Synthesis and Reactions of 1,3-Bis(diphenylphosphino-κ*P*)-2-methylallyl Complexes of Platinum

Bernard L. Shaw* and Jonathan D. Vessey
School of Chemistry, Leeds University, Leeds LS2 9JT, UK

Treatment of $[PtX_2(cod)]$ (cod = cycloocta-1,5-diene) with the diphosphine $(Ph_2PCH_2)_2C{=}CH_2$ gives the complexes $[PtX_2\{(Ph_2PCH_2)_2C{=}CH_2\}]$ (X = Cl **1a** or Me **1c**). The dichloro complex can be converted to give the corresponding diiodo complex by metathesis and isomerised by base (NaOH–EtOH) to give $[PtCl_2(Ph_2PCH_2CMe{=}CHPPh_2)]$ **2a**. Treatment of complexes **1a**, **1c** or **2a** with LiMe gives $[PtMe_2\{(Ph_2PCH)_2CMe\}]^-$ **3**, containing a symmetrical anionic diphosphine, which reacts with MeOH to give $[PtMe_2(Ph_2PCH_2CMe{=}CHPPh_2)]$ **2b**. Treatment of **1a** or **2a** with equimolar amounts of Cl_2 produces the corresponding tetrachloroplatinum(IV) complexes **4** and **5**, whilst treatment of **1c** with MeI gives $[PtMe_3I\{(Ph_2PCH_2)_2C{=}CH_2\}]$ **6**; **4**–**6** are all unstable in solution with respect to reductive elimination reactions, **4** and **5** giving **1a** and **2a** respectively whilst **6** gives $[PtMeI\{Ph_2PCH_2)_2C{=}CH_2\}]$. Treatment of **3** with electrophilic reagents such as MeI, $PhCH_2Br$, $SiMe_3Cl$ or PPh_2Cl gives complexes $[PtMe_2(Ph_2PCHRCMe{=}CHPPh_2)]$ (R = Me **7a**, $PhCH_2$ **7b**, $SiMe_3$ **7c** or PPh_2 **7d**). Treatment of the salt $[Pt\{(Ph_2PCH_2)_2C{=}CH_2\}_2]Cl_2$ **9** with $NaBH_4$ gives the platinum(0) compound $[Pt\{(Ph_2PCH_2)_2C{=}CH_2\}_2]$ **9**, whilst with $LiBu{-}Me_2NCH_2CH_2NMe_2$ it gives the unusual platinum(II) complex $[Pt\{Ph_2PCH_2C({=}CH_2)CHPPh_2\}_2]$ **10**, in which the Pt is bonded to two P and two C atoms and two of the phosphorus atoms are uncomplexed.

Recently, we reported that the allylic diphosphine ligand $(Ph_2PCH_2)_2C{=}CH_2$, when complexed to a Group 6 metal tetracarbonyl moiety, underwent prototropic rearrangement on treatment with sodium ethoxide in ethanol to give the corresponding complexes of the rearranged ligand *Z*-$Ph_2PCH{=}CMeCH_2PPh_2$.[1] We also reported that this rearranged ligand could be deprotonated by strong bases such as lithium bis(trimethylsilyl)amide to give the symmetrical 1,3-bis(diphenylphosphino)-2-methylallylmetal tetracarbonyl anions $[M\{Ph_2PCH{=}CMeCHPPh_2\}(CO)_4]^-$; these anions could in turn be alkylated by electrophiles to give various substituted diphosphine–metal tetracarbonyl complexes.[1] The $M(CO)_4$ moiety (M = Cr, Mo or W) is a relatively inert one and we wanted to find out whether similar prototropic rearrangement and deprotonation reactions could be effected when these ligands are complexed to a more labile metal–ligand system such as with platinum. In this paper we describe our results with platinum(II) and also with platinum-(0) and -(IV).

Chelating ditertiary phosphines are very important in coordination and organometallic chemistry and in associated areas of catalysis.[2] Usually the chelating diphosphine is made separately and then complexed to the metal. The strategy described in our previous paper and now used in the present paper is to effect the synthesis of new ditertiary phosphine ligands in the *complexed* state. This strategy can have advantages: for example, base-promoted migration of the C=C double bond in the free ligand $(Ph_2PCH_2)_2C{=}CH_2$ has been reported but a mixture of *E* and *Z* isomers of $Ph_2PCH{=}CMeCH_2PPh_2$ is formed[3] and of course the *E* isomer cannot be a chelating diphosphine. Additionally, the *free* anion $Ph_2PCH{=}CMeCHPPh_2^-$, generated from the free diphosphine $Ph_2PCH{=}CMeCH_2PPh_2$, might be attacked by electrophiles at both carbon and phosphorus centres, giving a complex mixture of products.

Results and Discussion

Treatment of $[Pt(cod)Cl_2]$ (cod = cycloocta-1,5-diene) with $(Ph_2PCH_2)_2C{=}CH_2$ in a 1:1 ratio gave $[PtCl_2\{(Ph_2PCH_2)_2C{=}CH_2\}]$ **1a**, in high yield. The new complex was fully characterised by elemental analysis (Table 1), ^{31}P (Table 2), ^1H (Table 3), ^{13}C (Table 4) and ^{195}Pt (Table 1) NMR spectroscopy, and mass spectrometry (Table 1). The other new complexes described in this paper were similarly characterised and only specially important or noteworthy features of the characterising data will be discussed further. The ^1H NMR spectrum of **1a** was second order and contained two triplet resonances, with an intensity ratio of 1:2, at δ 4.70 and 3.24 which we assign to the $C{=}CH_2$ and PCH_2 protons, respectively. In the $^1H\text{-}\{^{31}P\}$ spectrum these resonances became slightly broad singlets due to unresolved H–H coupling. The resonance due to the PCH_2 protons also showed a coupling to the platinum nucleus, $^3J(PtH)$ = 45.0 Hz. The dichloride **1a** readily underwent metathesis to the corresponding diiodide **1b** by treatment with NaI in refluxing acetone. In the $^1H\text{-}\{^{31}P\}$ NMR spectrum of **1b** the resonances due to the two types of methylene protons showed a resolvable mutual coupling, $^4J(HH) + {^4J}(HH)$ of 1.8 Hz. The $^{31}P\text{-}\{^1H\}$ spectra of **1a** and **1b** were similar although the value of $^1J(PtP)$ was about 200 Hz smaller for **1b** than for **1a**. The $^{195}Pt\text{-}\{^1H\}$ NMR spectrum of **1b** showed the expected shift found by replacing Cl^- ligands by I^-.[4]

The dimethylplatinum complex $[(PtMe_2\{(Ph_2PCH_2)_2C{=}CH_2\}]$ **1c** was made in high yield from $[Pt(cod)Me_2]$ and $(Ph_2PCH_2)_2C{=}CH_2$. It was fully characterised, *i.e.* by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopies in addition to elemental analysis and mass spectrometry. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the resonance due to the $Pt{-}CH_3$ groups appeared as a pseudo-first-order doublet of doublets, $^2J(P_{trans}C)$ = 101.2, $^2J(P_{cis}C)$ = 10.3 Hz with coupling to platinum $^1J(PtC)$ = 597 Hz.

We expected that the diphosphine ligand in complexes of type **1** could be isomerised by base/acid-catalysed movement of the C=C bond along the backbone, in a similar fashion to that observed for complexes of the same diphosphine with Mo or W, to produce complexes of *Z*-$Ph_2PCH_2CMe{=}CHPPh_2$.[1] Such an isomerisation was effected upon the dichloride **1a** using NaOEt in refluxing EtOH, followed by addition of HCl, giving $[PtCl_2(Ph_2PCH_2CMe{=}CHPPh_2)]$ **2a** as the only observed product. In the $^{31}P\text{-}\{^1H\}$ NMR the chemically inequivalent

Table 1 Elemental analytical[a] (C, H and Cl), mass spectral[b] and ^{195}Pt-{^{1}H}[c] NMR spectroscopic data

	Analysis (%)			Mass spectrum		
Compound	C	H	Cl	*m/z*	Assignment	^{195}Pt-{^{1}H} NMR
1a	48.4 (48.7)	3.75 (3.8)	10.05 (10.25)	655 (86)	$M - \mathrm{Cl}$[d]	−19 (t)
				618 (15)	655 − HCl	
1b	38.5 (38.5)	2.9 (3.0)	29.2 (29.1)[e]	873 (7)	M^+	−845 (t)
				746 (52)	$M - \mathrm{I}$	
				618 (5)	746 − HI	
1c	55.5 (55.45)	5.0 (4.95)	—	634 (11)	$M - \mathrm{CH_3}$	−170 (t)
				618 (7)	634 − CH_4	
1d	46.2 (45.75)	3.9 (3.85)	16.3 (16.65)[e]	761 (7)	M^+	−489 (dd)[f]
				746 (30)	$M - \mathrm{CH_3}$	
				634 (16)	$M - \mathrm{I}$	
				619 (14)	$M - \mathrm{CH_3I}$	
2a	48.45 (48.7)	3.7 (3.8)	10.1 (10.25)	655 (100)	$M - \mathrm{Cl}$[d]	−86 (dd)
				618 (11)	655 − HCl	
2b·C_6H_6	59.2 (59.4)	5.2 (5.25)	—	634 (71)	$M - \mathrm{CH_3}$	−199 (dd)
				618 (100)	634 − CH_4	
4·0.1CH_2Cl_2	43.45 (43.85)	3.3 (3.45)	19.0 (19.35)	—	—	—
5·0.25CH_2Cl_2	42.7 (43.35)	3.35 (3.4)	20.05 (20.4)	726 (8)	$M - \mathrm{Cl}$	—
				689 (11)	726 − Cl	
				653 (100)	689 − HCl	
				617 (17)	653 − HCl	
6	46.8 (47.05)	4.4 (4.45)	16.2 (16.05)[e]	761 (5)	$M - \mathrm{C_2H_6}$	+143 (t)
				746 (100)	761 − CH_3	
				634 (33)	761 − I	
				618 (36)	634 − CH_4	
7a	56.15 (56.1)	5.05 (5.15)	—	662 (2)	$M - \mathrm{H}$	−212 (dd)
				648 (10)	$M - \mathrm{CH_3}$	
				632 (6)	648 − CH_4	
7b	60.2 (60.1)	5.1 (5.2)	—	739 (2)	M^+	−226 (dd, br)
				724 (100)	$M - \mathrm{CH_3}$	
				708 (66)	724 − CH_4	
7c·0.4CH_2Cl_2	53.15 (53.1)	5.2 (5.45)	—	706 (61)	$M - \mathrm{CH_3}$	−162 (dd)
				690 (43)	706 − CH_4	
				675 (30)	690 − CH_3	
				618 (19)	706 − $SiMe_4$	
7d·0.5CH_2Cl_2	58.15 (58.05)	4.65 (4.8)	—	833 (19)	M^+	−178 (ddd)
				818 (81)	$M - \mathrm{CH_3}$	
				802 (100)	818 − CH_4	
8	60.15 (60.3)	4.7 (4.7)	6.6 (6.35)	1079 (70)	$M - \mathrm{Cl}$	−500 (qnt)[g]
				1043 (36)	1079 − Cl	
				858 (100)	1043 − PPh_2	
				804 (23)	858 − C_4H_6	
				655 (49)	1079 − $(Ph_2PCH_2)C{=}CH_2$	
				618 (26)	655 − HCl	
9	64.15 (64.4)	5.2 (5.0)	—	1044 (100)	$M + \mathrm{H}$	−525 (qnt)[h]
				858 (48)	$M - \mathrm{PPh_2}$	
				804 (50)	858 − C_4H_6	
				618 (16)	858 − PPh_2H	
10·0.5CH_2Cl_2	62.2 (62.6)	4.85 (4.75)	—	1042 (12)	$M + \mathrm{H}$	+38 (tt)[i]
				857 (6)	1042 − PPh_2	

[a] Calculated values in parentheses. [b] Figures quoted refer to the most intense peak in each profile and assignments are based on the ^{195}Pt isotope unless stated otherwise. Figures in parentheses indicate the intensity relative to the most intense peak in the spectrum, which was commonly below *m/z* = 200. [c] Recorded at 19.17 MHz in CD_2Cl_2 solution, at 301 K unless stated otherwise. t = Triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, qnt = quintet, tt = triplet of triplets, br = broad. [d] Assignment based on (^{194}Pt and ^{37}Cl) and (^{196}Pt and ^{35}Cl). [e] Analysis for I. [f] In $CDCl_3$ solution. [g] In Me_2CO–water (1:1) solution. [h] In C_6D_6 solution. [i] Recorded at 85.6 MHz.

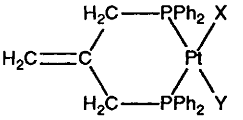
^{31}P nuclei show a mutual coupling, ^{2}J(PP), of 22 Hz. From selective ^{1}H-{^{31}P} decoupling experiments we showed that the resonance due to the alkenic phosphorus (=CHP) is at δ −7.2, ^{1}J(PtP) = 3415 Hz, and that for the allylic phosphine (CH_2P) is at δ 33.9, ^{1}J(PtP) = 3811 Hz. The increased value of ^{1}J(MP) for the allylic over the alkenic phosphorus is similar to that observed for the complex of the same ligand with $W(CO)_4$.[1] Somewhat analogous complexes, [PdX_2{$Ph_2PCH_2C(CF_3)$=CHPPh$_2$}] (X = Cl, Br or SCN), have been prepared by Carty and his co-workers[5] by hydrolysis of *cis*-[$PdX_2(Ph_2PC{\equiv}CCF_3)_2$].

Comparing the chemistry of compounds of types **1** and **2** with that of the corresponding complexes of Group 6 tetracarbonyls, one would predict that the deprotonation of an allylic carbon in the platinum compounds would be more facile due to the increased electron-withdrawing nature of the more oxidised metal. This is certainly the case for complexes of bis(diphenylphosphino)methane for which complexes the Group 6 metal carbons are deprotonated by LiMe but not by Li[$N(SiMe_3)_2$], whereas complexes of type [PtX_2{$(Ph_2P)_2CH_2$}] (X = Cl, Br or I) are deprotonated by Li[$N(SiMe_3)_2$].[6] The allylic diphosphine complexes **1a**, **1b** or **2a** reacted with either Li[$N(SiMe_3)_2$] or Li($NCMe_2CH_2CH_2CH_2CMe_2$) to give dark red solutions but these were shown by ^{31}P NMR spectroscopy to consist of complex mixtures. In contrast, treatment of **1a** or **2a** in tetrahydrofuran solution with 3 mole equivalents of LiMe gave a red-orange solution which was shown by ^{31}P NMR spectroscopy to consist of a single phosphorus-containing product

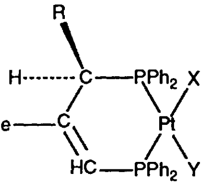
Table 2 $^{31}P\text{-}\{^1H\}$ NMR spectroscopic data[a]

Complex	δ	$^1J(PtP)$/Hz	$^2J(PP)$/Hz	Assignment	Complex	δ	$^1J(PtP)$/Hz	$^2J(PP)$/Hz	Assignment
1a[b]	1.2 (s)	3483	—	PCH_2	**7a**	40.3 (d)	1923	20	PCHMe
1b[b]	−4.4 (s)	3264	—	PCH_2		−2.3 (d)	1735	20	PCH=C
1c[b]	12.7 (s)	1810	—	PCH_2	**7b**[c]	43.4 (d)	1916	20	$PCHCH_2Ph$
1d	9.0 (d)	4044	23	PCH_2 *trans* to I		−1.7 (d)	1725	20	PCH=C
	5.9 (d)	1712	23	PCH_2 *trans* to Me	**7c**	33.1 (d)	1925	19	$PCHSiMe_3$
2a[b]	33.9 (d)	3811	22	PCH_2		−4.0 (d)	1788	19	PCH=C
	−7.2 (d)	3415	22	PCH=C	**7d**[b]	39.5 (dd)	1974	21, 140	$PPh_2CH\textit{P}Ph_2Pt$
2b[b]	39.7 (d)	1917	20	PCH_2		−1.3 (dd)	1753	21, 12[d]	PCH=C
	2.7 (d)	1731	20	PCH=C		−9.8 (dd)	105	140, 12[d]	$\textit{P}Ph_2CHPPh_2Pt$
3[e]	3.8 (s)	1830	—	PCH	**8**[b]	−8.3 (s)	2292	—	PCH_2
4[f]	−7.0 (s)	2074	—	PCH_2	**9**[g]	−1.7 (s)	3696	—	PCH_2
5[f]	22.8 (d)	2296	6	PCH_2	**10**[g]	18.6 (t)	2221	13.3[h]	PCH_2
	−14.9 (d)	2073	6	*P*CH=C		−13.0 (t)	50	13.3[h]	PCHPt
6	−34.1 (s)	1072	—	PCH_2					

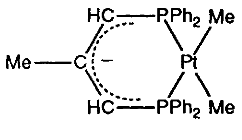
[a] In $CDCl_3$ solution at 301 K and 36.2 MHz, unless stated otherwise. [b] In CD_2Cl_2 solution. [c] Recorded at 330 K, see Discussion for the spectra at low temperatures. [d] $^4J(PP)$/Hz. [e] In tetrahydrofuran solution. [f] In $(CD_3)_2SO$ solution. [g] In C_6D_6 solution. [h] $^3J(PP) + {}^3J(PP)$/Hz.



1a X = Y = Cl
1b X = Y = I
1c X = Y = Me
1d X = Me, Y = I



2a R = H, X = Y = Cl
2b R = H, X = Y = Me
7a R = Me, X = Y = Me
7b R = CH2Ph, X = Y = Me
7c R = SiMe3, X = Y = Me
7d R = PPh2, X = Y = Me



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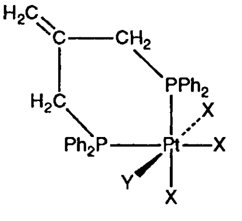
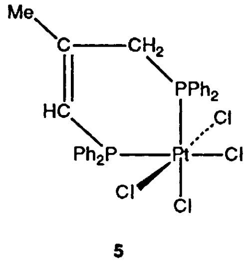


4 X = Y = Cl
6 X = Me, Y = I



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exhibiting a singlet resonance at δ 3.8 with $^1J(PtP) = 1830$ Hz. The platinum–phosphorus coupling indicated that the ^{31}P nuclei were each *trans* to a methyl group and so the complex was assigned the structure $[PtMe_2\{(Ph_2PCH)_2CMe\}]^-$ **3**, a symmetrical structure with the charge delocalized over three carbon atoms and stabilised by the co-ordinated phosphorus atoms. This anion was found to be long-lived in solution in a dry nitrogen atmosphere but reacted with moisture of MeOH to produce $[PtMe_2(Ph_2PCH_2CMe{=}CHPPh_2)]$ **2b**, a similar reaction to that observed with analogous compounds of Mo and W.[1]

This dimethyl complex **2b** could also be made in high yield by treating the unisomerised complex **1c** with 1 mole equivalent of LiMe, followed by MeOH, and was fully characterised. Two separate resonances for the chemically inequivalent Pt–Me groups were observed in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra but we were unable to assign either resonance to a particular methyl group.

One of the problems we encountered in attempting to deprotonate the dihalide complexes **1a**, **1b** or **2a** was their lack of solubility in solvents (such as tetrahydrofuran) suitable for use with strong bases. The dimethylplatinum complexes **1c** and **2b** are much more soluble but treatment with bases such as lithium tetramethylpiperidinide failed to generate the deprotonated complex **3**; a $PtMe_2$ moiety is less electron attracting than a PtX_2 moiety (X = halide).

Our inability to effect clean deprotonation of platinum(II) compounds of the types described above using reagents other than LiMe led us to attempt to prepare and deprotonate complexes of platinum(IV) which, having a more oxidised metal, might deprotonate with milder bases. Treatment of **1a** with an equimolar amount of Cl_2 gave the platinum(IV) complex $[PtCl_4\{(Ph_2PCH_2)_2C{=}CH_2\}]$ **4**, as a yellow microcrystalline solid in very high yield. The ^1H, ^{13}C and ^{31}P NMR spectra in $(CD_3)_2SO$ solution established that **4** was indeed a complex of platinum(IV) and we observed no products that might have resulted from the addition of Cl_2 to the C=C double bond in **1a**. In a similar way, **2a** was converted into $[PtCl_4(Ph_2PCH_2CMe{=}CHPPh_2)]$ **5**. These platinum(IV) complexes, **4** and **5**, were stable in dimethyl sulfoxide (dmso) solution for several hours but over a few days reverted to the platinum(II) complex from which each had been prepared (NMR evidence). Treatment of either **4** or **5** with either $Li[N(SiMe_3)_2]$ or $Li(NCMe_2CH_2CH_2CH_2CMe_2)$ also resulted in the reduction to the corresponding platinum(II) complex **2a** or **2b** and other unidentified products.

Treatment of the dimethylplatinum(II) complex **1c** with MeI resulted in oxidative addition to give the trimethylplatinum(IV) complex *fac*-$[PtMe_3I\{(Ph_2PCH_2)_2C{=}CH_2\}]$ **6**, which was characterised in solution by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopies but was isolated only in low yield due to its relatively rapid loss of ethane (identified in solution from a singlet resonance at δ 0.79 in the ^1H NMR spectrum) to give the monomethylplatinum(II) complex $[PtMe(I)\{(Ph_2PCH_2)_2{=}CH_2\}]$ **1d**, which was isolated in moderate yield. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1d** showed two doublet resonances with $^2J(PP) = 23$ Hz each with satellites due to coupling to ^{195}Pt. As would be expected[7] the coupling of the phosphorus in the *trans* position to iodide was very much larger than that of the phosphorus *trans* to methyl; hence the resonance at δ 9.0, $^1J(PtP) = 4044$ Hz is due to phosphorus *trans* to I whereas that at δ 5.9, $^1J(PtP) = 1712$ Hz, us due to phosphorus *trans* to Me. In the ^1H NMR spectrum the resonance at δ 3.26 with

Table 3 Proton and ^{1}H-{^{31}P} NMR spectroscopic data[a]

Complex	δ	Assignment	Coupling constant/Hz	Assignment
1a[b]	4.70	C=CH$_2$	4.8	^4J(PH) + ^4J(PH)
	3.24	PCH$_2$	13.8	^2J(PH) + ^4J(PH)
			45.0	^3J(PtH)
1b[b]	4.57	C=CH$_2$	4.9	^4J(PH) + ^4J(PH)
			1.8	^4J(HH) + ^4J(HH)
	3.21	PCH$_2$	12.6	^2J(PH) + ^4J(PH)
			1.8	^4J(HH) + ^4J(HH)
			54.5	^3J(PtH)
1c[c]	4.64	C=CH$_2$	6.8	^4J(PH) + ^4J(PH)
	3.46	PCH$_2$	12.2	^2J(PH) + ^4J(PH)
			18.3	^3J(PtH)
	0.62	PtMe$_2$	1.5	^3J(PH) + ^3J(PH)
			68.8	^2J(PtH)
1d[c]	4.51	C=CH	3.6	^4J(PH)
			3.3	^4J(PH)
			1.0	^2J(HH)
	4.45	C=CH	4.1	^4J(PH)
			2.4	^4J(PH)
			1.0	^2J(HH)
	3.26	PCH$_2$ *trans* to I	12.7	^2J(PH)
			0.6	^4J(PH)
			49.6	^3J(PtH)
	3.19	PCH$_2$ *trans* to Me	10.3	^2J(PH)
			1.7	^4J(PH)
			18.3	^3J(PtH)
	0.78	PtMe	7.1	^3J(PH)
			5.6	^3J(PH)
			57.4	^2J(PtH)
2a[b,c]	5.91	PCH=C	13.3	^2J(PH)
			2.2	^4J(PH)
			1.5	^4J(HH)
			55.3	^3J(PtH)
	3.10	PCH$_2$	12.3	^2J(PH)
			2.1	^4J(PH)
			76.8	^3J(PtH)
	1.83	CH$_3$	1.5	^4J(HH)
			1	^4J(PH)
			12.1	^5J(PtH)
2b[c]	6.00	PCH=C	5.7	^2J(PH)
			1.5	^4J(HH)
			18.8	^3J(PtH)
	3.10	PCH$_2$	9.9	^2J(PH)
			28.6	^3J(PtH)
	1.79	C=CMe	1.5	^4J(PH)
			1.5	^4J(HH)
			3	^5J(PtH)
	0.53	PtMe	8.4	^3J(PH)
			7.3	^3J(PH)
			69.2	^2J(PtH)
	0.47	PtMe	8.4	^3J(PH)
			7.0	^3J(PH)
			70.1	^2J(PtH)
4[d]	5.73 (br)	C=CH$_2$	—	—
	4.16	PCH$_2$	15.6	^2J(PH) + ^4J(PH)
			33.0	^3J(PtH)
5[d]	6.70	PCH=C	13.8	^2J(PH)
			2.8	^4J(PH)
			1.5	^4J(HH)
			28.6	^3J(PtH)
	4.22	PCH$_2$	15.7	^2J(PH)
			39.2	^3J(PtH)
	2.63	C=CMe	obscured	
6[c]	4.66 (br)	C=CH$_2$		
	4.22	PCH	13.2	^2J(HH) + ^4J(HH)
			12.7	^2J(PH) + ^4J(PH)
			≈ 0	^3J(PtH)
	3.58	PCH	16.8	^2J(PH) + ^4J(PH)
			13.2	^2J(HH) + ^4J(HH)
			15.6	^3J(PtH)
	1.22	PtMe *trans* to P	1.2	^3J(PH) + ^3J(PH)
			58.8	^2J(PtH)
	0.82	PtMe *trans* to I	6.5	^3J(PH)
			78.6	^2J(PtH)
7a	5.95	PCH=C	2.2	^2J(PH)

Table 3 (*continued*)

Complex	δ	Assignment	Coupling constant/Hz	Assignment
			1.4	$^{4}J(\mathrm{PH})$
			1.4	$^{4}J(\mathrm{HH})$
			25.8	$^{3}J(\mathrm{PtH})$
	3.22	$\mathrm{PC}\mathit{H}\mathrm{Me}$	14.1	$^{2}J(\mathrm{PH})$
			7.0	$^{3}J(\mathrm{HH})$
			0.9	$^{4}J(\mathrm{PH})$
			27.6	$^{3}J(\mathrm{PtH})$
	1.98	$\mathrm{C{=}CMe}$	1.4	$^{4}J(\mathrm{HH})$
	1.09	$\mathrm{PCH}\mathit{Me}$	15.5	$^{3}J(\mathrm{PH})$
			7.0	$^{3}J(\mathrm{HH})$
	0.56	PtMe	7.4	$^{3}J(\mathrm{PH})$
			7.4	$^{3}J(\mathrm{PH})$
			70.0	$^{2}J(\mathrm{PtH})$
	0.56	PtMe	7.6	$^{3}J(\mathrm{PH})$
			7.6	$^{3}J(\mathrm{PH})$
			68.6	$^{2}J(\mathrm{PtH})$
7b	6.06	$\mathrm{PCH{=}C}$	1.8	$^{2}J(\mathrm{PH})$
			1.8	$^{4}J(\mathrm{PH})$
			1.1	$^{4}J(\mathrm{HH})$
			25.2	$^{3}J(\mathrm{PtH})$
	3.53	$\mathrm{PC}\mathit{H}\mathrm{CH_2Ph}$	12.1	$^{2}J(\mathrm{PH})$
			12.1	$^{3}J(\mathrm{HH})$
			3.5	$^{3}J(\mathrm{HH})$
			1.4	$^{4}J(\mathrm{PH})$
			28	$^{3}J(\mathrm{PtH})$
	2.88	$\mathrm{PCHC}\mathit{H}$	13.1	$^{2}J(\mathrm{HH})$
			5.2	$^{3}J(\mathrm{PH})$
			3.5	$^{3}J(\mathrm{HH})$
	2.77	$\mathrm{PCHC}\mathit{H}$	13.1	$^{2}J(\mathrm{HH})$
			12.1	$^{3}J(\mathrm{HH})$
			6.3	$^{3}J(\mathrm{PH})$
	1.41	$\mathrm{C{=}CMe}$	1.1	$^{4}J(\mathrm{HH})$
	0.68	PtMe	7.4	$^{3}J(\mathrm{PH})$
			7.4	$^{3}J(\mathrm{PH})$
			70.3	$^{2}J(\mathrm{PtH})$
	0.60	PtMe	8.3	$^{3}J(\mathrm{PH})$
			7.2	$^{3}J(\mathrm{PH})$
			69.2	$^{2}J(\mathrm{PtH})$
7c	5.87	$\mathrm{PCH{=}C}$	1.3	$^{2}J(\mathrm{PH})$
			1.3	$^{4}J(\mathrm{HH})$
			1.2	$^{4}J(\mathrm{PH})$
			27.7	$^{3}J(\mathrm{PtH})$
	3.17	$\mathrm{PC}\mathit{H}\mathrm{SiMe_3}$	14.7	$^{2}J(\mathrm{PH})$
			2.6	$^{4}J(\mathrm{PH})$
			42.1	$^{3}J(\mathrm{PtH})$
	1.94	$\mathrm{C{=}CMe}$	1.3	$^{4}J(\mathrm{HH})$
	0.63	PtMe	7.1	$^{3}J(\mathrm{PH})$
			7.1	$^{3}J(\mathrm{PH})$
			70.1	$^{2}J(\mathrm{PtH})$
	0.44	PtMe	7.9	$^{3}J(\mathrm{PH})$
			7.2	$^{3}J(\mathrm{PH})$
			68.6	$^{2}J(\mathrm{PtH})$
	−0.41	$\mathrm{SiMe_3}$	6.6	$^{2}J(\mathrm{SiH})$
7d[b]	5.91	$\mathrm{PCH{=}C}$	2.6	$^{2}J(\mathrm{PH})$
			1.2	$^{4}J(\mathrm{HH})$
			1.0	$^{4}J(\mathrm{PH})$
			1.0	$^{4}J(\mathrm{PH})$
			29.1	$^{3}J(\mathrm{PtH})$
	4.59	PCHP	11.7	$^{2}J(\mathrm{PH})$
			1.6	$^{2}J(\mathrm{PH})$
			1.6	$^{4}J(\mathrm{PH})$
			33.1	$^{3}J(\mathrm{PtH})$
	1.26	$\mathrm{C{=}CMe}$	1.2	$^{4}J(\mathrm{HH})$
			1.2	$^{4}J(\mathrm{PH})$
	0.50	PtMe	8.1	$^{3}J(\mathrm{PH})$
			7.3	$^{3}J(\mathrm{PH})$
			69.0	$^{2}J(\mathrm{PtH})$
	0.40	PtMe	7.3	$^{3}J(\mathrm{PH})$
			7.3	$^{3}J(\mathrm{PH})$
			70.1	$^{2}J(\mathrm{PtH})$
8[b,c]	4.51 (br)	$\mathrm{C{=}CH_2}$		
	4.19 (br)	$\mathrm{PCH_2}$	32.2	$^{3}J(\mathrm{PtH})$
9[c,e]	3.83 (br)	$\mathrm{C{=}CH_2}$		
	3.15	$\mathrm{PCH_2}$	8.8	$^{2}J(\mathrm{PH}) + {}^{4}J(\mathrm{PH})$
			18.3	$^{3}J(\mathrm{PtH})$
10[e]	4.44	$\mathrm{C{=}CH}$	2.2	$^{2}J(\mathrm{HH})$
			1.7	$^{4}J(\mathrm{HH})$
			17.5	$^{4}J(\mathrm{PtH})$

Table 3 (*continued*)

Complex	δ	Assignment	Coupling constant/Hz	Assignment
	4.22	C=CH	2.2	^2J(HH)
			1.7	^4J(HH)
			12.0	^4J(PtH)
	4.06	PtCH	1.8	^4J(HH)
			64.0	^2J(PtH)
	3.63	PtPCH	13.8	^2J(HH)
			13.7	^2J(PH) + ^4J(PH)
			1.7	^4J(HH)
			1.7	^4J(HH)
	2.49	PtPCH	13.8	^2J(HH)
			12.4	^2J(PH) + ^4J(PH)
			1.8	^4J(HH)
			32.5	^3J(PtH)

[a] In $CDCl_3$ solution at 400.13 MHz and 301 K unless stated otherwise; br = broad. [b] In CD_2Cl_2 solution. [c] Recorded at 99.5 MHz. [d] In $(CD_3)_2SO$ solution at 323 K. [e] In C_6D_6 solution.

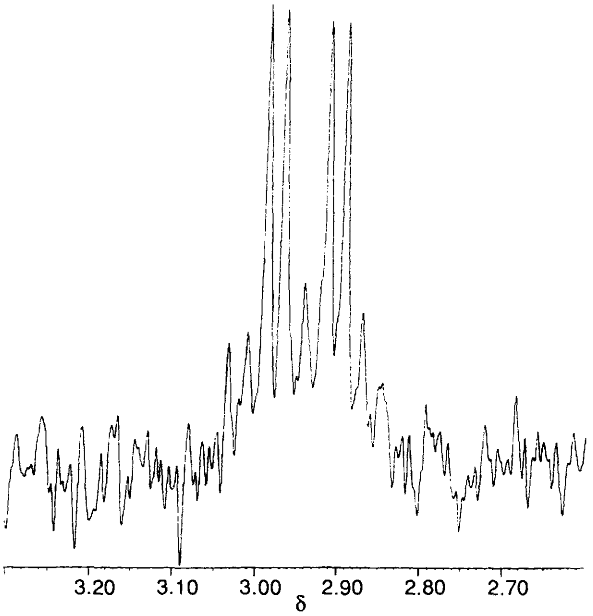


Fig. 1 The ^{29}Si-{^{1}H} NMR spectrum of complex **7c** in CD_2Cl_2 solution at 79.5 MHz. The couplings to both ^{31}P nuclei can be seen clearly; the smaller peaks are assigned to satellites due to coupling to platinum-195

^3J(PtH) = 49.6 Hz, is assigned to the CH_2 *trans* to iodide and the resonance at δ 3.19 with ^3J(PtH) = 18.3 Hz is assigned to the CH_2 *trans* to methyl. The C=CH_2 protons appeared as multiplets at δ 4.45 and 4.51 and although the couplings between these protons and the phosphorus nuclei and PCH_2 protons were resolved we did not assign the alkenyl resonances to any particular group of protons.

The formation of the anionic complex **3** allowed us to prepare derivatives of **2b** by treating this anion with electrophiles, *i.e.* to prepare complexes containing a substituted ligand of type *Z*-$Ph_2PCHRMe$=$CHPPh_2$; similar conversions were carried out in our previous work with complexes of Mo and W.[1] When a solution of **3** in tetrahydrofuran was treated with 1 mole equivalent of MeI the red-orange colour of the solution was discharged over a few seconds and in the ^{31}P-{^{1}H} NMR spectrum two new doublet resonances appeared which had chemical shifts and coupling constants similar to those for **2b**. The product was isolated and elemental analysis and spectroscopic data showed that it was the hoped-for methylated derivative **7a**. The position of the introduced methyl group α to the allylic phosphorus was shown by a quartet splitting of the PC*H*(Me) proton [^3J(HH) = 7.0 Hz] in the ^{1}H NMR spectrum. In addition, the loss of a plane of symmetry through the molecule was confirmed by the ^{13}C-{^{1}H} NMR spectrum wherein separate resonances were observed for the four PPh groups.

Treatment of the anion **3** with $PhCH_2Br$ gave the benzylated derivative [$PtMe_2${$Ph_2PCH(CH_2Ph)CMe$=$CHPPh_2$}] **7b**. The ^{31}P-{^{1}H} NMR spectrum of **7b** at 161.5 MHz and 301 K in dichloromethane was broad but, on cooling to 223 K, it showed the presence of two species: the major species gave two doublet resonances with satellites at δ 42.5 [^1J(PtP) = 1950] and −2.4 [^1J(PtP) = 1728 Hz] with ^2J(PP) = 20.0 Hz whilst the minor species, only about 1–2% of the whole, gave a pair of doublet resonances with satellites at δ 67.0 [^1J(PtP) = 1965] and 6.3 [^1J(PtP) = 1770 Hz] with ^2J(PP) = 20.4 Hz. The high-temperature limit for the process of interconversion was approached when the spectrum was recorded at 300 K and 36.2 MHz: under these conditions the whole spectrum consisted of two doublets with satellites, chemical shifts and coupling constants being similar to those of the major species. We have observed similar changes in the ^{31}P-{^{1}H} NMR spectra of complexes of Mo and W of *Z*-$Ph_2PCH(CH_2R')CMe$=$CHPPh_2$ (R′ = Me, CH=CH_2 or Ph) and ascribed them to conformational isomers related by rotation about the R′CH_2–CHP bond,[1] and it seems possible that the temperature dependence of the ^{31}P-{^{1}H} NMR spectrum of **7b** is due to a similar cause. The phenomenon was also detected in the ^{13}C-{^{1}H} NMR spectrum of **7b** in which several of the resonances were broad at 301 K but sharpened upon cooling to 233 K or warming to 325 K (see Table 4), and in the ^{195}Pt-{^{1}H} NMR spectrum in which the signal was very much broader than those for the other complexes we report.

Treatment of anion **3** with $SiMe_3Cl$ gave the trimethylsilyl derivative [$PtMe_2${$Ph_2PCH(SiMe_3)CMe$=$CHPPh_2$}] **7c**; this compound showed spectroscopic properties similar to those of the methylated complex **7a**. We recorded the ^{29}Si-{^{1}H} NMR spectrum of this compound (see Fig. 1) which appeared as a doublet of doublets at δ 2.94, ^2J(PSi) = 6.0 Hz, ^4J(PSi) = 1.6 Hz and which also exhibited coupling to the platinum nucleus, ^3J(PtSi) = 7.0 Hz.

Another derivative, [$PtMe_2${$Ph_2PCH(PPh_2)CMe$=$CHPPh_2$}] **7d**, was prepared by treating the anion **3** with PPh_2Cl. The ^{31}P-{^{1}H} NMR spectrum of this triphosphine complex **7d** showed three doublet of doublet resonances assigned to P_a, P_b and P_c, with satellites due to coupling to ^{195}Pt (see Fig. 2). The shifts of P_a and P_b are similar to those of other complexes of type **7** and these atoms are clearly shown to be bound to the platinum by the size of the coupling constants, ^1J(PtP) = 1974 and 1753 Hz, respectively; the resonance for P_c also showed coupling to the platinum, ^3J(PtP) = 105 Hz. The ^{195}Pt-{^{1}H} NMR spectrum of **7d** appeared as a double doublet of doublets with the magnitudes of the couplings to the three ^{31}P nuclei in agreement with those found in the ^{31}P spectrum.

It should be noted that the ^{195}Pt NMR spectra of the five complexes **2b** and **7a**–**7d** had chemical shifts within about 60 ppm of each other, with no obvious relationship between

Table 4 ^{13}C-{^{1}H} NMR spectroscopic data[a]

					Aromatics					
Complex	HC=*C*	H*C*=C	P*C*HR	C=C*C*H$_3$	P*C*$_{ipso}$	P*C*$_{ortho}$	P*C*$_{meta}$	P*C*$_{para}$	PtCH$_3$	Others
1a[b]	134.2[c] —	119.7 (t) (9.6[d])	36.9 (t) (42.7[e])	—	129.1 (m) (65.1[e])	134.1 (t) (10.1[f])	128.9 (t) (10.5[g])	131.9 (s) —	—	—
1b[b]	134.1 (s) —	119.1 (t) (9.0[d])	36.8 (t) (41.8[e])	—	130.9 (m) (74.6[e])	134.3 (br) —	128.6 (t) (11.3[g])	131.7 (s) —	—	—
1c[h]	138.2 (s) —	116.9 (t) (8.6[d])	39.3 (t) (27.5[e])	—	132.9 (m) (43.9[e])	133.5 (t) (10.3,[f] *18.3*)	128.0 (t) (9.2[g])	129.7 (s) —	4.6 (dd) (101.2,[i] 10.3,[i] *597*)	
1d	136.1 (dd) (4.9,[i] 1.5,[i] *14.5*)	117.7 (t) (8.8[d])	38.7 (dd) (33.3, 7.4,[d] *30*)	—	133.5 (d) (46.1)	134.0 (d) (10.5,[i] *13.3*)	128.3 (d) (11.0[d])	130.9 (d) (2.7[j])	2.6 (dd) (94.3,[i] 5.4, *450*)	—
			38.6 (dd) (23.5, 3.6,[d] *22*)		129.3 (dd) (59.6, 1.2,[d] *47.2*)	133.5 (d) (10.7,[i] *32.8*)	127.9 (d) (10.1[d])	130.1 (d) (2.3[j])		
2a[b]	153.5 (dd) (4.4,[i] 4.4,[i] *30*)	116.3 (dd) (63.7, 12.2[d])	31.2 (dd) (36.0, 16.0[d])	29.9 (dd) (13.6[d])	128.9 (d) (69.4)	133.9 (d) (11.5[i])	129.0 (d) (11.0[d])	132.2 (d) (1.9[j])	—	—
					127.9 (d) (64.2)	133.8 (d) (11.8[i])	128.9 (d) (11.6[d])	131.8 (d) (1.9[j])		
2b	150.4 (dd) (7.3,[i] 3,[i] *8*)	119.1 (dd) (43.9, 12.2[d])	32.2 (dd) (25, 9,[d] *8*)	30.5 (dd) (12.2,[d] 2.5[d])	*k*	133.4 (d) (11.0[i])	128.2 (d) (9.8[d])	130.0 (d) (2.4[j])	3.6 (dd) (102.8,[i] 6.7[i])	—
						133.3 (d) (11.0[i])		129.7 (d) (2.4[j])	2.3 (dd) (95.2,[i] 6.7[i])	
4[l]	134.7 (t) (4.3[i])	127.7 (br)	32.4 (t) (46.4[e])	—	128.0 (t) (67.9[e])	138.5 (br s)	131.5 (t) (11.4[g])	136.1 (br s)	—	—
5[l]	161.7 (dd) (5.8,[i] 3.7[i])	116.7 (dd) (64.2, 11.5[d])	30.7 (dd) (34.4, 12.8[d])	33.5 (dd) (15.4,[d] 4.3[d])	128.8 (d) (66.4)	138.8 (d) (7.2[i])	131.6 (d) (12.3[d])	136.1 (s) —	—	—
					128.1 (d) (72.7)	138.4 (d) (7.0[i])	131.3 (d) (11.6[d])	135.9 (s) —		
6[b,m]	137.5 (t) (1.8[i])	120.4 (t) (9.0[d])	39.1 (t) (26.2[e])	—	129.4 (m) (46.9[e])	134.7 (t) (7.7[f])	127.8 (t) (8.8[g])	130.3 (s) —	12.7 (t) (1.8,[i] *624.5*)	—
					129.3 (m) (45.4[e])	133.9 (t) (8.3[f])	127.6 (t) (9.2[g])	130.2 (s) —	5.8 (dd) (115.9,[i] 8.0,[i] *501.4*)	
7a	157.8 (dd) (10.8,[i] 1.0,[i] *5.4*)	117.1 (dd) (43.4, 11.5[d])	32.5 (dd) (27.2, 10.8,[d] *3.8*)	30.5 (dd) (12.4,[d] 4.4[d])	135.8 (dd) (51.1, 3.0,[d] *18.4*)	134.2 (d) (12.0,[i] *19.8*)	128.2 (d) (9.8[d])	130.1 (d) (1.8[j])	4.4 (dd) (95.1,[i] 6.4,[i] *609.9*)	18.5 (d) (7.6,[i] *24.2*)
					133.1 (d) (44.6, *19.4*)	134.1 (d) (10.9,[i] *18.0*)	128.1 (d) (9.3[d])	129.8 (d) (2.1[j])	3.9 (dd) (99.6,[i] 7.3,[i] *604.5*)	
					132.2 (d) (41.6, *18.8*)	133.7 (d) (11.5,[i] *22.9*)	127.7 (d) (9.6[d])	129.9 (d) (2.0[j])		
					131.1 (dd) (38.1, 3.0,[d] *28.6*)	132.1 (d) (10.9,[i] *14.3*)	127.6 (d) (9.5[d])	128.8 (d) (2.0[j])		
7b	156.8 (d)[n] (9.3[i])	118.2 (br) (42.5, 10.8[d])	41.4 (dd) (23.9, 10.5[d])	32.7 (dd)[n] (12.8,[d] 4.2[d])	136.3 (br d) (52.1)	135.6 (d) (12.3,[i] *23.6*)	128.5 (d) (9.9[d])	130.5 (d) (2.1[j])	4.4 (dd) (95.4,[i] 6.5,[i] *612.9*)	39.1 (d)[n] (11.3[i])
					132.5 (d) (44.3, *19.3*)	134.5 (d) (11.0,[i] *19.0*)	128.1 (d) (9.5[d])	130.3 (d) (1.7[j])	4.0 (dd) (110.4,[i] 7.4,[i] *606.0*)	139.0 (d) (14.4[d])
					132.1 (d) (41.0, *17.4*)	134.1 (d) (11.9,[i] *23.5*)	127.9 (d) (9.5[d])	130.0 (d) (2.0[j])		128.6 (s) 128.0 (s) 126.1 (s)
					131.4 (dd) (37.0, 3.0,[i] *30.6*)	131.7 (br) (10.6[i])	127.7 (d) (9.6[d])	128.7 (d) (1.8[j])		
7c	155.9 (d) (12.2[i])	114.8 (dd) (45.2, 12.7[d])	32.0 (dd) (10.7, 10.7[d])	34.3 (dd) (12.5,[d] 4.9[d])	137.4 (dd) (52.5, 3.6[d])	135.3 (d) (11.6,[i] *17.9*)	128.1 (d) (9.5[d])	130.1 (d) (2.0[j])	4.0 (dd) (94.9,[i] 6.7[i])	0.2 (d) (2.1[d])
					135.9 (d) (37.2)	135.1 (d) (11.5,[i] *18.7*)	128.1 (d) (9.2[d])	130.0 (d) (2.2[j])	2.7 (dd) (101.4,[i] 6.9[i])	
					131.7 (d) (43.3)	132.7 (d) (11.8,[i] *22.0*)	127.9 (d) (9.6[d])	129.6 (d) (1.8[j])		
					130.9 (dd) (39.6, 3.9[d])	131.7 (d) (11.0,[i] *14.7*)	127.6 (d) (9.7[d])	128.5 (d) (2.0[j])		
7d	153.3 (br d) (10.3)	119.5 (br dd) (46.0, 11.5[d])	37.0 (br ddd) (26, 21, 9[d])	32.7 (dd) (10.3,[d] 4.0[d])	*k*	*k*	*k*	*k*	5.3 (br dd) (95.8,[i] 6.5,[i] *610*)	
									3.4 (dd) (101.5,[i] 7.2,[i] *609.0*)	
8[o]	131.2 (br s) —	122.5 (br) —	35.9 (t) (20.8[p])	—	126.0 (m) (31.5[p])	133.9 (br s) —	129.7 (br s) —	133.1 (br s) —		

Table 4 (*continued*)

Complex	HC=*C*	H*C*=C	P*C*HR	C=C*C*H$_3$	Aromatics P*C*$_{ipso}$	 P*C*$_{ortho}$	 P*C*$_{meta}$	 P*C*$_{para}$	PtCH$_3$	Others
9^h	139.0 (s) —	115.0 (br) —	44.6 (t) (20.8^p)	—	141.2 (m) (35.4^p)	132.4 (br) —	127.3 (br) —	127.0 (br) —		
10^q	150.6 (s) (*39.8*)	105.8 (m) (15.9^g)	44.1 (m) (88.9,^{i} 43.8, (14.6,^{i} 8.0^d) 37.9 (t) (35.8^e)	—	*k*	*k*	*k*	*k*	—	—

^{a} Recorded in CDCl$_3$ solution at 301 K and an operating frequency of 100.6 MHz unless stated otherwise. Figures in parentheses are coupling constants to ^{31}P and, unless otherwise shown, are ^1J(PC); italicised figures are couplings to ^{195}Pt; m = multiplet. ^{b} In CD$_2$Cl$_2$ solution. ^{c} Obscured. ^{d} ^3J(PC). ^{e} ^1J(PC) + ^3J(PC). ^{f} ^2J(PC) + ^4J(PC). ^{g} ^3J(PC) + ^5J(PC). ^{h} Recorded at 22.5 MHz. ^{i} ^2J(PC). ^{j} ^4J(PC). ^{k} Resonance not assigned. ^{l} In (CD$_3$)$_2$SO solution at 323 K. ^{m} Recorded at 253 K. ^{n} Resonance broad at 301 K but sharp at 223 K. Data refer to the spectrum at 223 K. ^{o} In 1:1 (CD$_3$)$_2$CO–D$_2$O solution. ^{p} Value for *N* doublet. ^{q} In C$_6$D$_6$ solution.

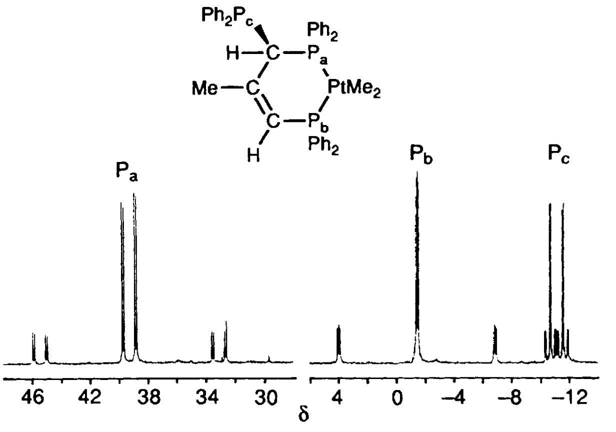
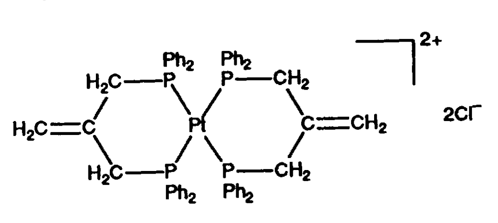


Fig. 2 The ^{31}P-{^{1}H} NMR spectrum of complex **7d** in CD$_2$Cl$_2$ solution at 161.5 MHz showing the three resonances for the three nuclei P$_a$, P$_b$ and P$_c$



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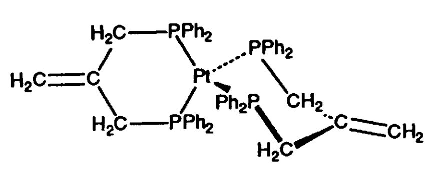

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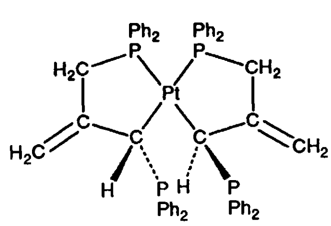

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chemical shift and steric or electronic properties of the group α to the phosphorus. The chemical shift of the ^{195}Pt resonance of anion **3** (δ −208) was very close to that of **2b**, which suggests that the charge delocalisation in the anionic complex is restricted to the C$_3$ chain. The fast atom bombardment (FAB) mass spectra of the methyl complexes of platinum, **1c** and **7a**–**7d**, all showed the loss of one methyl group followed by a methane molecule as the principal fragmentation pathway.

From the reactions that have been carried out on complexes of (Ph$_2$P)$_2$CH$_2$ (dppm), it is clear that a residual positive charge facilitates deprotonation. For example, [Pt(dppm)$_2$]Cl$_2$ is deprotonated by KOH–EtOH to give [Pt(dppm − H)$_2$][8] and analogous reactions with complexes of palladium suggest that deprotonation can be brought about by weak bases such as NEt$_3$ or Na$_2$CO$_3$.[9] By contrast, [PtCl(dppm)(PEt$_3$)]$^+$ requires NaH to effect deprotonation.[10] We have therefore attempted to prepare cationic platinum complexes containing two (Ph$_2$PCH$_2$)$_2$C=CH$_2$ ligands with the expectation that they might deprotonate more readily than neutral species.

Treatment of PtCl$_2$ with 2 mole equivalents of (Ph$_2$PCH$_2$)$_2$C=CH$_2$ in EtOH gave the salt [Pt{(Ph$_2$PCH$_2$)$_2$C=CH$_2$}$_2$]Cl$_2$ **8**, which was fully characterised. The ^{31}P-{^{1}H} NMR spectrum showed a single resonance, with satellites, although the value of ^1J(PtP) was somewhat solvent dependent: 2292 Hz in CD$_2$Cl$_2$ solution and 2228 Hz in Me$_2$CO–water solution. The ^{195}Pt-{^{1}H} NMR spectrum consists of binomial quintet at δ −500. In the FAB mass spectrum the parent ion appeared at 1079 (for ^{195}Pt) which was in excellent agreement with [Pt{(Ph$_2$PCH$_2$)$_2$C=CH$_2$}$_2$]Cl$^+$ and the first fragmentation pathway involved loss of Cl to give *m*/*z* = 1043. We attempted to effect a prototropic shift reaction on the dicationic complex **8** in a similar way to the isomerisation of **1a** to **2a**, *i.e.* by heating it with NaOEt in EtOH solution, but instead of isomerising the carbon backbone of the diphosphine the major product of the reaction was the platinum(0) complex [Pt{(Ph$_2$PCH$_2$)$_2$C=CH$_2$}$_2$] **9**; this complex was prepared more cleanly and in higher yield by treating the platinum(II) dication **8** with NaBH$_4$ in EtOH. The pure complex was isolated as a bright yellow microcrystalline solid. In the mass spectrum the parent ion was centred at *m*/*z* 1044 with the principal fragmentation routes being loss of PPh$_2$ followed by loss of C$_4$H$_6$.

We attempted to deprotonate the dicationic platinum(II) complex **8** using the reagents Li[N(SiMe$_3$)$_2$] or Li(NCMe$_2$CH$_2$CH$_2$CH$_2$CMe$_2$) in the hope of obtaining a neutral species [Pt{(Ph$_2$PCH)$_2$CMe}$_2$] with two anionic ligands, however these reagents produced mixtures which contained a large proportion of the platinum(0) complex **9** (^{31}P-{^{1}H} NMR evidence). In contrast, when the dicationic complex **8** was treated with 3 mole equivalents of LiBu in C$_6$H$_6$, in the presence of 1 equivalent of Me$_2$NCH$_2$CH$_2$NMe$_2$ per Li, a dark red solution was obtained. Addition of MeOH and removal of the solvent left a pale yellow solid, which from elemental analysis and mass spectral data appeared to be the required neutral species formed by double deprotonation of **8**. This product was unstable in many common organic solvents

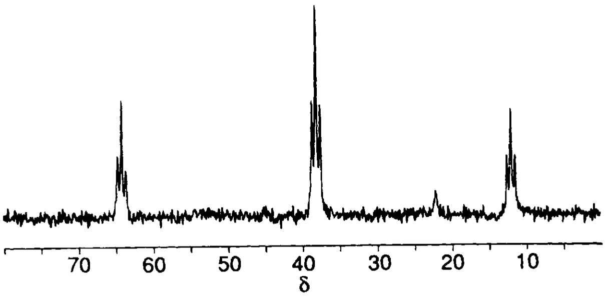

Fig. 3 The ^{195}Pt-{^{1}H} NMR spectrum of complex **10** in CD_2Cl_2 solution at 85.6 MHz

but ^{1}H, ^{13}C and ^{31}P NMR spectra of moderate quality were obtained. The ^{31}P-{^{1}H} NMR spectrum consisted of two triplet resonances, at δ 18.6 and −13.0, with coupling constants to platinum of 2221 and 50 Hz, respectively. The chemical shift value of δ −13.0 and the very small coupling to platinum (50 Hz) clearly showed that two of the phosphine groups were no longer co-ordinated to the platinum. The ^{195}Pt-{^{1}H} NMR spectrum consisted of a triplet of triplets resonance pattern (see Fig. 3). The ^{1}H NMR spectrum of the product showed five resonances assigned to protons in the backbone of the diphosphine; two of these, at δ 2.49 and 3.63, showed a mutual coupling of 13.8 Hz, typical of geminal protons, in addition to second-order coupling to ^{31}P. The ^{31}P coupling appeared to be non-limiting and so we concluded that the PCH_2 groups were not mutually *trans* across the metal centre. As the PCH_2 protons were inequivalent, the complex did not have a plane of symmetry containing the Pt–P bonds. Two resonances, at δ 4.22 and 4.44, showed a mutual coupling of 2.2 Hz and were assigned to inequivalent protons in an intact $C=CH_2$ group. The remaining resonance, at δ 4.06, showed coupling to platinum of 64.0 Hz, a value typical for a proton on a carbon atom directly bonded to a platinum. It thus appeared that the neutral complex formed by the deprotonation reaction contained two identical bidentate ligands, each bonded to the platinum by one phosphorus and one carbon, forming a five-membered ring; we therefore formulate this complex as **10**. The carbon atoms attached to the metal are therefore chiral centres but only one diastereoisomer was observed, the two unco-ordinated PPh_2 groups presumably being on opposite sides of the co-ordination plane for steric reasons. The ^{13}C-{^{1}H} NMR spectrum provided corroborative evidence for the assignment of the structure. Four non-phenyl resonances were observed, with one at δ 44.1 showing a complex coupling pattern but which clearly contained one coupling constant ^2J(PC) of *ca.* 90 Hz indicating the position of the metal-bound carbon atom as being *trans* to a ^{31}P donor atom. The displacement of a co-ordinated phosphine by a carbanion in the α position has also been observed in the deprotonation of $[\{Pt(PPh_3)\}_2(\mu\text{-dppm-}P,P')_2]^{2+}$ by KOH to give $[\{Pt(PPh_3)\}_2(\mu\text{-dppm-}P,P')(\mu\text{-dppm} - \text{H-}P,C)]$.[11]

Experimental

The general methods and instrumentation used were the same as those reported in recent papers from this laboratory.[1] The ^{195}Pt NMR spectra were recorded using a JEOL FX90-Q F.T. or Bruker AM-400 spectrometer and referenced using the 21.4 MHz (Goodfellow) scale,[4] ^{29}Si NMR spectra using a Bruker AM-400 spectrometer with an operating frequency for ^{29}Si of 79.5 MHz and referenced to $SiMe_4$, and FAB mass spectra using a VG Autospec with 8 kV acceleration, samples being contained in a *m*-nitrobenzyl alcohol mull.

Preparations.—$[PtCl_2\{(Ph_2PCH_2)_2C=CH_2\}]$ **1a**. The compound $(Ph_2PCH_2)_2C=CH_2$ (0.580 g, 1.37 mmol) was added to a stirred suspension of $[Pt(cod)Cl_2]$ (0.505 g, 1.35 mmol) in CH_2Cl_2 (10 cm^3). The required product was precipitated within 5 min. Diethyl ether (10 cm^3) was added and the product was filtered off, washed with more Et_2O and dried. It formed white *microcrystals*. Yield 0.890 g, 95%.

$[PtI_2\{(Ph_2PCH_2)_2C=CH_2\}]$ **1b**. The dichloride **1a** (0.274 g, 0.397 mmol) was refluxed in Me_2CO (10 cm^3) with NaI (1.6 g) for 5 h; at the end of this time yellow *microcrystals* had been deposited. These were filtered off and washed with EtOH. Water was added to the washings and a second crop of the product was isolated. Total yield 0.326 g, 94%.

$[PtMe_2\{(Ph_2PCH_2)_2C=CH_2\}]$ **1c**. A solution of $(Ph_2PCH_2)_2C=CH_2$ (0.396 g, 0.933 mmol) in benzene (10 cm^3) was added to a solution of $[PtMe_2(cod)]$ (0.311 g, 0.934 mmol) in benzene (2 cm^3). After 5 min the solvent was removed under reduced pressure and the residue triturated with Me_2CO (2 cm^3) and EtOH (5 cm^3). The required dimethylplatinum complex **1c** was collected as white *microcrystals* and washed with EtOH. Yield 0.510 g, 84%.

$[PtMe(I)\{(Ph_2PCH_2)_2C=CH_2\}]$ **1d**. Methyl iodide (1 cm^3) was added to a solution of the dimethylplatinum complex **1c** (0.020 g, 0.030 mmol) in CH_2Cl_2 (2 cm^3) and the resultant solution cooled to 275 K. After 2 h at 275 K only the resonance due to the trimethylplatinum(IV) complex **6** was apparent in the ^{31}P NMR spectrum. The solvent was evaporated under reduced pressure at 275 K to leave a colourless oil. This oil, when redissolved in $CDCl_3$ at 275 K, was shown to consist of **6** and **1d**. Only **1d** remained in solution after 12 d at 275 K. Addition of EtOH (0.5 cm^3) to the solution allowed the product to be collected as pale yellow *crystals*. Yield 0.015 g, 63%. In a separate experiment **6** was isolated in 27% yield by triturating the initial crude product with EtOH.

$[PtCl_2(Ph_2PCH_2CMe=CHPPh_2)]$ **2a**. Complex **1a** (0.150 g, 0.217 mmol) was heated in refluxing EtOH (10 cm^3) with NaOEt (0.3 cm^3 saturated solution in EtOH) for 15 min during which time the solution became very dark red. Concentrated HCl solution was then added dropwise until the reaction mixture was acidic and this caused the discharge of most of the colour. The solvent was removed under reduced pressure, the residue extracted with CH_2Cl_2 and the extract passed through a Florisil column. Evaporation of the solvent gave the dichloride **2a** as off-white *microcrystals* which could be recrystallised from EtOH. Yield 0.045 g, 30%.

$[PtMe_2(Ph_2PCH_2CMe=CHPPh_2)]$ **2b**. A suspension of the dichloride **1a** (0.100 g, 0.145 mmol) in dry tetrahydrofuran (9 cm^3) under Ar was treated with LiMe (0.8 cm^3 of 0.8 mol dm^{-3} solution in Et_2O, 0.64 mmol). The mixture was then stirred for 15 min during which time the dichloride dissolved to give a bright orange-red solution of anion **3**. Methanol was then added and the colour immediately discharged. The solvent was removed under reduced pressure and the product extracted into benzene. The benzene solution was filtered through a Celite column and the solvent was then removed under reduced pressure. The residue was triturated with EtOH which gave the required dimethylplatinum complex **2b** as white *microcrystals*. Yield 0.058 g, 62%.

$[PtCl_4\{(Ph_2PCH_2)_2C=CH_2\}]$ **4**. Chlorine (0.6 cm^3 of 0.85 mol dm^{-3} solution in CCl_4, 0.51 mmol) was added to a stirred solution of the dichloride complex **1a** (0.340 g, 0.490 mmol) in CH_2Cl_2 (25 cm^3). The solution, which immediately became yellow, was stirred for 20 min during which time the tetrachloroplatinum(IV) complex **4** was obtained as yellow *microcrystals*. The solid was filtered off, washed with CCl_4 and dried. Yield 0.322 g, 86%.

$[PtCl_4(Ph_2PCH_2CMe=CHPPh_2)]$ **5**. This complex was obtained in 87% yield using the same method as that for **4**, above, but starting from **2a**.

$[PtMe_2\{Ph_2PCH(Me)CMe=CHPPh_2\}]$ **7a**. Methyllithium (0.22 cm^3 of 1.17 mol dm^{-3} solution in Et_2O, 0.26 mmol) was added to a solution of the dimethyl complex **1c** (0.171 g, 0.26 mmol) in dry tetrahydrofuran (5 cm^3) under Ar. The solution became bright orange-red and was stirred for 5 min before MeI (16 mm^3, 0.26 mmol) was added; the colour was immediately discharged. The solvent was removed under reduced pressure and benzene (5 cm^3) and water (1 cm^3) were added to the residue which was then evaporated again before benzene was added and the solution dried over $MgSO_4$. The solution was then filtered using a Celite column and concentrated to approximately 2 cm^3 after which EtOH (5 cm^3) was added to give complex **7a** as an off-white *microcrystalline solid.* Yield 0.104 g, 60%.

Complexes **7b**–**7d** were prepared similarly from **1a** but using 3 mole equivalents of LiMe and $PhCH_2Br$ (**7b**, 66% yield), $SiMe_3Cl$ (**7c**, 29%) or PPh_2Cl (**7d**, 63%).

$[Pt\{(Ph_2PCH_2)_2C{=}CH_2\}_2]Cl_2$ **8**. Platinum(II) chloride (0.400 g, 1.50 mmol) and $(Ph_2PCH_2)_2C{=}CH_2$ (1.31 g, 3.08 mmol) were suspended in EtOH (25 cm^3) and stirred under N_2 for 24 h. The resulting white *microcrystalline solid* was washed with EtOH and then Et_2O before being dried under vacuum. Yield 1.455 g, 87%.

$[Pt\{(Ph_2PCH_2)_2C{=}CH_2\}_2]$ **9**. Complex **8** (0.247 g, 0.222 mmol) was suspended in EtOH (10 cm^3) under N_2 and $NaBH_4$ (0.5 g) was added. The resulting yellow suspension was stirred for 10 min before water (5 cm^3) was added. The yellow *microcrystalline solid* was filtered off and dried over P_4O_{10}. Yield 0.174 g, 75%.

$[Pt\{Ph_2PCH_2C({=}CH_2)CHPPh_2\}_2]$ **10**. Butyllithium (1.15 cm^3 of a 1.6 mol dm^{-3} solution in hexanes, 1.84 mmol) and $Me_2NCH_2CH_2NMe_2$ (278 mm^3, 1.84 mmol) were dissolved in dry C_6H_6 (5 cm^3) under Ar and added over 15 min to a stirred suspension of complex **8** (0.512 g, 0.460 mmol) in C_6H_6 (5 cm^3). The solution became dark red. Stirring was continued for 10 min before MeOH (1 cm^3) was added and the solvent removed from the resulting colourless solution. Methanol was added to the residue to give complex **10** as an off-white *microcrystalline solid* which was filtered off and dried *in vacuo*. Yield 0.220 g, 46%.

Acknowledgements

We thank the SERC for a post-doctoral fellowship (to J. D. V.) and for other support. We thank Johnson-Matthey for a very generous loan of platinum salts.

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Received 27*th November* 1991; *Paper* 1/06015E