^{13}C NMR Spectra of α,α'-Tetracyanosubstituted Platinacyclobutanes

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Abstract

The natural abundance ^{13}C NMR spectra of some bis-(triphenylphosphino)tetracyano substituted platinacyclobutanes are described. Coupling constants and chemical shifts are compared with the available literature data of similar compounds. A correlation is found between $\mathrm{C{-}\widehat{Pt}{-}C}$, $\mathrm{P{-}\widehat{Pt}{-}P}$ angles and $J(\mathrm{Pt{-}C_\alpha})$ coupling constants. The influence on NMR parameters of the nature of the ancillary ligands, the ring size and substitution on α carbons, is discussed.

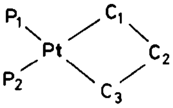
Introduction

There has been considerable interest in the chemistry of platinacyclobutanes in the last years, particularly because such complexes are useful models for metallacyclobutanes thought to be intermediates in many catalytic reactions (1–7].

The stable six-coordinate platinum(IV) analogues are easily prepared by oxidative addition of cyclopropanes to platinum(II) derivatives [1, 2, 7], but oxidative addition of cyclopropanes to Pt(0) complexes is restricted to rings [8–11] bearing electronwithdrawing substituents. Platinum(II) cyclobutanes with a purely hydrocarbon annulus have been prepared by thermolysis of dineopentylbis-(triethylphosphino)platinum(II) [5, 6] or by electrochemical reduction of Pt(IV) derivatives [4]. In spite of the available structural [4, 5, 10–12] and mechanistic [2–4, 6, 7] data, little is known about the electronic characteristics of these species.

Within our studies on the NMR parameters of platinum metallocycles [13, 14] here we report briefly the natural abundance ^{13}C spectra of $\overline{\mathrm{Pt{-}C(CN)_2{-}CH_2{-}C}}\mathrm{(CN)_2L_2}$, (L = PPh$_3$, PMePh$_2$, AsPh$_3$) from CDCl$_3$ solutions. ^{13}C NMR spectra of platinacyclobutanes have been reported for $\overline{\mathrm{Pt{-}CH_2{-}CH_2{-}C}}\mathrm{H_2(PPh_3)_2}$ [4], $\overline{\mathrm{Pt{-}CH_2{-}CH_2{-}C}}\mathrm{H_2X_2(L)}$ (X = Cl, Br; L = 2py, bipy) [15] and $\overline{\mathrm{Pt{-}CH_2{-}CHR_1{-}C}}\mathrm{HR_2(Cl)_2(L)_2}$ (L = nitrogenous base) [2].

Phosphino Pt(II) cyclobutanes (Scheme 1) have crystal structures heavily distorted from a square planar arrangement [4, 5, 10, 11], reaching the maximum distortion in the cyanosubstituted derivatives.



Scheme 1.

The dihedral (twist) angle between the P$_1$PtP$_2$ and C$_1$PtC$_3$ planes ranges from 1.8° to 18° and the puckering angle between the C$_1$PtC$_3$ and C$_1$C$_2$C$_3$ planes is more than 20° in all the three examined structures. Cyclobutane derivatives of Pt(II) and Pt(IV) bearing nitrogenous ancillary ligands like bipyridyl (bipy) or pyridine (py), show on the contrary crystal structures very close to planarity [4, 12]. Pt–C$_1$ bond length ranges from 2.08 to 2.16 Å, the smallest value being found for the unsubstituted ring.

Experimental

The compounds were prepared as reported elsewhere [8, 10, 13, 14]. ^{13}C NMR spectra were recorded from deuterated chloroform (Stohler) solutions in 10 mm sample tubes. TMS was used as internal standard. A Bruker WP 80 spectrometer equipped with a BNC 28 computer was used. Spectral width was 4500 Hz, digital resolution 1.1 Hz; flip angle 30° and pulse interval 0.9 s in broad band proton decoupled spectra, flip angle 60° and pulse interval 5 s in gated proton undecoupled spectra.

Results

Values of ^{13}C NMR parameters are shown in Tables I and II. In the [^{1}H] broad band decoupled

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TABLE I. ^{13}C NMR Data of Platinacyclobutanes and Selected Platinum Dialkyl and Platinum Olefin Complexes

Compound	Chemical shift (ppm from TMS) (^{13}C–^{195}Pt coupling constant (Hz))			Reference
	C$_\alpha$	C$_\beta$	CN	
$\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(As(C_6H_5)_3)_2$	−30.7 (365)	49.5 (180)	119.9 (85)	this paper
$\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(P(C_6H_5)_3)_2$	−23.1	48.4 (160)	120.3 (76)	this paper
$\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(P(C_6H_5)_2CH_3)_2$	−26.8 (450)	48.3 (155)	120.6 (77)	this paper
$\overline{Pt-CH_2-CH_2-C}H_2(P(C_6H_5)_3)_2$	−17.61 (400)	30.52 (150)		4
$Pt(CH_2{=}CH_2)(P(C_6H_5)_3)_2$	36.9 (194)			14
$Pt(C(CN)_2{=}C(CN)_2)(P(C_6H_5)_3)_2$	21.4 (290)		114.1 (49)	14
$Pt(CH_2CH_3)_2(P(C_6H_5)_3)_2$	16.2 (700)	15.7		4

TABLE II. ^{13}C NMR Data of Complexed and Free Arsine and Phosphines. Chemical shifts, ppm from TMS (^{13}C, ^{195}Pt coupling constants, Hz)

Compound	Carbon atoms					Reference
	ipso (^2J(Pt–C))	*ortho* (^3J(Pt–C))	*meta*	*para*	CH$_3$ (^2J(Pt–C))	
$\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(As(C_6H_5)_3)_2$	130.90	134.90	130.00	132.00		this paper
$As(C_6H_5)_3$	140.69	134.46	129.40	129.19		20
$\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(P(C_6H_5)_3)_2$	128.00 (26)	135.20 (17?)	128.90	131.90		this paper
$(P(C_6H_5)_3$	137.20	133.60	128.40	128.50		21
$\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(P(C_6H_5)_2CH_3)_2$	129.90 (26)	133.90 (18?)	130.00	132.70	14.2 (29)	this paper
$P(C_6H_5)_2(CH_3)$	139.90	131.70	128.00	127.90	12.0	22

spectrum of $\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(AsPh_3)_2$ assignment of the propane moiety was made assuming that $^1J[^{195}Pt, ^{13}C]$ is larger than $|^2J[^{195}Pt, ^{13}C]|$ and that the noticeably high field resonances are due to C$_\alpha$ in analogy with $\overline{Pt-CH_2-CH_2-C}H_2(PPh_3)_2$ [4] and with $\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(PPh_3)_2$ and $\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(PMePh_2)_2$. Assignment in the aromatic region was made as follows: the *ipso* carbon was assumed to originate the smallest peak, with satellites obscured by other resonances. Amongst the other signals only the low field intense peak shows evidence of coupling with ^{195}Pt ($|J| < 10$ Hz) and was attributed to the *ortho* carbon. Different intensities allowed the remaining two attributions.

In the phosphine derivatives the propane signals are further split by coupling with ^{31}P, the spectral patterns being identical in the two compounds. Apart from intensity no significant difference between central resonances and the corresponding ^{195}Pt satellites could be detected at our level of sensitivity. The central multiplets of C$_\alpha$ and CN are X parts of AA'X spectra; the former shows large splitting and strong differences between the two $^2J[^{31}P, ^{13}C]$; in the latter the splitting is much smaller and the effect of the differences in $^3J[^{31}P, ^{13}C]$ values is just observable. The annular C$_\beta$ gives the expected A$_2$X regular triplet ($|^3J[P, C_\beta]| = 4.5$ Hz) which in the [^{1}H] gated undecoupled spectrum of $\overline{Pt-C(CN)_2-CH_2-C}(CN)_2(PMePh_2)_2$ becomes a regular triplet of triplets ($^1J[C_\beta, H] = 138$ Hz to be compared with $^1J[C_\beta, H] = 135$ Hz observed for $\overline{Pt{-}CH_2{-}CH_2{-}C}H_2Cl_2(py)_2$ [15]). Also the central resonances of the phosphine carbons appear as X parts of AA'X spectra apart from the *para*. The quaternary *ipso* carbon gives low intensity resonances noticeably split by coupling with phosphorus atoms. *Ortho* and *meta* carbons give intense multiplets with smaller splittings. *Para* gives a single signal, coupling with phosphorus originating here just a significant broadening. ^{195}Pt satellites can be observed for the *ipso* and the *ortho* carbons, $|^3J[^{195}Pt, ^{13}C]|$ constants being larger than in the arsine complex.

Discussion

The multiplets due to carbon phosphorus couplings and the presence of ^{195}Pt satellites are in agreement with the expected kinetic stability of these complexes [8].

In unsubstituted platinum organometallics moving from Pt(II) dialkyls, to Pt(II) platinacyclobutane to Pt(0)ethene, $^1J[^{195}Pt, ^{13}C]$ decreases from 700 to 400 to $\cong$200 Hz and the $P{-}\widehat{Pt}{-}P$ angle increases (Tables I and III). It is likely that the dominant factor in explaining these trends is the variation of the $C{-}\widehat{Pt}{-}C$ angle (Figs. 1 and 2) or of the ring size. Noteworthy along the purely organic aliphatic series open chain, cyclobutane, cyclopropane, $^1J[^{13}C, ^{13}C]$ decreases from 40 to 10 Hz. Considering our tetracyanosubstituted compounds, the differences in $^1J[^{195}Pt, ^{13}C]$ values and $P{-}\widehat{Pt}{-}P$ angles between $Pt[C(CN)_2{=}C(CN)_2](PPh_3)_2$ and $\overline{Pt{-}C(CN)_2{-}CH_2{-}C}(CN)_2L_2$ have in the $C{-}\widehat{Pt}{-}C$ angle their main factor (Table I; Fig. 1). But our results indicate that these parameters depend heavily also on other factors. Indeed substitution at the α carbons causes just minor variations at the $C{-}\widehat{Pt}{-}C$ angles, but the $P{-}\widehat{Pt}{-}P$ angles are noteworthy smaller in the tetracyanosubstituted than in the corresponding unsubstituted compounds (Fig. 2). $^1J[^{195}Pt, ^{13}C]$ feels substitution at the α carbons [14] as well as changes of L, varying from 450 to 365 Hz when PPh_2Me is substituted with $AsPh_3$ (Table I); furthermore its values are lower in six-coordinate Pt(IV) platinacyclobutanes with nitrogenous ligands [2, 15].

The coupling between platinum and the annular β carbon (Table I) seems to be more dependent on the nature of the ligand atoms directly bound to platinum than on the kind of phosphine or on substitution at C_α (Table I). It becomes weaker in analogous Pt(IV) derivatives ($\cong$100 Hz). As the $Pt{-}C_\beta$ distances in $\overline{Pt(II){-}CH_2{-}CH_2{-}C}H_2(bipy)$ and $\overline{Pt(IV){-}CH_2{-}CH_2{-}C}H_2(Cl)_2(bipy)$ are 2.67 and 2.76 Å respectively direct interaction could play some role in determining the value of these coupling constants. In this respect it is worth mentioning that the $|^3J|$ values close to 100 Hz relative to coupling between platinum and annular protons observed in $\overline{Pt{-}CH_2{-}CH_2{-}C}H_2(L)_2$, ($L = PPh_3$, PEt_3, PMe_3, t-BuNC) and $\overline{Pt{-}CH_2{-}CH_2{-}C}H_2(bipy)$ have been attributed to direct Pt–H interaction [1, 4]. Indeed these values are dramatically influenced by changes in the molecule. Thus in $\overline{Pt{-}C(CN)_2{-}CH_2{-}C}(CN)_2(PPh_3)_2$ and $\overline{Pt{-}C(CN)_2{-}CH_2{-}C}(CN)_2(PEt_3)_2$ these $|^3J[^{195}Pt, ^1H]|$ are 38 and 28 Hz respectively and in Pt(IV) derivatives they are just 2.5 Hz.

Also the $|^2J|$ relative to the coupling between platinum and the CN carbon is significantly higher for $AsPh_3$ than for PPh_3 or PPh_2Me complexes. These values are noticeably larger than the corresponding ones in $Pt[C(CN)_2{=}C(CN)_2](PPh_3)_2$ (49 Hz) and in $Pt[CH(CN){=}CH(CN)](PPh_3)_2$ (52 Hz) [14], but close to the $|^2J(Pt, H_\alpha)|$ ($\cong$80 Hz) usually observed in the unsubstituted platinacyclobutanes [4].

One of the most striking features of platinacyclobutanes is the strong shielding of the α carbons in the Pt(II) and Pt(IV) derivatives. In this respect these compounds are unique among platinum organometallics. In fact comparison of cyclobutane,

TABLE III. X-ray Structural Data of Platinacyclobutanes and Other Selected Platinum Organometallics

Compound	Structural data (°)		Reference
	$C{-}\widehat{Pt}{-}C$	$P{-}\widehat{Pt}{-}P$	
$Pt(CH_2{=}CH_2)(P(C_6H_5)_3)_2$	39.7	111.6	16
$Pt(C(CN)_2{=}C(CN)_2)(P(C_6H_5)_3)_2$	41.5	101.4	17
$\overline{Pt{-}CH_2{-}C(CH_3)_2{-}C}H_2(P(C_2H_5)_3)_2$	67.3	103.01	5
$\overline{Pt{-}C(CN)_2{-}CH_2{-}C}(CN)_2(P(C_6H_5)_3)_2$	68.8	96.99	10
$\overline{Pt{-}CH_2{-}CH_2{-}CH_2{-}C}H_2(P(C_6H_5)_3)_2$	80.9	98.8	18
$Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$	85.5	94.09	5
$Pt(CH_3)_2(P(C_6H_5)_2(CH_3))_2$	81.9	97.75	19

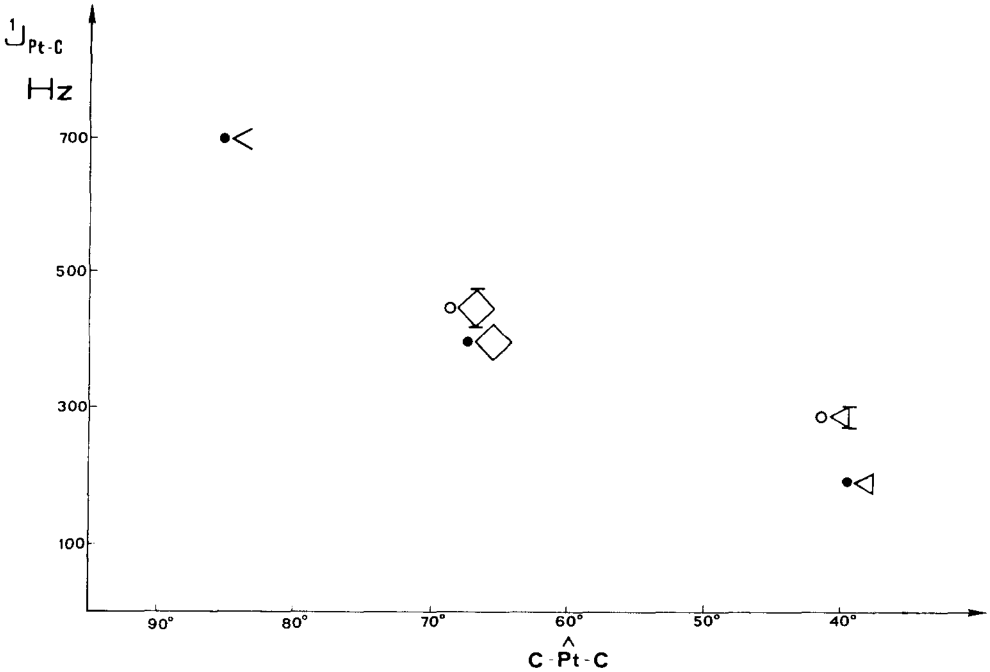

Fig. 1. Plot of $^1J(^{195}Pt-^{13}C)$ values *vs.* the $C-\hat{Pt}-C$ angles (Tables I and III) for bis-phosphine platinum derivatives. <: coupling constant of $Pt(CH_2CH_3)_2(P(C_6H_5)_3)_2$, $C-\hat{Pt}-C$ angle of $Pt(CH_3)_2(P(C_6H_5)_2CH_3)_2$; ◇: coupling constant of $\overline{Pt-CH_2-CH_2-CH_2}(P(C_6H_5)_3)_2$, $C-\hat{Pt}-C$ angle of $\overline{Pt-CH_2-C(CH_3)_2-CH_2}(P(C_2H_5)_3)_2$; ◁: $Pt(CH_2=CH_2)(P(C_6H_5)_3)_2$; ⊼ indicates α dicyano substitution.

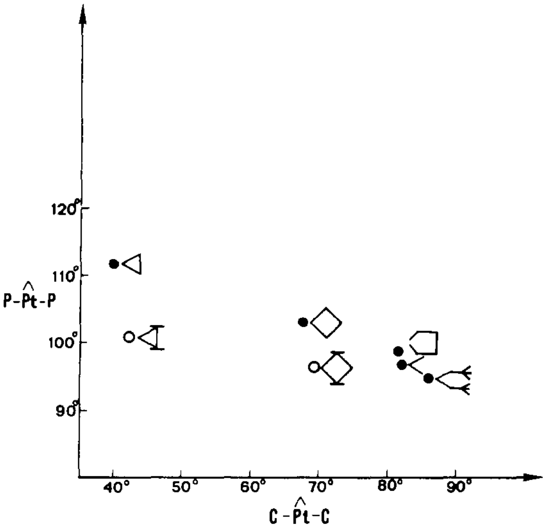

Fig. 2. Plot of the $P-\hat{Pt}-P$ *vs.* the $C-\hat{Pt}-C$ angles of bis-phosphine platinum derivatives. <: $Pt(CH_3)_2(P(C_6H_5)_2CH_3)_2$; ◇: $\overline{Pt-CH_2-C(CH_3)_2-CH_2}(P(C_2H_5)_3)_2$; ◁: $Pt(CH_2-C(CH_3)_3)_2(P(C_2H_5)_3)_2$; ◁: $Pt(CH_2=CH_2)(P(C_6H_5)_3)_2$; □: $\overline{Pt-CH_2-CH_2-CH_2-CH_2}(P(C_6H_5)_3)_2$; ⊼ indicates α dicyano substitution.

n-pentane and cyclopropane respectively with bis-(triphenylphosphino)platinacyclobutane, bis-(triphenylphosphino)platinumdiethyl and bis-(triphenylphosphino)platinumethylene shows that the substitution of CH_2 with $Pt(PPh_3)_2$ has a shielding effect on the α carbons of ≅40 ppm in the first, but of only 6 ppm in the second and a deshielding effect of ≅40 ppm in the third case. After introduction of four CN groups in α positions the α carbons move 5.5 ppm upfield, while the β carbons undergo a deshielding of 18 ppm. This has to be compared with the 15.5 upfield shift observed for the α carbons moving from $Pt(CH_2=CH_2)(PPh_3)_2$ to $Pt[C(CN)_2=C(CN)_2](PPh_3)_2$. Furthermore in the $\overline{Pt-C(CN)_2-CH_2-C(CN)_2}L_2$ series the shifts of α carbons depend clearly on L, their resonance moving to higher fields increasing the ligand donor properties.

The chemical shifts of the phosphine and arsine carbons (Table II) show the usual behaviour: after complexation the *ipso* carbon is strongly shielded and the *para* is deshielded, its shift variation monitoring the electronic charge donated by L.

Conclusions

The angular dependence of $|^1J[^{195}Pt, ^{13}C_\alpha]|$ seems to be related to different platinum 6s and carbon 2s characters of the MOs involved in platinum–carbon bonds.

Within the $\overline{Pt-C(CN)_2-CH_2-C(CN)_2}L_2$ series the C_α shielding increases with the expected increase of the electronic charge. Extension of such a correlation to all the compounds considered in this paper would indicate that donation of electronic charge from the $Pt(PPh_3)_2$ moiety is poorer in platinum olefins that in platinum(II) dialkyls and platinacyclobutanes in agreement with a formulation of the former compound as Pt(0) adducts and of the latter as Pt(II) complexes. But the difference observed between platinum dialkyls and platinacyclobutanes is not straightforward to explain through variations in the electronic charge and thus suggests that other factors have to be taken into account to understand these ^{13}C chemical shifts. In this respect it is also worthwhile mentioning that ring α carbons in Pt(II) and Pt(IV) cyclopropanes show small differences in shielding in spite of the expected significant difference in electronic charge.

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