

The Relationships between ^{13}C Nuclear Magnetic Resonance Parameters, *trans*-Influences, and Ligand Reactivities for Methylplatinum Compounds

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Summary ^{13}C n.m.r. parameters for a series of neutral and cationic methylplatinum compounds are reported and discussed in terms of *trans*-influences and ligand reactivities of these complexes.

WE report new ^{13}C n.m.r. data¹ for a variety of methylplatinum complexes (see Table) which show that these parameters can yield valuable information regarding *trans*-influences and ligand reactivities.

^{13}C and ^1H n.m.r. data for cationic and neutral methylplatinum complexes

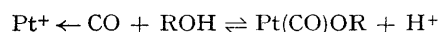
Complex	^{13}C Data				^1H Data			
	Pt-Me $\delta(\text{CH}_3)$	Pt-C $^1J(\text{Pt-C})$	Me-As $\delta(\text{CH}_3)$	Other $\delta(\text{C})$	Pt-Me $\delta(\text{Me})$	Pt-C $^2J(\text{Pt-H})$	Me-As $\delta(\text{Me})$	Other $\delta(\text{Me})$
<i>cis</i> -PtMe ₂ A ₂	-4.1	689 ± 2	11.6	19 ± 2	77.5	11.3		
<i>trans</i> -PtMeClA ₂	-28.4	643 ± 3	7.9	53 ± 2	81.4	21.3		
<i>fac</i> -Me ₃ PtA ₃ I	{ -0.8 ^c 2.0 ^h	{ 623 ± 3 ^c 556 ± 3 ^d	8.6	7 ± 2	72.8 ^c 63.6 ^d	7.0		
<i>trans</i> -[PtMe ₂ (CO)]PF ₆	-6.9	470 ± 3	10.0	42 ± 2	0.91 ^c 1.23 ^d			
<i>trans</i> -[PtMe ₂ (CNCH ₃)]PF ₆	-13.9	476 ± 3	9.6	50 ± 2	0.65	24.8		
<i>trans</i> -[PtMe ₂ (C(OCH ₃)CH ₃)]PF ₆	-15.9	360 ± 3	9.5	44.2 ^h 70.6 ⁱ	0.36	23.6 ^f	3.39	~12.8
<i>trans</i> -[PtMe ₂ (NCC ₆ F ₅)]PF ₆	-25.5	616 ± 3	8.3	321.0 ^j	0.11	25.5	4.86 ^f 2.55 ^h	6.0

^a Obtained at 25.2 MHz with a Varian system operating in the Fourier transform mode. (CD₂CO solutions (25–30 w/v) were examined (ca. 36°C) and peak positions measured (±0.1 p.p.m.) relative to internal Me₄Si; $J(\text{Pt-C})$ values are given in Hz. ^b Recorded in CHCl₃ at 31° at 100 MHz, δ in p.p.m. relative to Me₄Si internal ref., $J(\text{Pt-H})$ in Hz. ^c Me *trans* to I. ^d Me *trans* to AsMe₃. ^e Not observed at probe temperature due to exchange (ref. 14). ^f Obtained at -30°. ^g Carbonyl carbon. ^h α -carbon methyl. ⁱ Methoxyl. ^j Carbene carbon. ^k CNMe carbons were not observed—probably due to broadening owing to the ¹⁴N quadrupole. ^l C₄F₅CN carbons not measured. Satisfactory analytical data were obtained for all compounds not previously reported.

The *trans*-influence² is believed to arise from a rehybridisation of platinum σ -orbitals in response to changes in orbitals on the ligand used in σ -bonding.^{2,3} Thus, within a series, {e.g. *trans*-[PtH(L)(PEt₃)₂]⁺} as the σ -donor properties of the ligand L, increase so the Pt-L bond gains in Pt 's' and 'd' and loses 'p' character; conversely the bond *trans* to the ligand gains in Pt 'p' and loses 's' and 'd' character.⁴ ¹J-(¹⁹⁵Pt-³¹P) and ¹J(¹⁹⁵Pt-¹H) for tertiary phosphine- and hydrido-platinum complexes are believed to be dominated by the Fermi contact contribution and within a compound or a related series {e.g. *cis*-PtMeCl(PR₃)₂ or *trans*-[PtH(L)-(PEt₃)₂]⁺} the magnitude of these platinum coupling constants has been related specifically to the α^2_{Pt} term—the Pt 6s orbital contribution in the Pt-P or Pt-H bond.^{2,4,5} Since the Pt-C bond of a methylplatinum group is covalent and σ in character, values of ¹J(¹⁹⁵Pt-¹³C) should similarly reflect the hybridisation of platinum and the nature of the *trans*-ligand. That this is so may be seen in the values of ¹J(¹⁹⁵Pt-¹³C) (see Table) for the compound *fac*-Me₃Pt(AsMe₃)₂ and for the series *trans*-[PtMe(L)(AsMe₃)₂]⁺. Hence, we obtain the decreasing *trans*-influence series of L, C(OMe)Me > CO \geq MeNC > C₆F₅CN. Previously for some cationic methylplatinum complexes, we have formulated *trans*-influence series on values of ²J(¹⁹⁵Pt-C-¹H) for the methylplatinum group and assumed that this indirect coupling was proportional to the Pt 's' character used in the Pt-C bond.⁶ A plot of ²J(¹⁹⁵Pt-C-¹H) against ¹J(¹⁹⁵Pt-¹³C) for the complexes *trans*-[PtMe(L)(AsMe₃)₂]⁺ gives a straight line which passes through the origin and therefore supports the use of ²J(¹⁹⁵Pt-C-¹H) in the elucidation of the *trans*-influence of L. It is significant that ¹J(¹⁹⁵Pt-¹³C) for the methylplatinum group in *trans*-[PtMe(L)(AsMe₃)₂] is 470 and 476 Hz when L = CO and CNMe respectively. We have recently noted⁷ the similar n.m.r. *trans*-influence of methyl and trifluoromethyl groups in complexes *trans*-[PtX(L)-(PMe₂Ph)₂]⁺ where X = Me or CF₃. Thus it appears that the *trans*-influence of a ligand is dominated by the nature of its σ -bonding orbital and that its electronegativity and π -acceptor properties have little effect on the *trans*- σ -bond.

The complexes *trans*-[PtMe(L)(AsMe₃)₂]⁺ where L = CO and C(OMe)Me, allow a comparison of ¹J(¹⁹⁵Pt-¹³C) for approximately *sp*³, *sp*², and *sp* hybridised carbon atoms. Since the 's' character of the carbon hybrid orbital used in the Pt-C bond is contained within the Fermi contact equation for ¹J(¹⁹⁵Pt-¹³C), the observed magnitudes of these couplings, CO > C(OMe)Me > Me is not surprising [cf. ref. 8 for hydrocarbons where ¹J(¹³C-¹H) \sim 125 for C(*sp*³), \sim 160 for C(*sp*²), and \sim 250 for C(*sp*)] and therefore this order does not necessarily correlate with bond strength.

The carbonyl carbon resonance in *trans*-[PtMe(CO)(AsMe₃)₂]⁺ occurs at a higher field than that of any previously reported^{9,10} metal carbonyl complex; and in fact, it is slightly shielded relative to carbon monoxide. This together with the high value of ν_{CO} 2098 cm⁻¹, indicates little Pt 'd' to carbonyl π^* -bonding. This lack of Pt π -backbonding is responsible for the susceptibility of the carbonyl carbon atom towards nucleophilic attack¹¹



The central carbon of the C(OMe)Me moiety at 321.1 p.p.m. downfield from Me₄Si clearly indicates the marked positive charge on this carbon; indeed a comparison with ¹³C shieldings for organic compounds shows that this deshielding is comparable to that found for tertiary alkyl carbonium ion carbons.¹² We have previously proposed¹³ that the formation and reactivity of these cationic alkoxy-carbene complexes may be interpreted as reactions of platinum-stabilised or platinum-induced carbonium ions. Recently Randall *et al.*¹⁰ reported ¹³C n.m.r. data for (CO)₆CrC(OMe)Me in which the carbene carbon appeared at +362.2 p.p.m. from Me₄Si. Thus we feel that all metal-carbene complexes may be considered as metal stabilised carbonium ions, a model which closely reflects their chemical and physical properties.

(Received, October 14th, 1971; Com. 1817)

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