^{13}C Nuclear Magnetic Resonance Spectra of the Complexes *cis*-[$\mathrm{PtMe_2(XMe_2Ph)_2}$] (X = P or As)

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Summary ^{13}C and new ^{1}H n.m.r. data for the complexes *cis*-[$\mathrm{PtMe_2(XMe_2Ph)_2}$](X = P or As) are given including the first measurements of platinum-195–carbon-13 coupling.

RECENT papers[1] have shown some of the potentialities of ^{13}C n.m.r. spectroscopy for the study of organo-transition metal complexes. We now report the first ^{13}C n.m.r. studies on organo-platinum complexes including the first measurements of $^{1}J(^{195}\mathrm{Pt}–^{13}\mathrm{C})$. Data for the two complexes studied, *cis*-[$\mathrm{PtMe_2(XMe_2Ph)_2}$] (X = P or As), are given in the Table. Some ^{1}H n.m.r. data for these two complexes have been reported previously;[2,3] we now have more accurate and also new ^{1}H n.m.r. data (Table).

The data show that on replacing phosphorus by arsenic $^{1}J(^{195}\mathrm{Pt}–^{13}\mathrm{C})$ and $^{2}J(^{195}\mathrm{Pt}–\mathrm{H})$ increase and $^{1}J(^{13}\mathrm{C}–\mathrm{H})$ (platinum–methyl) decreases. The increased $^{1}J(^{195}\mathrm{Pt}–^{13}\mathrm{C})$ possibly reflects a greater platinum–carbon bond strength since ν(Pt–C) also increases in going from the dimethylphenylphosphine complex to the dimethylphenylarsine complex; 536 and 523 cm^{-1} (for P);[2] 545 and 535 cm^{-1} (for As).[3] Couplings involving the methyl groups bonded to phosphorus or arsenic show the opposite trends to those bonded to platinum; thus, on replacing phosphorus by arsenic, $^{2}J(^{195}\mathrm{Pt}–^{13}\mathrm{C})$ and $^{3}J(^{195}\mathrm{Pt}–\mathrm{H})$ decrease and $^{1}J(^{13}\mathrm{C}–\mathrm{H})$ increases (Table). In the complex *cis*-[$\mathrm{PtMe_2(PMe_2Ph)_2}$] a platinum-methyl carbon-13 nucleus is strongly coupled to one phosphorus but only weakly coupled to the other phosphorus and the couplings are opposite in sign. It is likely that the strong coupling is to the phosphorus in mutually *trans*-position since one invariably finds, in complexes of the platinum metals (M) with phosphines, that ^{2}J(P–M–P) (*trans*) and ^{2}J(P–M–H) (*trans*) are much larger and opposite in sign to ^{2}J(P–M–P) (*cis*)[4] and ^{2}J(P–M–H) (*cis*)[5] respectively.

^{13}C (22·62 *MHz*) *and* ^{1}H (90 *MHz*) *n.m.r. data for the complexes* cis-[$\mathrm{PtMe_2(XMe_2Ph)_2}$] (X = P *or* As). J-*values in Hz. Measured at* ca.25° *in dichloromethane. The* ^{13}C *spectra were measured with random noise decoupling of the protons.*

	X = P	X = As
$^{1}J(^{195}\mathrm{Pt}–^{13}\mathrm{C})$	594 ± 5	685 ± 5
$\delta(\mathrm{Pt}^{13}\mathrm{CH_3})$[a]	−3·3 ± 0·1	+3·0 ± 0·1
$^{1}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$	1818·9 ± 0·2	—
$\delta(^{31}\mathrm{P})$[b]	+11·2 ± 0·1	—
$^{1}J(^{13}\mathrm{C}–^{1}\mathrm{H})$ (Pt–$\mathrm{CH_3}$) ..	132·0 ± 0·2	125·9 ± 0·2
$^{2}J(^{195}\mathrm{Pt}–\mathrm{C}–^{1}\mathrm{H})$	67·1 ± 0·1	77·2 ± 0·2
$^{2}J(^{31}\mathrm{P}–\mathrm{Pt}–^{13}\mathrm{C})$ (*trans*)[c] ..	104 ± 2	—
$^{2}J(^{31}\mathrm{P}–\mathrm{Pt}–^{13}\mathrm{C})$ (*cis*)[c] ..	9 ± 1	—
$^{3}J(^{31}\mathrm{P}–\mathrm{Pt}–\mathrm{C}–^{1}\mathrm{H})$ *trans*)[c]	8·2 ± 0·2	—
$^{3}J(^{31}\mathrm{P}–\mathrm{Pt}–\mathrm{C}–^{1}\mathrm{H})$ (*cis*)[c] ..	6·3 ± 0'2	—
$^{1}J(^{31}\mathrm{P}–^{13}\mathrm{CH_3})$	32 ± 1	—
$^{2}J(^{195}\mathrm{Pt}–\mathrm{X}–^{13}\mathrm{CH_3})$ ..	28 ± 1	20 ± 1
$\delta(\mathrm{X}^{13}\mathrm{CH_3})$[a]	−15·1 ± 0·1	−10·6 ± 0·1
$^{2}J(^{31}\mathrm{P}–\mathrm{C}–^{1}\mathrm{H})$	7·7 ± 0·1	—
$^{3}J(^{195}\mathrm{Pt}–\mathrm{X}–\mathrm{C}–^{1}\mathrm{H})$ ..	20·1 ± 0·1	11·0 ± 0·1
$^{1}J(^{13}\mathrm{C}–^{1}\mathrm{H})$ (X–$\mathrm{CH_3}$) ..	128·8 ± 0·2	133·9 ± 0·2
$^{2}J(^{31}\mathrm{P}–\mathrm{Pt}–^{31}\mathrm{P})$	*ca.* 0	—

[a] Relative to internal $\mathrm{Me_4Si}$. [b] Relative to external 85% $\mathrm{H_3PO_4}$. [c] The signs of the *cis*- and *trans*-coupling constants are opposite.

The reduced coupling constant[6] $^{1}K(^{195}\mathrm{Pt}–^{13}\mathrm{C})$ for *cis*-[$\mathrm{PtMe_2(PMe_2Ph)_2}$] is 915 × 10^{20} cm^{-3}, compared with $^{1}K(^{199}\mathrm{Hg}–^{13}\mathrm{C})$ for [$\mathrm{HgMe_2}$] of 1276 × 10^{20} cm^{-3}.[7]

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