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Preliminary communication

The synthesis, structure, and reactions of some simple unsaturated σ-hydrocarbylplatinum(II) complexes

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SUMMARY

Trimethyltin compounds Me_3Sn–R (R = CH=CH$_2$, CF=CF$_2$, or C≡CPh) are selective reagents for the synthesis of unsaturated hydrocarbyl derivatives such as *trans*-$PtCl(R)(PPhEt_2)_2$, by R/Cl exchange or oxidative addition (*e.g.*, to $Pt(PPh_3)_3$); single crystal X-ray analyses of two such compounds (R = CH=CH$_2$ or C≡CPh) show that the *trans*-influence of R has only a low sensitivity to hybridisation at carbon, with $sp^3 > sp \geqslant sp^2$.

There has been much interest in the nature of the transition metal–carbon bond with reference to unsaturated ligands, particularly in platinum chemistry, and speculation on the binding in terms of the Chatt–Dewar model. X-ray crystallographic studies have provided most of the experimental results. One approach to the problem is through study of the effect of hybridisation at carbon on the ligand *trans*-influence. In this context it is noteworthy that NMR coupling constant data on appropriate complexes have been interpreted to give an NMR *trans*-influence order of $C(sp^3) \simeq C(sp^2) > C(sp^1)$. We now present data on the synthesis, structure, and reactions of some simple vinyl, fluorovinyl, and acetylide derivatives of platinum(II).

A feature of the syntheses (A or B in Table 1) is the use of the selective reagents Me_3SnR; in increasing order of reactivity R = CH=CH$_2$ < CF=CF$_2$ < C≡CPh. For R = CH=CH$_2$, the *trans*-monovinyl derivatives of platinum are obtained exclusively by R/Cl ligand exchange [*e.g.*, using *cis*-$PtCl_2(PPhEt_2)_2$], (method A), in contrast to routes employing (i) $(CH_2{=}CH)_4Sn$, which affords very poor yields, (ii) $CH_2{=}CHMgBr$ from which $PtBr_2P_2$ was chiefly obtained, and (iii) $CH_2{=}CHLi$. For R = CF=CF$_2$ or C≡CPh,

TABLE 1

Compound	*Method* [a]	*Yield (%)*	*ν(Pt–Cl) (Nujol) (cm^{-1})*	*M.p. (°C)*
trans-$Pt(Cl)(CH{=}CH_2)(PPhEt_2)_2$	A	50	270	108
trans-$Pt(Cl)(CF{=}CF_2)(PPhEt_2)_2$	A	74	285	99
trans-$Pt(CF{=}CF_2)_2(PPhEt_2)_2$ [b]	A	68	–	109
trans-$Pt(Cl)(C{\equiv}CPh)(PPhEt_2)_2$	A	90	283	108
$PtCl_2(CH{=}CH_2)(PPhEt_2)_2$	C	90	328 and 255	175–178
$PtI_2Me(CH{=}CH_2)(PPhEt_2)_2$	C	50	–	129–131
trans-$Pt(CF{=}CF_2)(SnMe_3)(PPh_3)_2$	B	75	–	171–174

[a] A, R/Cl ligand exchange; B, oxidative addition to $Pt(PPh_3)_3$; C, oxidative addition to Pt^{II} of MeX or X_2. [b] Refinement of X-ray structure in progress.

method A affords good yields of either the *trans*-mono or *trans*-bis derivatives, stoicheiometrically controlled. Oxidative addition, method B, of Me_3SnR to PtP_3 or similar Pt^0 complexes gives *cis*-$PtR(SnMe_3)P_2$ ($R = CF{=}CF_2$ and $P = PPh_3$ or $PPhMe_2$; $R = C{\equiv}CPh$ [2] and $P = PPh_3$ or PPh_2Me].

For platinum, X-ray analyses are available for only two unsaturated σ-hydrocarbyl derivatives, *cis*-$Pt(C{\equiv}C{-}CN)CN(PPh_3)_2$ [3], and $Pt(C_6H_9)(CH_2COPh)$(diphos), [where C_6H_9 = 1-cyclohexenyl, and diphos = 1,2-bis(diphenylphosphino)ethane] [4], and the present results complete a series of hydrocarbyl ligands in the hybridisation states *sp*, sp^2, and sp^3. Selected bond lengths and angles for *trans*-$PtCl(R)(PPhEt_2)_2$ ($R = CH{=}CH_2$ or $C{\equiv}CPh$), are shown in Figs. 1 and 2. As assessed by Pt–Cl bond lengths, the ligands $-CH{=}CH_2$ and $-C{\equiv}CPh$ exert a very similar *trans*-influence. only slightly less than for the alkyl group in *trans*-$Pt(Cl)(CH_2SiMe_3)(PPhMe_2)_2$ [Pt–Cl 2.415(5) Å] [5], but greater than that for carbene in *cis*-$Pt(Cl)_2[C(NPhCH_2)_2](PEt_3)$ [Pt–Cl 2.363(3) Å] [6]. We conclude that the *trans* influence of these *monohapto* hydrocarbyl ligands falls in the order $sp^3 > sp > sp^2$, but that it is not very sensitive to the hybridisation state of the ligating carbon. Studies using the acetyl group [7] have shown that ligand electronegativity is also of little importance, the

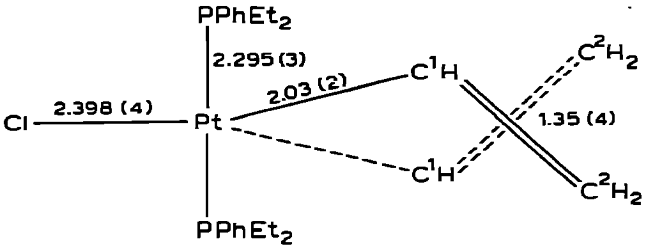

Fig. 1. *trans*-$PtCl(CH{=}CH_2)(PPhEt_2)_2$: ∠ Pt–C(1)–C(2) 126.9(19)°. Crystal data: orthorhombic, *a* 10.686(2), *b* 13.832(4), *c* 16.129(4) Å, *Z* = 4; *Pbcn* (No. 60, D_{2h}^{14}); *R* 4.4%, *R* 6.0% for 1420 absorption-corrected independent diffractometric data. The vinyl group is disordered about a C_2 axis passing through Pt and Cl.

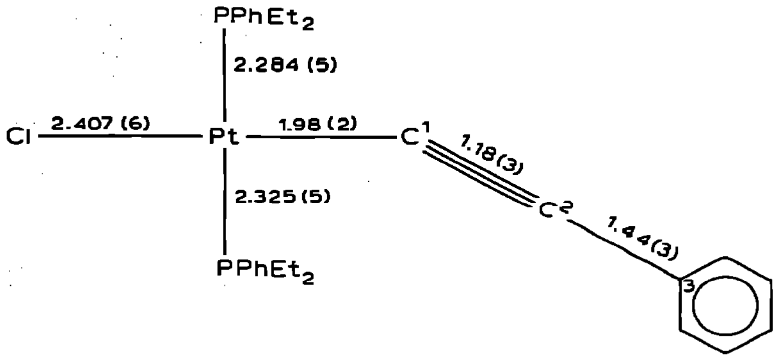

Fig. 2. *trans*-PtCl(C≡CPh)(PPhEt$_2$)$_2$: ∠ Pt–C(1)–C(2) 162(3)°, ∠ C(1)–C(2)–C(3) 174(2)°. Crystal data: monoclinic, *a* 12.359(3), *b* 13.015(3), *c* 9.031(2) Å, *β* 101.65(3)°; *Z* = 2; $P2_1$, (No. 4, C_2^2): *R* 4.7%, *R* 4.9% for 1883 independent diffractometric data.

trans-influence being chiefly controlled by the identity and formal charge (neutral < uninegative) of the ligating atom; note some relevant σ_I constants Me, –0.05; CH=CH$_2$, 0.15 (ref. 8); C≡CH, 0.20 (ref. 9), C≡CPh, 0.14 (ref. 9).

The new complexes are unsaturated in two senses, both with regard to the ligand R and to the metal. When R = CH=CH$_2$, addition takes place exclusively at the latter position for halogen (Cl$_2$, Br$_2$) and methyl halides (MeBr, MeI), (see Table 1). Another interesting reaction is shown in Scheme 1 and may relate to the *trans*-effect of the ligands R in (I). Clark and Manzer[10] showed that the methyl complex (R = Me) does not react with aromatic amines; in contrast. using n-butylamine we readily obtained cationic carbene complexes from the vinyl or phenylacetylide analogues.

Scheme 1

$$\mathrm{PtCl(R)P_2} \xrightarrow[\mathrm{MeOH}]{\mathrm{AgPF_6}} \mathrm{[Pt(R)(MeOH)P_2]^+PF_6^-} \xrightarrow{\mathrm{CNC_6H_4OMe}\text{-}p}$$

$$trans\text{-}\mathrm{[Pt(R)P_2(CNC_6H_4OMe}\text{-}p)]^+\mathrm{PF_6^-} \xrightarrow[\text{Reflux, 1 h}]{\text{n-BuNH}_2} trans\text{-}\mathrm{[(Pt(R)P_2\{C(NHBu\text{-}n)NHC_6H_4OMe}\text{-}p\}]^+\mathrm{PF_6^-}$$

(I) (II)

(1) R = CH=CH$_2$, P = PPhEt$_2$ gives (II) (m.p. = 129°)
(2) R = C≡CPh, P = PPh$_2$Me gives (II) (m.p. = 192–194°)

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