Synthesis of α-Functionalised-alkylplatinum(II) Complexes by Oxidative Addition of Geminal Dihalides to Platinum(0) Substrates; *X*-Ray Structure of *cis*-[Pt(CH$_2$I)I(PPh$_3$)$_2$]†

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Summary The reaction of [Pt(η-C_2H_4)(PPh$_3$)$_2$] with CHRXY (CH_2I_2, CH_2Br_2, CH_2BrCl, CH_2BrI, CH_2ClI, or $CHBr_3$) affords *trans*- (and usually also *cis*-) [Pt(CHRX)(PPh$_3$)$_2$Y], whereas [Pt(PEt$_3$)$_3$] and CH_2I_2 yield *trans*-[Pt(CH$_2$PEt$_3$)I(PEt$_3$)$_2$]I; *X*-ray analysis of the title compound to *R* 0·064 shows Pt–P (*trans* to I) 2·228(6), Pt–P (*trans* to CH$_2$I) 2·355(7), Pt–C 2·08(2), and Pt–I 2·658(3) Å, ∠PPtP 97·1(2), and ∠CPtI 83·3(5)°.

We report a series of stable α-halogenoalkyls of Pt^{II}, (**1**)—(**8**), equations (1) and (3). Such compounds may be key intermediates to a wider range of functionalised alkyls of transition metals, as illustrated by equation (3). Data on a selection of complexes are in the Table and the Figure shows details of the molecular geometry of a rare *cis*-halogenoalkyl of Pt^{II} characterised by *X*-ray crystallography {*cf*. *cis*-[Pt(PPh$_3$)$_2$RX], R = CF$_2$ClCOCF$_2$, X = Cl;[1a] R = (CF$_3$)$_2$CH, X = F;[1b] or *cis*-[Pt(CF$_3$)Cl(*cis*-PPh$_2$-CH=CHPPh$_2$)][1c]}.

Compounds (**1**)—(**9**) have been identified by microanalysis and/or n.m.r. and i.r. spectra. The ^{31}P n.m.r. spectra show singlets for the *trans*-complexes (**1b**)—(**8b**) whereas the *cis*-isomers (**1a**)—(**8a**) have coupled doublets arising from the coupling $^2J(^{31}P Pt ^{31}P)$; for both there are ^{195}Pt satellites. The ^{1}H n.m.r. spectra reveal a triplet for *trans*-complexes due to $^3J(^1H^{31}P_2)$, but a doublet for the *cis*-isomers caused by $^3J(^1H^{31}P\text{-}trans)$, and for each there are appropriate ^{195}Pt satellites.

$$\begin{array}{c}[Pt(\eta\text{-}C_2H_4)(PPh_3)_2] + CHRXY \\ \Big\downarrow {\scriptstyle C_6H_6,\,24\,h \atop 25\,°C} \\ [Pt(CHRX)(PPh_3)_2Y]\end{array} \qquad (1)$$

a; *cis*
b; *trans*

(**1**), R = H, X = Y = I
(**2**), R = H, X = Y = Br
(**3**), R = H, X = Cl, Y = Br
(**4**), R = H, X = I, Y = Cl
(**5**), R = H, X = Cl, Y = I
(**6**), R = H, X = I, Y = Br
(**7**), R = H, X = Br, Y = I
(**8**), R = X = Y = Br

$$[Pt(PEt_3)_3] + CH_2I_2 \xrightarrow[25\,°C]{C_6H_6,\ 24\,h} trans\text{-}[Pt(CH_2PEt_3)I(PEt_3)_2]I \qquad (2)$$

(**9**)

$$trans\text{-}[PtBr(CH_2Br)(PPh_3)_2] \xrightarrow[Me_2CO\ reflux]{excess\ NaI} trans\text{-}[Pt(CH_2I)I(PPh_3)_2] \qquad (3)$$

The oxidative addition (equation 1) of CH_2I_2 yields a mixture of *cis*-(**1a**) and *trans*-(**1b**) products. Heating the mixture in CH_2Cl_2 causes complete conversion into the thermodynamically preferred isomer (**1b**). For CH_2Br_2 or CH_2Cl_2 additions there is progressive (Cl > Br > I) preponderance of *trans*-product at 25 °C, whereas CH_2BrCl yields mainly *trans*-[PtBr(CH$_2$Cl)(PPh$_3$)$_2$] (**3b**); CH_2IBr and CH_2ICl give complicated mixtures, including for the latter the

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† No reprints available.

TABLE. Data for some α-functionalised-alkyls of platinum(II).

		^{31}P N.m.r. (CH_2Cl_2)			^{1}H N.m.r. (CD_2Cl_2)		
Complex	M.p./°C	Chemical shift (δ, p.p.m.)[a]	$^2J(^{31}PPt^{31}P)$ /Hz	$^1J(^{31}P^{195}Pt)$ /Hz	Chemical shift (δ)[b]	$^2J(^1HC^{195}Pt)$ /Hz	$^3J(^1HCPt^{31}P)$ /Hz
(**1a**)	290—293 (decomp.)	124·1, 126·9	17	4224, 1826	3·1	36	10
(**1b**)		117·9		3066	2·3	36	9
(**2a**)		121·5, 122·9	17	4414, 1748	3·4	39	7
(**2b**)	220 (decomp.)	114·7		3103	2·8	43	9
(**3b**)	218 (decomp.)	114·3		3130	3·0	53	9
(**10**)	149—152	137·6,[c] 99·1	92·8[d]	2473			

[a] Relative to $P(OMe)_3$. [b] Relative to $SiMe_4$. [c] In EtOH. [d] $^2J(^{31}PC^{195}Pt)$.

halogen-scrambled products (**1b**) and $[Pt(CH_2Cl)Cl(PPh_3)_2]$. This suggests a free-radical mechanism (*cf.* ref. 2 for MeI addition to Pt^0), as do the observations of Scherer and Jungmann of photoinitiation for the CH_2Cl_2 reaction and its inhibition by duroquinone.[3]

Reaction (2) is related to one observed by Moss and Spiers, equation (4).[4] The possibility that for both reactions (2) and (4) there is an intermediate phosphonium salt, such as (**10**) (m.p. 222—226 °C), gains credence from its formation by reaction (5), employing the conditions of reaction (2). Against this, it is possible that the α-halogenoalkyl-Pt^{II} complexes may be precursors of ylide-Pt^{II} analogues; *e.g.* (**1**) with an excess of PEt_3 in CH_2Cl_2 at 25 °C yields (**9**).

$$[Pt(PPh_3)_4] + CH_2ClI \xrightarrow{\text{ref. 4}} cis\text{-}[Pt(CH_2PPh_3)(PPh_3)_2Cl]I \quad (4)$$

$$PEt_3 + CH_2I_2 \rightarrow \underset{(\mathbf{10})}{[P(CH_2I)Et_3]I} \quad (5)$$

Halogenoalkylmetal complexes are notoriously unstable. For example (transient) α-halogenomethyls of zinc (Simmons–Smith reaction) and mercury (Seyferth reaction) are useful carbenoids. There are few clear prior examples of d^8 complexes, $[Ir(CH_2Cl)(CO)(PMe_2Ph)_2]$[5] and *cis*-[Pt(CHClMe)-Cl(diphos)],[6] although an Rh^{III},[7] an Os^{II},[8] and three Ir^{III}[9] compounds have recently been described. Additionally, the complexes *trans*-$[Pt(CH_2Cl)Cl(PR_3)_2]$ (R = Bu^n or Ph)[10] were identified by ^{31}P n.m.r. spectroscopy; the latter was obtained not only as a mixture with the *cis*-isomer but also as the pure solid, and decomposes to yield the Pt^{II} dichloride upon photolysis.[3] Oxidative additions of CH_2Cl_2 to Rh^I,[7] Ir^I (also CH_2Br_2, $CHBr_3$, or CH_2I_2),[9] Pt^{II},[3,10] or Sn^{II} (CH_2Br_2 or CH_2I_2)[11] substrates have previously been reported; $[Pt(PPh_3)_4]$ and $CHCl_3$, $CH_2Cl(SMe)$, or $CH_2Cl(CN)$ gave $[PtCl_2(PPh_3)_2]$,[12] *trans*-$[Pt(CH_2SMe)Cl(PPh_3)_2]$,[13] or $[Pt(CH_2CN)Cl(PPh_3)_2]$,[14] respectively.

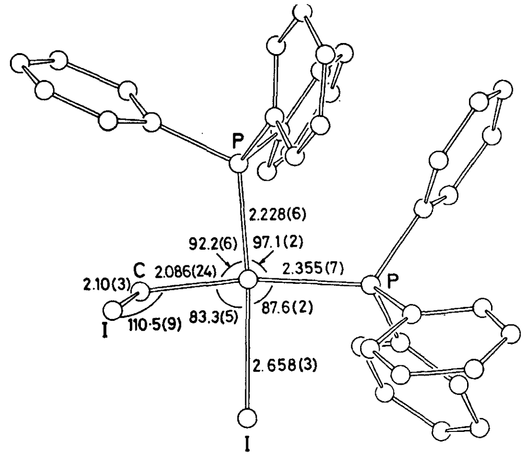

FIGURE. Schematic representation of the molecular structure of *cis*-$[Pt(CH_2I)I(PPh_3)_2]$ (**1a**) (projection of the molecule normal to the plane of the platinum environment) with some important bond lengths (Å) and angles (degrees).

The structure of the complex (**1a**) has been determined by *X*-ray crystallography.

Crystal data: $C_{37}H_{32}I_2P_2Pt.CH_2Cl_2$, triclinic, space group $P\bar{1}$, $a = 13{\cdot}03(1)$, $b = 12{\cdot}75(1)$, $c = 12{\cdot}51(1)$ Å, $\alpha = 65{\cdot}89(6)$, $\beta = 85{\cdot}99(6)$, $\gamma = 76{\cdot}69(7)$°, $Z = 2$. The structure was determined at room temperature (295 K) from 3183 independent 'observed' diffractometer reflections (Mo-K_α radiation). Current R: 0·064.‡

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‡ Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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