

Preliminary communication

SYNTHESIS OF YLIDEPLATINUM(II) COMPLEXES VIA α -FUNCTIONALISED ALKYLPLATINUM(II) INTERMEDIATES AND SOME COMPARATIVE DATA ON PALLADIUM(II) COMPLEXES; X-RAY STRUCTURE OF *trans*-[Pt(CH₂PEt₃)I(PEt₃)₂] I

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(Received December 16th, 1981)

Summary

The reaction of [Pt(PEt₃)₃] with CH₂I₂ affords *trans*-[Pt(CH₂PEt₃)I(PEt₃)₂] I and is believed to proceed via the α -functionalised alkyl *cis*-[Pt(CH₂I)I(PEt₃)₂], because similar ylides are obtained from *cis*- or *trans*-[Pt(CH₂X)(PPh₃)₂X] (X = Cl, Br, or I) with PR₃ (PEt₃, PBuⁿ₃, PMePh₂, PEtPh₂, or PPh₃); *cis*-[Pd(CH₂I)I(PPh₃)₂] does not react with excess PPh₃, but with PEt₃ yields *trans*-[Pd(CH₂PEt₃)I(PPh₃)₂] I; the X-ray structure of *trans*-[Pt(CH₂PEt₃)I(PEt₃)₂] I (current *R* = 0.045) shows Pt—P(1) 2.332(7), Pt—P(2) 2.341(8), Pt—C 2.08(2), and Pt—I 2.666(2) Å, and angles (a) C(1)—Pt—I, P(1), P(2): 176.9(8), 91.6(6), 93.4(6), (b) I—Pt—P(1), P(2): 87.1(2), 88.5(2), and (c) P(1)—Pt—P(2), 166.8(3), and (d) Pt—C(1)—P(3), 118(1)°.

We have recently described the synthesis of α -functionalised derivatives of platinum(II), *trans*- (and also often *cis*-) [Pt(CHRX)(PPh₃)₂Y] (R = H and X and Y are Cl, Br, or I; or CHRXY = CHBr₃), by oxidative addition of the appropriate geminal dihalide CHRXY to [Pt(η -C₂H₄)(PPh₃)₂] [1]. We also noted that a deceptively similar pair of reagents, CH₂I₂ + [Pt(PEt₃)₃], afforded a quite different product, an ylideplatinum(II) complex *trans*-[Pt(CH₂PEt₃)I(PEt₃)₂] I.

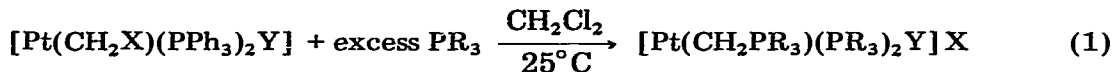
TABLE I
 ^{31}P NMR DATA FOR SOME YLIDEPLATINUM(II) COMPLEXES (IN CH_2Cl_2)

<i>trans</i> - $[\text{Pt}(\text{CH}_2\text{P}^{\text{A}})_2\text{P}^{\text{B}}\text{X}]_2\text{Y}$									
<i>trans</i> - $[\text{Pt}(\text{CH}_2\text{PR}_2)_2(\text{PR}_3)_2\text{X}]_2\text{Y}$									
No.	R	X	Y	Chemical shift P^{A} δ (ppm)	$^2J(^{31}\text{PC}^{195}\text{Pt})$ (Hz)	Chemical shift P^{B} δ (ppm)	$^2J(^{31}\text{P}^{195}\text{Pt})$ (Hz)	Chemical shift P^{C} δ (ppm)	$^2J(^{31}\text{P}^{195}\text{Pt})$ (Hz)
I	Et	I	I	98.9	92.8	137.2	2466		
II	Bu ⁿ	I	I	83.0	105.1	144.3	2466		
III	Et	Br	Br	98.3	100.1	133.0	2505		
IV	Et	Cl	Cl	97.7	107.4	130.4	2532		

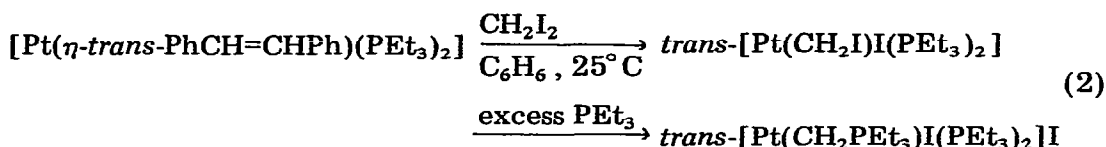
<i>cis</i> - $[\text{Pt}(\text{CH}_2\text{P}^{\text{A}})_2\text{P}^{\text{B}}\text{P}^{\text{C}}]_2\text{I}$											
<i>cis</i> - $[\text{Pt}(\text{CH}_2\text{PR}_2)_2(\text{PR}_3)_2\text{X}]_2\text{Y}$											
No.	R ₃	X	Y	Chemical shift P^{A} δ (ppm)	$^2J(^{31}\text{PC}^{195}\text{Pt})$ (Hz)	$^3J(^{31}\text{PRPtC}^{31}\text{P})$ (Hz)	Chemical shift P^{B} δ (ppm)	$^1J(^{31}\text{PC}^{195}\text{Pt})$ (Hz)	Chemical shift P^{C} δ (ppm)	$^1J(^{31}\text{P}^{195}\text{Pt})$ (Hz)	$^2J(^{31}\text{P}^{195}\text{Pt})$ (Hz)
V	MePh ₂	I	I	114.2	46	7	143.6	2223	142.3	3704	17
VI	EtPh ₂	I	I	105.0	59	5	126.5	2234	127.9	3928	19
VII	Ph ₃	I	I	108.7	49	5	128.6	2261	122.9	3794	17

^a Relative to P(OMe)₃.

We now find that there is a clear relationship between these two apparently disparate observations*. Accordingly we report a general synthesis of cationic ylide-platinum(II) complexes such as I–VII (see Table 1), as shown in eq. 1. This procedure, whereby an α -halogenomethylplatinum(II) complex is caused to react with an appropriate tertiary phosphine, may be regarded as a Men-



schutkin-type reaction of a metalloalkyl halide ($\text{RX} + \text{NR}_3 \rightarrow [\text{NR}_4]\text{X}$) and may have some generality for organometallic chemistry, as also evident from (i) eq. 2 (N.B. the use of PPh_3 is not obligatory), (ii) Klein and Hammer's preparation of $[\text{Co}(\text{CH}_2\text{PMe}_3)_2\text{Cl}_2]$ from $[\text{Co}(\text{PMe}_3)_4]$ and CH_2Cl_2 [2], (iii) Feser and Werner's synthesis of $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CH}_2\text{PMe}_3)(\text{PMe}_3)_2]\text{I}_2$ from $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CH}_2\text{I})(\text{PMe}_3)_2]\text{I}$ [3], and of some related cationic ylide-rhodium(III) complexes [4], and (iv) Botha, Moss, and Pelling's conversion of $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_n(\text{CH}_2\text{Cl})]$ ($\text{M} = \text{Fe}$ and $n = 2$, or $\text{M} = \text{W}$ and $n = 3$) into $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_n(\text{CH}_2\text{PPh}_3)]^+$ [5]. Ylide-transition metal complexes are well-known, but are generally made from a phosphorus ylide [6].



Reaction of *cis*- $[\text{Pt}(\text{CH}_2\text{I})\text{I}(\text{PPh}_3)_2]$ with excess of PEtPh_2 in CH_2Cl_2 is quite slow at 25°C , taking several days to reach equilibrium; ^{31}P NMR data recorded during this time show the presence of three *cis*-ylide-platinum(II) complexes, which we attribute to initial Menschutkin-type nucleophilic I^-/PPh_3 exchange at C_α followed by sequential displacements of the two PPh_3 ligands.

We believe that the formation of the ylide-platinum(II) complex is metal-assisted, involving initial formation of a five-coordinate 18-electron platinum(II) complex $[\text{Pt}(\text{CH}_2\text{X})(\text{PR}_3)(\text{PPh}_3)_2\text{Y}]$ and a subsequent 1,2-shift to yield the isomeric 16-electron complex $[\text{Pt}(\text{CH}_2\text{PR}_3)(\text{PPh}_3)_2\text{Y}]\text{X}$. Consistent with this is the failure of *cis*- $[\text{Pd}(\text{CH}_2\text{I})(\text{PPh}_3)_2]\text{I}$ to react with excess PPh_3 , although with the more basic PEt_3 the novel ylide-palladium(II) complex *cis*- $[\text{Pd}(\text{CH}_2\text{PEt}_3)\text{I}(\text{PPh}_3)_2]\text{I}$ is obtained. The iodomethyl precursor (the first halogenomethylpalladium(II) complex) is obtained from $[\text{Pd}(\text{PPh}_3)_4]$ and CH_2I_2 . This offers an interesting contrast to the corresponding reaction of $[\text{Pt}(\text{PPh}_3)_4]$ with CH_2ClI , leading to *cis*- $[\text{Pt}(\text{CH}_2\text{PPh}_3)\text{Cl}(\text{PPh}_3)_2]\text{I}$, and proposed to proceed via $[\text{P}(\text{CH}_2\text{Cl})\text{Ph}_3]\text{I}$ [7]. In the light of the present results this is unlikely, and reaction 1 is almost certainly implicated. NMR data on some of the new palladium compounds are in Table 2.

The structure of *trans*- $[\text{Pt}(\text{CH}_2\text{PEt}_3)\text{I}(\text{PEt}_3)_2]\text{I}$ (I) has been determined by X-ray crystallography and important molecular parameters for the cation are shown in Fig. 1. A feature is the significantly greater than tetrahedral bond angle

*Some of these results were presented at the International Conference on the Chemistry of the Platinum Group Metals, Bristol, 1981 (Abstracts, C5; see also C48 by J.R. Moss et al.).

TABLE 2

DATA FOR SOME α -FUNCTIONALISED ALKYLs OF PALLADIUM(II) AND AN YLIDE-PALLADIUM(II) COMPLEX

Complex	^{31}P NMR (CHCl_3)		^1H NMR (CDCl_3)	
	Chemical shift δ (ppm) ^a	$^2J(^{31}\text{Ppd}^{31}\text{P})$ (Hz)	Chemical shift δ (ppm) ^b	$^3J(^1\text{HCPd}^{31}\text{P})$ (Hz)
<i>cis</i> -[Pd(CH ₂ I)(PPh ₃) ₂]I	{ 109.7 122.3	7	3.47	10.6
<i>cis</i> -[Pd(CH ₂ Br)(PPh ₃) ₂]Br	{ 110.2 119.5	35		
<i>trans</i> -[Pd(CH ₂ Cl)(PPh ₃) ₂]Br	113.9		3.03	9.5
<i>cis</i> -[Pd(CH ₂ PEt ₃)I(PPh ₃) ₂]I	{ 108.6 122.6 119.6 ^c	22	3.63	13

^a Relative to P(OMe)₃. ^b Relative to SiMe₄. ^c For ylide phosphorus.

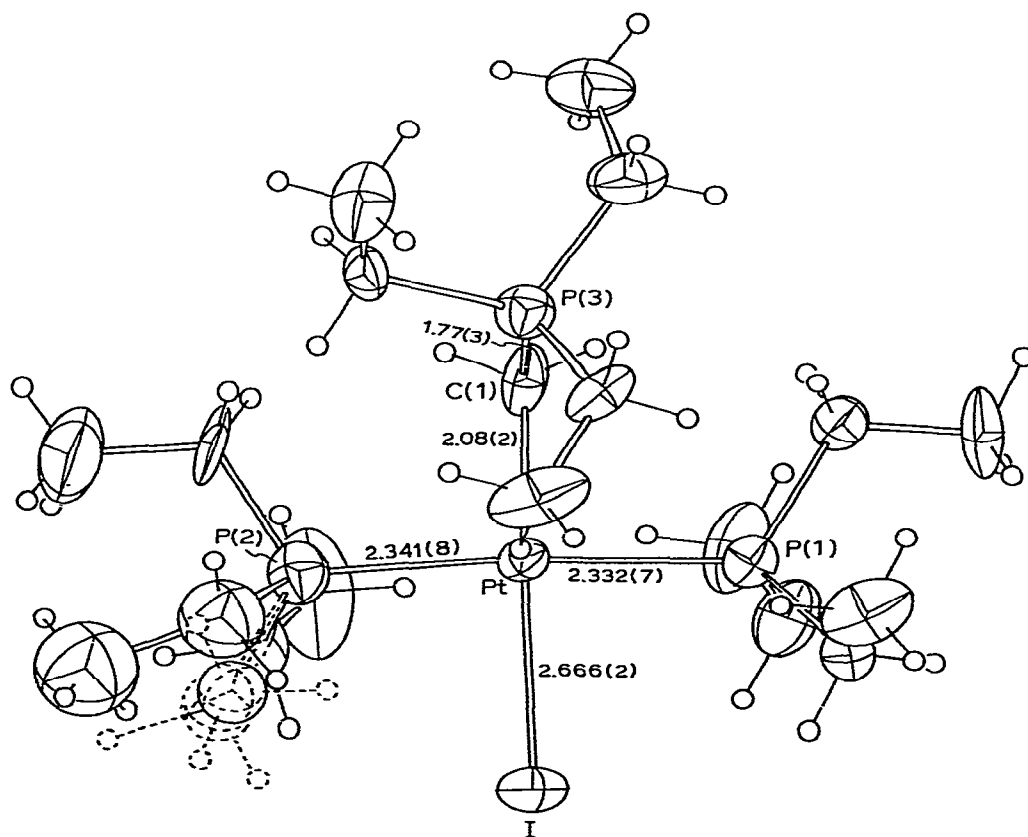


Fig. 1. Projection of the molecular structure of *trans*-[Pt(CH₂PEt₃)I(PEt₃)₂]⁺ normal to the plane of the platinum environment. The ethyl substituents of one of the PEt₃ groups are disordered as shown. Bond lengths about the platinum are as shown; associated angles are: C(1)—Pt—I, P(1), P(2): 176.9(8), 91.6(6), 93.4(6); I—Pt—P(1), P(2): 87.1(2), 88.5(2); P(1)—Pt—P(2), 166.8(3); Pt—C(1)—P(3), 118(1)^σ.

at C_α, 118(1)[°]; cf., 112.5(3)[°] in [Pd{CH(SiMe₃)PMe₂Ph}Cl(COD)]⁺ [8], 118[°] in [Ni{CH(Me)P(C₆H₁₁)₃}](CO)₃] [9], 117.2(34) in [Au{CH₂S(O)Me₂}Me₃] [10], and 114.89(71) in [Au(CH₂PPh₃)Me₃]; these appear to be the only crystallo-

graphically authenticated non-chelating ylide-transition metal complexes.

Crystal data: $C_{19}H_{47}I_2P_3Pt$, monoclinic, $P2_1/c$, $a = 16.926(4)$, $b = 15.129(5)$, $c = 11.523(4)$ Å, $\beta = 90.96(2)^\circ$, $Z = 4$. The structure was determined at 295 K from 1562 independent "observed" diffractometer reflections (Mo- K_α radiation). Current $R = 0.045^*$.

We are grateful to S.E.R.C. and I.C.I. (P.P.L., Runcorn) for the award of a CASE studentship to N.J.K.

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*Atom coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.