		t(4·6)	t(4·8)		t(13·1)
2-MethallylPd$(PEt_2Ph)_2^+$	71·0	136·3	23·7	130·8	128·7	130·3	Et: CH_2 18·5 and 17·9
				t(5·2)	t(4·6)		2 × t(12·9)
	t(15·9)	t(7·5)					CH_3 8·4 and 8·1

[a] Relative to Me_4Si.
[b] Tertiary carbon not positively identified.
[c] t = triplet [splitting between components in Hz = $\frac{1}{2}(J_{PC}-J_{P'C})$].

would be misleading or the structures inferred would be wrong.

It is interesting to note the long range shielding effects operative in ^{13}C n.m.r. The ethyl group in bis-diethylphenylphosphine derivatives of π-2-methallyl palladium are markedly anisochronous, while in the analogous π-allyl palladium derivatives no such nonequivalence is observed.

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[1] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.
[2] F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1916, and references therein.
[3] B. E. Mann, B. L. Shaw, and R. E. Stainbank, *J.C.S. Chem. Comm.*, 1972, 151.
[4] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.
[5] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 774.