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RING SIZE EFFECTS ON SOME ^{13}C, ^{31}P AND ^{195}Pt NMR PARAMETERS IN THE SERIES $\{Ph_2P(CH_2)_nPh_2\}Pt(CH_3)_2$

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Summary

The ^{31}P, ^{13}C, and ^{195}Pt NMR spectra of the compounds $\{Ph_2P(CH_2)_nPPh_2\}$-$Pt(CH_3)_2$ were studied and compared with the spectra of the acyclic analogue, *cis*-$(Ph_2PCH_3)_2Pt(CH_3)_2$. Comparison with structural data showed that irregularities in the NMR parameters can be explained on the basis of the existence of angle strain for four-membered but not for five-membered rings.

Introduction

A large number of metallocyclic compounds have been described [1—5]. In these systems a wide range of elements such as C, N, O, P, S, can be incorporated in the ring together with a metal atom. The ring sizes can also vary considerably, from three to six atoms, and even some very large ring systems have been reported [6]. It was noticed that the chemical and spectroscopic properties are frequently different from those of acyclic systems [3]. The phosphorus-containing ring systems have received much attention [7]. Interesting are the anomalous ^{31}P chemical shifts of four- and five-membered ring systems. These shifts are characteristic and can be used for structural assignments. However, a satisfactory interpretation of these shifts is still lacking. A number of crystal structure determinations of chelating and acyclic compounds of palladium and platinum are now available [8,9]. These structural data can be used for comparison with NMR results. In this study, an attempt has been made to correlate the NMR data for various nuclei (^{31}P, ^{13}C and ^{195}Pt) with the angle strain determined by X-ray diffraction in similar complexes. For this purpose we have studied the series $\{Ph_2P(CH_2)_nPPh_2\}Pt(CH_3)_2$ (n = 1—4).

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TABLE 1

^{195}Pt AND ^{31}P NMR DATA (δ, ppm)

δ ^{195}Pt relative to *cis*-$(Ph_2PCH_3)_2Pt(CH_3)_2$; 19.27 MHz. $\delta(dpmp)_2Pt(CH_3)_2$ = −1043 with respect to *cis*-$Pt(SMe_2)_2Cl_2$. δ ^{31}P relative to H_3PO_4 85%; 40.5 MHz. The data for $Ph_2P(CH_2)_nPPh_2PtCl_2$ are from ref. 5.

Compound	δ ^{195}Pt	J(Pt—P)		δP		$\Delta\delta P$		ΔR	
	R = CH_3	R = CH_3	R = Cl	R = CH_3	R = Cl	R = CH_3	R = Cl	R = CH_3	R = Cl
$Ph_2PCH_2PtR_2$	+703.9	1427	3078	40.4	64.3	+17.4	+41.3	+51.9	+73.6
$Ph_2P(CH_2)_2PPh_2PtR_2$	−9.2	1783	3618	−54	−45.3	−57.9	−57.8	−23.4	−25.5
$Ph_2P(CH_2)_3PPh_2PtR_2$	+4.7	1767	3420	−3.2	+5.6 [a]	−20.5	−11.7	+14.0	
$Ph_2P(CH_2)_4PPh_2PtR_2$	−58.6	1847	—	−18.8	−13.4 [a]	−38.8	−33.4	−4.3	
$(Ph_2PCH_3)_2PtR_2$	0	1834	3622	−6.4	−2.2	−34.5	−32.3	—	—
$\{(t\text{-}Bu)_2PC_4H_8\}Pt\{(t\text{-}bu)_3P\}Cl$	+685	2348/2692		−10.4/−68.8		—	+53		+58.4

[a] These complexes are not monomeric.

TABLE 2

^{13}C AND ^{31}P NMR DATA FOR THE PHOSPHINES (δ, ppm)

In $CDCl_3$ δ ^{13}C with respect to TMS, δ ^{31}P with respect to 85% H_3PO_4 (upfield = +). t = triplet; d = doublet.

Compound	$\delta CH_2(1)$	$\delta CH_2(2)$	$^1J(P_1C)$	$J(P_2C)$	$\delta C_1 J$(P—C)	$\delta C_2 J$(P—C)	$\delta C_3 J$(P—C)	δC_4	J(PP)	δP
dppm	28.0(t)	—	24		138.9(7.8)(t)	132.7(20.5)(t)	128.2(6.8)(t)	128.5		+23.0
dppe	23.7(t)	—	15 [a]	15 [a]	138.1(13.6)(t)	132.6(18.5(t)	128.3(7.8)(t)	128.5	34	+12.5
dppp	29.6(t)	22.3(16.6)(t)	12.4	17	138.6(13.6)(d)	132.6(18.6)(d)	128.3(6.8)(d)	128.4	0	+17.3
dppb	27.7(d)	23.4(13.7)(t)	16	0	138.8(13.7)(d)	132.6(18.5)(d)	128.2(5.9)(d)	128.3	0	+20.0
dpmp	12.3(d)	—	14	—	140.3(12.7)(d)	132.0(18.6)(d)	128.2(6.8)(d)	128.2	—	+28.1

[a] The signs are opposite; probably $^1J(P_1C)$ is negative.

Experimental

The phosphines and the corresponding complexes were prepared by published procedures [10] except that a slight modification was used in case of the complexes. The reactions were carried out in diethyl ether for dppe, dppp and dppb (bis(diphenylphosphino)ethane,-propane and -butane, respectively). The insoluble product was washed with diethyl ether and dried. The complexes (dppm)$Pt(CH_3)_2$ (dppm = bis(diphenylphosphino)methane) and (dpmp)$_2$Pt-$(CH_3)_2$ (dpmp = diphenylmethylphosphine) were prepared in hexane, washed with hexane, and dried. The products were obtained in quantitative yield.

Molecular weight determinations by vapor pressure osmometry showed that all the complexes are monomeric in chloroform. $(t\text{-}C_4H_9)_2P\dot{C}_4H_8\dot{P}tClP(t\text{-}C_4H_9)_3$ was prepared by Goel's method [11] from $PtCl_2$(benzonitrile) and $(t\text{-}C_4H_9)_3P$ in boiling toluene.

Spectroscopic measurements

The ^{31}P NMR spectra were recorded on a Varian XL 100 instrument, the ^{13}C NMR spectra on a Bruker WP 80. The ^{195}Pt NMR spectra were recorded on a Bruker WH 90 by Dr. J.W. Marsman of the Institute of Organic Chemistry TNO, Utrecht, with financial assistance of S.O.N.

Results

The ^{31}P NMR chemical shifts for the complexes, except for those for dppb-$Pt(CH_3)_{2\,g}$, were previously published by Appleton [10] and are listed in Table 1. ΔR is defined as the difference between the coordination chemical shift of a *cis*-disubstituted phosphine complex, and the coordination chemical shift of an analogous phosphorous atom in a chelate complex [3]. As shown in Table 1, ΔR is large and upfield for four-membered ring compounds and downfield for five-membered ring compounds. For larger rings ΔR becomes smaller; for even membered rings an upfield shift is found and for odd membered rings a downfield shift is found.

The ^{13}C NMR spectra of the free diphosphines (Table 2) dppm and dppe show triplet resonances for the C(1), C(2) and C(3) carbon atoms of the aromatic rings (Fig. 1). For the other diphosphines these carbon atoms appear as doublets. Thus dppm and dppe result in $^2J(^{31}P—^{31}P) > |^1J(P_1C) + ^3J(P_2C)|$ (20.5) and $^3J(^{31}P—^{31}P) > |^1J(P_1C) + ^4J(P_2C)|$ (18.5) respectively, because the spin system is AA′X (X = ^{13}C). For the other diphosphines $^4J(^{31}P—^{31}P) << J(PC)$ (18.6) and $^5J(^{31}P—^{31}P) << J(PC)$ (18.5) holds.

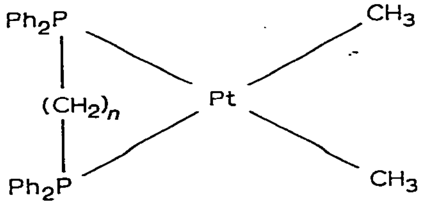

Fig. 1. Structure of the compounds $\{Ph_2P(CH_2)_nPPH_2\}Pt(CH_3)_2$.

TABLE 3

^{13}C NMR DATA FOR THE COMPLEXES (δ, ppm)

+ = downfield, J(PP) ranges from 5–8 Hz. Of the aromatic C atoms, C_1 is obscured; C_2 was found between 132.1 and 133.4 (J(PC) = 10–12 Hz); C_3 was found between 127.8 and 129.0 (J(PC) = 9–10 Hz); C_4 was found between 129.5 and 130.5 (J(PC) = 0 Hz).

Compound	δCH_3	^2J(CP *trans*)	^2J(CP *cis*)	^1J(Pt–CH_3)	$\delta CH_2(1)$	$\delta CH_2(2)$	$^1J(P_1C(1))$	$J(P_2C(1))^2$	$J(PtC_1)$	$\Delta CH_2(1)$
dppm	–27.9	106	6	640	19.7	—	26		6	–8.3
dppe	1.0	102	7	610	29.7	—	30	15	21.5	+6
dppp	5.0	100	10	595	27.4	21.0	~28	~5	—	–2.2
dppb	5.8	96	10	600	28.6	23.4	~28	~2	—	+0.9
dpmp	5.3	110	8	600	13.9	—	30	2	20	+1.7

The bridging carbon atom in dppm shows the expected triplet (A_2X system) resonance, but for dppe only a slightly broadened singlet is observed, accompanied by two small peaks at 37 Hz on either side of the main peak. Apparently $^1J(^{31}P—^{13}C) = {}^2J(^{31}P—^{13}C)$. For $^3J(^{31}P—^{31}P)$ a value of 32 ± 2 Hz was computed. In monodentate dppe complexes $^3J(PP)$ has comparable values, e.g. (dppe)Mo(CO)$_5$ $^3J(PP) = 26$ Hz [14]. For dppp two triplets were found, thus $^1J(P_1C) = {}^3J(P_2C)$ because $^4J(PP) \approx 0$. Dppb shows a doublet for C_1 ($^1J(P_1C_1)$ and a broadened triplet for C_2, thus $^2J(P_1C_2) \approx {}^3J(P_2C_2)$.

In the complexes the aromatic parts of the ^{13}C spectra are all very similar (Table 3). The *para*-carbon atoms appear as singlets and the others as triplets, with the middle peak somewhat smaller than the outside ones. The pattern represents the X part of an AA'X system. Thus $^2J(^{31}P—^{31}P) \approx |J(P_1C) + J(P_2C)|$ (10 Hz) even in the complex with dppm. For other (dppm) complexes larger couplings were found [12]. The comparative values for $^2J(^{31}P—^{31}P)$ of all the complexes show that a normal *cis* coupling is present, and therefore no noticeable coupling is transmitted through the carbon skeleton. The resonance of the phosphorus bound aromatic C atom is only found in the complex (dpmp)$_2$Pt(CH$_3$)$_2$ as a doublet ($J(^{13}C—^{31}P) = 44$ Hz, $J(^{13}C—^{195}Pt) = 16$ Hz. In the other complexes this resonance is obscured by the *ortho*-carbon atoms. The bridging C atom in (dppm)Pt(CH$_3$)$_2$ appears as a triplet (A_2X system) with an exceptionally small $J(^{13}C—^{195}Pt)$ coupling (6 Hz) [10]. In the other complexes the pattern is more complex (Fig. 2) because the system is an AA'X case.

The computed coupling constants are compiled in Table 3. For (dpmp)$_2$Pt(CH$_3$)$_2$ no satisfactory fit of calculated and observed patterns was obtained; therefore, the system was treated as an ABX case. The phosphorus atoms are assumed to be rendered magnetically and chemically inequivalent by the isotope effect of ^{13}C [13,14].

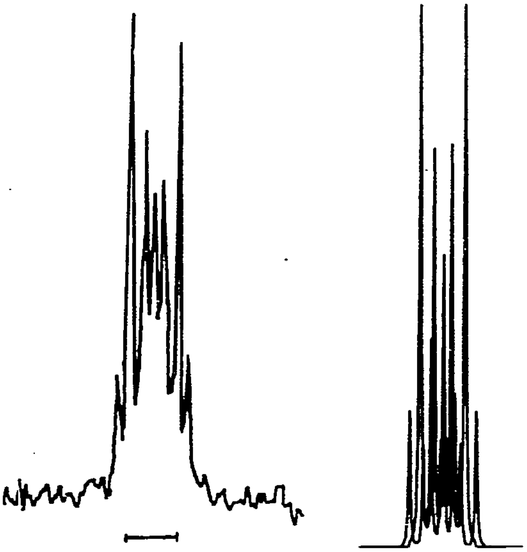

Fig. 2. Observed and calculated pattern for the NMR spectrum of the bridging carbon atoms in {Ph$_2$P-(CH$_2$)$_2$PPh$_2$}Pt(CH$_3$)$_2$. (|———|) ■G

The chemical shifts of the bridging carbon atoms resemble the trend in the ^{31}P shifts for the same compounds. Thus an upfield shift is found for the dppm complex and a downfield shift for the dppe complex. The *cis* and the *trans* $^{2}J(^{31}P—^{13}C)$ couplings with the platinum bound methyl groups are all very similar and therefore not very sensitive to ring size effects.

The $^{1}J(^{195}Pt—^{13}C)$ couplings also show few irregularities. The only exception is the four-membered ring compound for which a marked increase of this coupling was found. The larger coupling shows a stronger bonding between the metal and the methyl group. A strong carbon—platinum bond is also reflected in an upfield shift of the methyl carbon atoms. The ^{195}Pt chemical shifts do not differ substantially except for the dppm complex, in which a large downfield shift was found. A downfield shift is also found for $[(t\text{-}Bu)_2P\overline{C_4H_8)}Pt(P(t\text{-}Bu)_3]$-Cl and for other four-membered ring compounds [15]. Also a decrease of $^{1}J(^{195}Pt—^{31}P)$ is found in four-membered rings with respect to acyclic compounds.

Discussion

The ^{195}Pt NMR shifts of the series $Ph_2P(CH_2)_nPPh_2Pt(CH_3)_2$ are all very similar, except for $(dppm)Pt(CH_3)_2$ for which a large deviation was found. Crystal structure determinations, however, shows deviations of about —5° for (dppe)-$PdCl_2$ [9] and +5° for $(Me_3P)_2PtCl_2$ [8] from the theoretical PPtP angle of 90° (Table 4). Apparently, only the large deviations which are found in four-membered ring systems, have significant influence on the ^{195}Pt chemical shifts. The ^{195}Pt NMR shift of $[(t\text{-}C_4H_9)_2P\overline{C_4H_8P}tP(t\text{-}C_4H_9)_3Cl]$ was comparable with that of $(dppm)Pt(CH_3)_2$; therefore, the magnitude of the chemical shift was determined by the ring size. The number of phosphorus atoms in the ring has no large influence on the chemical shift.

The angles around phosphorus and carbon in the six-membered ring of $(dppp)PdCl_2$ are larger than normal but no irregularities were found for the ^{31}P and ^{13}C NMR parameters of $dpppPt(CH_3)_2$. On the other hand, the angles around phosphorus and carbon for $(dppe)PdX_2$ are virtually without strain. Irregularities are found, however, for the ^{13}C and ^{31}P NMR parameters of $(dppe)Pt(CH_3)_2$. For both nuclei a remarkable downfield shift was found. For other phosphorus containing five-membered rings the expected ring strain will be small, but a large downfield ^{31}P chemical shift was found irrespective of the kind of metal or other constituents of the ring. Therefore angle deformations

TABLE 4

IMPORTANT CRYSTALLOGRAPHIC DATA

	PMP	MPC(1)	PC(1)C(2)	C(1)C(2)C(3) (angles)	ref.
$dppmPdCl_2$	73°	94.7	93.0 [a]		9
$dppePdCl_2$	85°	108.5	107.9/108.2		9
$dpppPdCl_2$	90°	115.9	112.9/118.1	117.0	9
$(tmp)_2PtCl_2$	96°	107			8

[a] PCP angle.

are probably not responsible for the anomalous ^{31}P and ^{13}C chemical shifts of five-membered ring compounds. More likely the change of the charge of a coordinated atom influences the charge of the other one via the carbon skeleton of the ring. When a larger carbon chain connects both coordinating atoms this effect is much smaller.

For four-membered rings large deviations from the normal bond angles are found for all the atoms in the ring. Large deviations are also found for the NMR parameters. The large downfield ^{195}Pt shift, the small $^{1}J(^{31}\text{P}—^{195}\text{Pt})$, the small $^{2}J(^{195}\text{Pt}—^{13}\text{C})$ (bridging C), the large $^{1}J(^{195}\text{Pt}—^{13}\text{C})$ (CH_3) and the upfield ^{13}C shift for the methyl carbon atom probably all result from the distortion around the platinum atom. The ^{31}P chemical shift to high field probably reflects the distortion around this atom. However, the electronic differences are probably large and may also partly determine the chemical shift. Possibly the same effects determine the chemical shift of the bridging C atom. From these results it appears that only large angle deformations can be directly correlated with NMR parameters. The chemical shift and the coupling constants of the metal atom with neighbouring nuclei are the best indications of angle strain.

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