The Use of ^{13}C Nuclear Magnetic Resonance Spectroscopy in Determining the Stereochemistry of Tertiary Phosphine or Tertiary Arsine Complexes of Transition Metals

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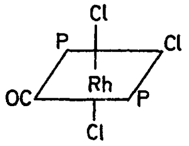
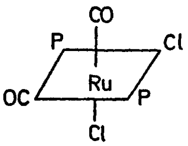
Summary ^{13}C N.m.r. spectroscopy is shown to be very useful in studying the stereochemistry of tertiary phosphine– or tertiary arsine–transition metal complexes.

THE stereochemistry of metal complexes containing two equivalent tertiary methylphosphine ligands has often been elucidated from the ^1H n.m.r. resonance pattern of the methyl groups.[1–4] Apart from a few exceptions involving complexes of Cr^0, Mo^0, W^0, and Mn$^{\text{I}}$,[2,3,5] two mutually *trans* tertiary methylphosphine ligands give a 1:2:1 triplet methyl resonance pattern [since $|^2J(\text{P–P})|$ is several hundred Hz and $|^2J(\text{P–}CH_3)-^4J(\text{P–CH}_3)|$ only a few Hz] and equivalent *cis* tertiary methylphosphine ligands give a 1:1 doublet pattern [since $|^2J(\text{P–P})|$ is then only a few Hz].[2–4,6] This method of determining the stereochemistry of tertiary phosphine–metal complexes is also applicable to tertiary t-butylphosphine complexes, and, in favourable cases to triethylphosphine but is not generally applicable to the great majority of tertiary phosphines because of the complexity of their ^{1}H n.m.r. spectra.


(I)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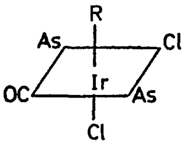
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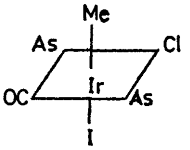
(IV)

Our present results show that this limitation will probably not apply to ^{13}C n.m.r. spectroscopy, for example with [RhCl$_3$(CO)(PBu$^n_2$Ph)$_2$)] configuration (I), *trans*-[PdCl$_2$(PBu$^n_2$Bu^t)$_2$], and [RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] configuration (II) ^{13}C n.m.r. spectroscopy with 'random noise' decoupling of the protons readily shows that the tertiary phosphines are mutually *trans*. Thus for [RhCl$_3$(CO)(PBu$^n_2$Ph)$_2$] 1:2:1 triplet resonances are observed for six of the eight different kinds of carbon atom in the tertiary phosphine, namely, the α-CH$_2$, β-CH$_2$, and γ-CH$_2$ of the n-butyl group, and the *o*-carbon, *m*-carbon, and the carbon of the phenyl group directly attached to the phosphorus. The δ-CH$_3$ of the n-butyl group and the *p*-carbon of the phenyl group appear as broad singlets; the coupling to phosphorus being too small to resolve. Similar results are obtained for the other two complexes mentioned above (see Table).

If the tertiary phosphines are mutually *cis* a 1:1 doublet for the resonances of the carbon atoms, is observed, as already reported for *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$].[8] It is very probable that values of $|J(\text{P–}^{13}\text{C})-J(\text{P}^1\text{–}^{13}\text{C})|$ will generally only be a few Hz or a few tens of Hz and hence when $|^2J(\text{P–P}^1)|$ is several hundreds of Hz, as it commonly is for many metal complexes with mutually *trans*-phosphine ligands (see above), the ^{13}C resonances will consist of 1:2:1 triplets but when $|^2J(\text{P–P})|$ is small (*cis*-phosphines) the ^{13}C resonances will consist of doublets.

The ^{13}C n.m.r. data for some tertiary phosphine complexes measured in CH$_2$Cl$_2$ *with complete proton decoupling. The* ^{13}C *chemical shifts are with respect to* Me$_4$Si *and are in the sense of increasing frequency. The resonances are singlets unless stated otherwise,* t = 1:2:1 *triplet.*

Compound	δ (^{13}C) (±0·2;	$|J$:P–C) + (P–C)$|$ ± 1Hz)
mer-[RhCl$_3$(CO)(PBu$^n_2$Ph)]		
α-CH$_2$	21·4t	29·5
β-CH$_2$	26·3t	2
γ-CH$_2$	25·3t	13·2
δ-CH$_3$	14·1	*ca.* 0
P-C <	134·0t	40
o-C	131·8t	8·5
m-C	129·8t	8·5
p-C	131·7	*ca.* 0
trans-[PdCl$_2$(PBu$^n_2$Bu^t)$_2$]		
α-CH$_2$	20·2t	23·0
β-CH$_2$	28·3	*ca.* 0
γ-CH$_2$	26·0t	14·3
δ-CH$_3$	14·6	*ca.* 0
–CMe$_3$	33·7t	23·0
–C(CH$_3$)$_3$	29·2t	4·5
[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$], configuration (II).		
α-CH$_2$	17·2	28
β-CH$_3$	7·6	*ca.* 0
		δ (^{13}C)
[IrCl$_2$(CO$_2$Me)(CO)(AsMe$_2$Ph)$_2$]	AsMe$_2$	7·6 7·8
[IrCl$_2$(CH$_2$CMe : CH$_2$)(CO)(AsMe$_2$Ph)$_2$]	AsMe$_2$	8·6 5·7
[IrClIMe(CO)(AsMe$_2$Ph)$_2$]	AsMe$_2$	6·5 16·0
[IrClIMe(CO)(AsEt$_2$Ph)$_2$]	AsCH_2	14·1 17·1
	AsCH$_2$$CH_3$	9·3 9·8

^{13}C N.m.r. spectroscopy will also be useful in studying tertiary arsine–metal complexes. Thus the complexes [IrCl$_2$(CO$_2$Me)(CO)(AsMe$_2$Ph)$_2$][4] and [IrCl$_2$(CH$_2$CMe : CH$_2$)(CO)(AsMe$_2$Ph)$_2$][9] have been assigned the stereochemistry (III) from i.r. and ^{1}H n.m.r. spectroscopic studies and in agreement with this we now find that the two arsenic methyls give resonances with different shifts, since there is no plane of symmetry along an arsenic–iridium bond. Similarly the complex [IrClIMe(CO)(AsMe$_2$Ph)$_2$] of configuration (IV)[4] shows two As–Me ^{13}C resonances and a similar doubling occurs for both the ^{13}CH$_2$ and the ^{13}CH$_3$ resonances of the ethyl groups in [IrClIMe(CO)(AsEt$_2$Ph)$_2$], showing that the arsines must be mutually *trans*.

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