Carbon-13 Nuclear Magnetic Resonance Study of the Styrene–Platinum(II) Bond

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Summary ^{13}C N.m.r. and i.r. spectroscopic studies of a series of *para*-substituted styrene–platinum(II) complexes indicate a significant ionic contribution to the styrene–platinum bond.

There is considerable current interest in the study of metal–carbon bonds using Fourier transform ^{13}C n.m.r. techniques.[1] We report here the effect of *para*-substituents Y in the series of complexes *trans*-$[(p\text{-}YC_6H_4CH{=}CH_2)PtCl_2(NC_5H_4Me)]$ (I) on the nature of the styrene–Pt bond as elucidated by ^{13}C n.m.r. spectroscopy.

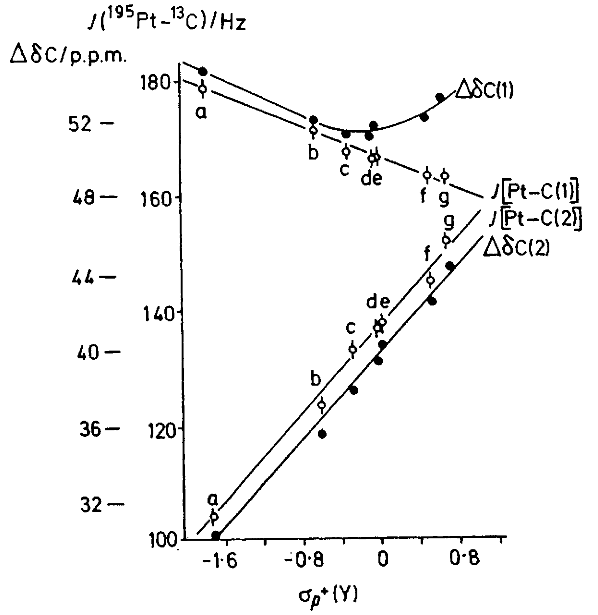


Figure. *A plot of* $J(^{195}Pt\text{-}^{13}C)$ *and* $\Delta\delta C$ (*the upfield shift on co-ordination*) *for* C(1) *and* C(2) *in* (I) *vs.* σ_p^+ (Y). a—g *as in formulae.*

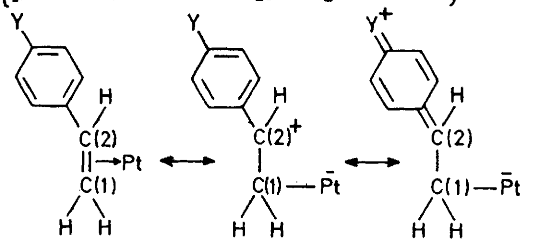
Plots of J ($^{195}Pt\text{-}^{13}C$) or $\Delta\delta C$ (the upfield shift on co-ordination to Pt) for the olefinic carbons C(1) and C(2) of (I) *vs.* Brown's σ_p^+ constant for Y[2] are shown in the Figure. Good linear correlations are obtained of J ($^{195}Pt\text{-}^{13}C$) for C(1) and C(2) and $\Delta\delta C(2)$ with $\sigma_p^+(Y)$. Several factors are apparent: (i) $J[^{195}Pt\text{-}^{13}C(1)] > J[^{195}Pt\text{-}^{13}C(2)]$ and $\Delta\delta C(1) > \Delta\delta C(2)$, (ii) the differences in the n.m.r. parameters for C(1) and C(2) are greatest for electron donor Y groups and least for electron acceptor Y groups, (iii) $J(^{195}Pt\text{-}^{13}C)$ and $\Delta\delta C$ for C(2) are considerably more sensitive to changes in Y than are the C(1) values, (iv) electron donor Y groups decrease markedly the value of $\Delta\delta C(2)$ and $J[^{195}Pt\text{-}^{13}C(2)]$ whilst increasing $J[^{195}Pt\text{-}^{13}C(1)]$, (v) $\Delta\delta C(1)$ varies non-linearly with σ_p^+. Polarization of the olefin π-electrons by Y, as in the V.B. representations (II), (III), and (IV), provides a reasonable rationalisation of points (i)—(iv). Electron donor Y groups would increase the contribution of (III) and/or (IV) to the overall styrene–Pt bonding, *i.e.*, the equilibrium position of Pt relative to the styrene C=C bond lies closer to C(1) for electron donor Y groups. It is a reasonable assumption that for (III) and (IV) $J[^{195}Pt\text{-}^{13}C(1)] >> J[^{195}Pt\text{-}^{13}C(2)]$ and that $\Delta\delta C(1) > \Delta\delta C(2)$.† A linear correlation between $\delta(^{13}C)$ and $\sigma_p^+(Y)$ has been recently reported for the series of carbonium ions $p\text{-}YC_6H_4\text{-}C^+Ph_2$.[3] An X-ray study of $[(PhCH{=}CH_2)PdCl_2]_2$ shows C(1) to be closer to the co-ordination plane than C(2).[4]

Table

Y	Pre-dominantly ν(C=C) (V)	ν(PtC_2) *asym* (V)	ν(PtC_2) *asym* (I)	ν(PtC_2) *sym* (I)	ν(PtCl) *trans* to styrene (V)
NMe_2	1206	554	546	480	298
NO_2	1275	463	449	388	315

The structural significance of the large changes in the ^{13}C n.m.r. parameters (Figure) has been determined by i.r. studies of complexes (I) and (V). Linear correlations of the important ligand vibrational modes[5] with σ_p^+ of Y were obtained. Unambiguously identified modes (cm^{-1}) for Y= NMe_2 and NO_2 are in the Table. Electron donor Y groups decrease ν(C=C) whilst increasing the *sym* and *asym* ν(PtC_2) modes suggesting that Y donor groups favour an increase in Pt–C bond strength at the expense of the C=C bonding. Consistent with this ν(Pt–Cl) *trans* to styrene in (V) is also dependent on Y, decreasing from 315 cm^{-1} for Y = NO_2 to 298 cm^{-1} for Y = NMe_2. The i.r. observations may also be accounted for in terms of greater contributions of (III) and (IV) to the overall bonding when Y is an electron donor group [*i.e.* Pt closer to C(1) with increased olefin–Pt σ-bonding]. The logarithms of the equilibrium constant for the system $[(YC_6H_4CH{=}CH_2)(5\text{-acetoxynortricyclenyl})Pd(hfacac)]$ also vary linearly with σ_p^+ (Y).[6] Electron donor Y groups *increase* the co-ordinative ability of the styrene.[6]

trans–$\{[p\text{-}YC_6H_4C(2)H{=}C(1)H_2]PtCl_2(NC_5H_4Me)\}$ (I)



(II) (III) (IV)

$K^+\{[p\text{-}YC_6H_4C(2)H{=}C(1)H_2]PtCl_3\}^-$ (V)

a; Y = NMe_2
b; Y = OEt
c; Y = Me
d; Y = H
e; Y = Cl
f; Y = COMe
g; Y = NO_2

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† The increase in $\Delta\delta C(1)$ for Y = NMe_2 and OBu (Figure) may be associated with greater shielding by Pt expected for a carbon atom more σ-bonded to platinum(II).[1]

The above results clearly illustrate (i) the sensitivity of ^{13}C n.m.r. parameters to changes in metal–carbon bonding modes, (ii) that the co-ordinated olefinic π-electrons are easily polarized, and (iii) that remote electron donor substituents on an olefin can markedly enhance the co-ordinative ability and *trans*-influence of olefins on Pt^{II}. On consideration of (ii) and (iii) it is conceivable that polarized intermediates similar to (III) and stabilized through solvation would contribute to the large kinetic *trans*-effect exhibited by co-ordinated olefins, not necessarily by an increase in Pt–olefin $d \rightarrow \pi^*$ back bonding but rather by an increased σ-donation and *trans*-influence.

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