The *trans*-Influence of the Ligand Trimethylsilylmethylide ($Me_3SiCH_2^-$) in Platinum(II) Complexes and the Crystal Structure of a Platinum(II) Alkyl

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Summary Spectroscopic and crystallographic data are presented for *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$; by comparison of data for *cis*-$[Pt(CH_2Y)_2(PMe_2Ph)_2]$ and *trans*-$[PtCl(CH_2Y)(PMe_2Ph)_2]$ (Y = H, Ph, or Me_3Si) it is concluded that the *trans*-influence of the ligands decreases in the order $Ph_2MeSi^- > YCH_2^-$, and that the group Y has a minor role.

TRANSITION-METAL compounds MR_n containing $Me_3SiCH_2^-$ ligands are often very stable.[1] This has been attributed largely to kinetic effects. On the other hand, in compounds such as π-$C_5H_5Mo(CO)_3CH_2SiMe_3$, the Si–C bond is readily cleaved by nucleophiles.[2] In organic compounds both Me_3Si and Me_3SiCH_2 groups are normally assumed to release electrons by an inductive mechanism, though for the Me_3Si group this can be masked by $(p\text{–}d)\pi$ bonding[3] (but see ref. 4). Furthermore, the Me_3SiCH_2 group has an exceptionally large electron-releasing effect when attached to an electron-deficient or π-bonded carbon atom,[4,5] and this is attributed to hyperconjugation (σ–π conjugation) from the Me_3SiCH_2 bond.[4] In transition-metal complexes the electronic effect of this and similar ligands is still an open question.

It has been shown, from i.r.[6] and structural data[7] on *trans*-$[PtCl(SiMePh_2)(PMe_2Ph)_2]$, that Ph_2MeSi– is a ligand of exceptionally strong *trans*-influence and comparison with Me_3SiCH_2– is thus of interest. We have therefore investigated, by spectroscopic and *X*-ray methods, the structural features of platinum(II) complexes containing the ligand Me_3SiCH_2–.

The J (^{195}Pt–^{31}P) coupling constants for *cis*-$[PtR_2P_2]$ complexes and ν (Pt–Cl) for *trans*-$[PtClRP_2]$ complexes, (P = tertiary phosphine), are presented in Table 1, together with comparative data. These relate to eight compounds, four of them previously unknown, which were fully characterized by elemental analyses, and i.r. and n.m.r. spectra. It was remarkably difficult to prepare $[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$ from either (i) $[PtCl_2(PMe_2Ph)_2]$ and Me_3SiCH_2Li or Me_3SiCH_2MgCl, or (ii) *cis*-$[Pt(CH_2SiMe_3)_2(PMe_2Ph)_2]$[8] and HCl, because stepwise replacement was difficult to control, and this was much more evident than for the related $[PtClMe(PMe_2Ph)_2]$.[9] Ultimately, route (ii) proved practicable, provided the chlorodealkylation was carried out at −78°. The synthesis of *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$ was completed (see equation) by conversion of the *cis*-isomer into a *cis–trans* equilibrium mixture (in about equal

TABLE 1

trans-*Influence in* Pt^{II} *complexes and some spectroscopic data*

R	J (^{195}Pt–^{31}P) (kHz)[a] for *cis*-$[PtR_2(PMe_2Ph)_2]$	ν (Pt–Cl) (cm^{-1})[b] for *trans*-$[Pt(Cl)R(PMe_2Ph)_2]$
Me	1·846	284 (ref. 9)
$PhCH_2$	1·933[c]	
Me_3SiCH_2	1·999[d]	272[e]
Ph_2MeSi	1·559 (ref. 11)	242 (ref. 6)
Cl	3·549 (ref. 12)	340

[a] From ^{31}P n.m.r. in C_6H_6, or (R = Cl) CH_2Cl_2. [b] In polyethylene discs. [c] *cis*-$[Pt(CH_2Ph)_2(PPhMe_2)_2]$, m.p. 136°, in 43% yield from the *cis*-dichloride + 2RMgCl in Et_2O at 20°. [d] *cis*-$[Pt(CH_2SiMe_3)_2(PMe_2Ph)_2]$, m.p. 51·5—52°, in 81% yield from the *cis*-dichloride in C_6H_6 + 2RLi in Et_2O at 0°. [e] *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$, m.p. 118°, in 100% yield from *cis*-$[Pt(Cl)R(PMe_2Ph)_2]$ {itself obtained, m.p. 100°, in 93% yield from *cis*-$[Pt(CH_2SiMe_3)_2(PMe_2Ph)_2]$} + HCl (1 mol) in Et_2O at −78°] and a trace of PMe_2Ph.

TABLE 2

trans-*Influence in* Pt^{II} *complexes and some* X*-ray data*

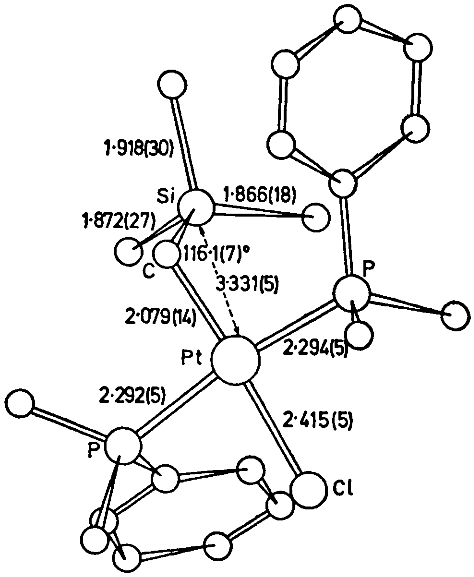
Compound	L	(Pt–L) Å	[Pt–Cl(*trans* to L)] Å
trans-[PtCl(CH$_2$SiMe$_3$)(PMe$_2$Ph)$_2$]	C	2·079(14)	2·415(5)
cis-[PtCl$_2$CH{CH$_2\overset{+}{N}$H$_2$CH(Me)Ph}CH$_2$CH$_2$CH═CH$_2$][a]	C	2·05	2·430
trans-[PtCl(SiMePh$_2$)(PMe$_2$Ph)$_2$][b]	Si	2·29	2·45(1)
trans-[PtCl$_2$(PEt$_3$)$_2$][c]	Cl	2·294(9)	2·294(9)

[a] Ref. 13. [b] Ref. 7, 14. [c] Ref. 15.

amounts) by addition of a trace of PMe$_2$Ph followed by chromatographic separation. The formation of an equilibrium mixture in this way is unusual (*cf.*, methyl analogue), and may be due to steric effects, as has been argued for [PtX$_2$P$_2$] isomerizations (X = Cl, Br; and P = PMe$_3$, PEt$_3$, or PPr$_3$).[10]

The structure of *trans*-[PtCl(CH$_2$SiMe$_3$)(PMe$_2$Ph)$_2$] has been determined by *X*-ray methods. The compound crystallizes well in a monoclinic unit cell of dimensions $a = 8{\cdot}919(4)$, $b = 21{\cdot}723(7)$, $c = 13{\cdot}865(3)$ Å, $\beta = 113{\cdot}88(3)°$. The space group is *Cc*. The structure was solved from 2573 diffractometric intensity data, corrected for absorption, and refined by full-matrix least-squares methods to a conventional *R*-factor of 0·039. Structural details are presented in the Figure and Table 2, with comparative data.

Both the spectroscopic and crystallographic data (Tables 1 and 2) support the following conclusions: (a) the *trans*-influence of the alkyl ligands YCH$_2^-$ is large compared with that of chloride, but still considerably smaller than that of Ph$_2$MeSi$^-$; (b) the *trans*-influence of YCH$_2^-$ is not significantly influenced by the nature of Y, when Y = H, Ph, or SiMe$_3$.



$$cis\text{-}[\mathrm{Pt(CH_2SiMe_3)_2(PMe_2Ph)_2}] \xrightarrow[-78°]{\mathrm{HCl}} cis\text{-}[\mathrm{PtCl(CH_2SiMe_3)(PMe_2Ph)_2}] \underset{\mathrm{PMe_2Ph}}{\overset{\text{trace}}{\rightleftharpoons}} trans\text{-}[\mathrm{PtCl(CH_2SiMe_3)(PMe_2Ph)_2}]$$

Since the *trans*-influence of the Me$_3$SiCH$_2$– is little different from that of the Me– ligand, and markedly smaller than that of the Ph$_2$MeSi– ligand, it is concluded that electrons are not released by hyperconjugation from Me$_3$Si–C or H–C bonds to platinum in the platinum(II) complexes examined.

We thank the S.R.C. for support and Engelhard, Ltd., for a loan of platinum.

(*Received, 20th March* 1972; *Com.* 448.)

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