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Chemistry and crystal structure of $[ClPt(NMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2)]Cl$ containing a tridentate ylide ligand *

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Abstract

Treatment of *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ with Me_2NNH_2 in hot benzene gives the title compound (**1a**) in high yield. Similar treatment of $[PtX_2(PPh_2CH{=}CH_2)_2]$, X = Br or I, gives the corresponding bromo- or iodo-complexes $[XPt(NMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2)]X$, X = Br or I. **1a** with NH_4PF_6 gives the corresponding PF_6 salt $[ClPt(NMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2)][PF_6]$, which with dilute HCl and NH_4PF_6 gives $[ClPt(NMe_2NH_2CH_2CHPPh_2CH_2CH_2PPh_2)][PF_6]_2$. Treatment of **1a** with $NaBH_4$ gives a neutral hydrido complex, formulated as $[HPt(NMe_2NHCH_2CPPh_2CH_2CH_2PPh_2)]$. The crystal structure of **1a** has been determined. NMR data are given.

Introduction

For reasons discussed previously [1], one would expect the vinyl double bond of the coordinated vinylphosphine, $Ph_2PCH{=}CH_2$, to be less activated towards Michael addition or nucleophilic attack than the vinylidene double bond of chelated $Ph_2PC({=}CH_2)PPh_2$ (vdpp). We have found this to be the case for complexes of the types $[M(CO)_4(\text{vdpp-}PP')]$ (M = Mo or W), which readily undergo Michael addition with a variety of amines or hydrazines [2], whereas complexes of the type *cis*-$[M(CO)_4(PPh_2CH{=}CH_2)_2]$ (M = Mo or W) show no tendency to add on amines or hydrazines [3]; these coordinated bisdiphenyl(vinyl)phosphines will, however, undergo Michael addition, when treated with *cis*-$[M(CO_4(PPh_2H)_2]$ in the presence of $KOBu^t$ [4].

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* This paper is dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday. We value his many contributions to chemistry and the help and support he has given to younger people over the years.

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However, we have shown that platinum(II) or palladium(II) halides are very highly activating when coordinated to vdpp, which then, even at low temperatures, undergoes Michael additions readily [5,6]. We thus thought that platinum(II) halides might be sufficiently activating to cause the vinyl double bond of coordinated $PPh_2CH{=}CH_2$ to undergo Michael additions. We have shown previously that *N*,*N*-dimethylhydrazine adds particularly rapidly and cleanly to the vinylidene double bond of coordinated vdpp. We have therefore studied the action of Me_2NNH_2 on *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$.

Results and discussion

Treatment of *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ with an excess of Me_2NNH_2 in boiling benzene for one hour gave a colourless solution from which colourless crystals separated on cooling in very high yield. Elemental analytical data (C,H,N and Cl) (Table 1) are in agreement with the composition $C_{30}H_{34}Cl_2N_2P_2Pt$, i.e. a 1 : 1 adduct. This complex was soluble in water or acetone and is formulated as the chloride salt $[C_{30}H_{34}ClN_2P_2Pt]Cl$. It was shown to be a 1 : 1 electrolyte in nitrobenzene solution from its electrical conductivity of 19.2 Ω^{-1} cm^2 mol^{-1} at 20 °C [7]. The most noteworthy feature of the ^{31}P-$\{^1H\}$ NMR spectrum of $[C_{30}H_{34}ClN_2P_2Pt]Cl$ is the presence of one P-atom not directly bonded to platinum, since its resonance at δ 21.9 ppm shows a coupling to platinum-195 of only 93 Hz, while the other

Table 1

Microanalytical data [a] for bicyclo complexes of platinum

Complex	C	H	N	Halogen
$\{[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Cl\}$	48.2(48.0)	4.45(4.55)	4.0(3.75)	9.4(9.45)
$\{[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]PF_6\}$ $\cdot\frac{1}{4}CH_2Cl$ [b]	41.1(41.2)	4.2(41.2)	3.3(3.2)	n.d.
$\{[BrPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Br\}$ $\cdot\frac{3}{4}CH_2Cl_2$ [b]	41.1(40.9)	4.1(4.1)	3.05(3.1)	n.d.
$\{[IPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]I\}$ $\cdot\frac{1}{4}CH_2Cl_2$ [b]	37.55(37.5)	3.5(3.6)	2.7(2.85)	24.7(26.0) [c]

[a] In %, calculated values in parentheses. n.d.-not determined. [b] The presence of solvent crystallisation confirmed by ^1H NMR spectroscopy. [c] Iodine only.

Table 2

^{31}P-$\{^1H\}$ NMR [a] data for the title complex (**1a**) and its derivatives

	δP_A	$^1J(PtP_A)$	δP_B	$^2J(PtB_B)$	$^3J(P_AP_B)$
1a	3.7	3530	21.9	93	7
1b	3.4	3498	21.2	93	10
1c	2.7	3452	20.4	81	10
1d	4.0	3562	21.7	105	5
2	4.15	3565	21.7	105	7
3	12.5	3652	27.4	37	<1

[a] Recorded at 40.25 MHz in CD_2Cl_2 at 21 °C. Chemical shifts (δ) in ppm relative to 85% H_3PO_4 and coupling constants (J) in hertz. P_A is phosphorus bound to platinum.

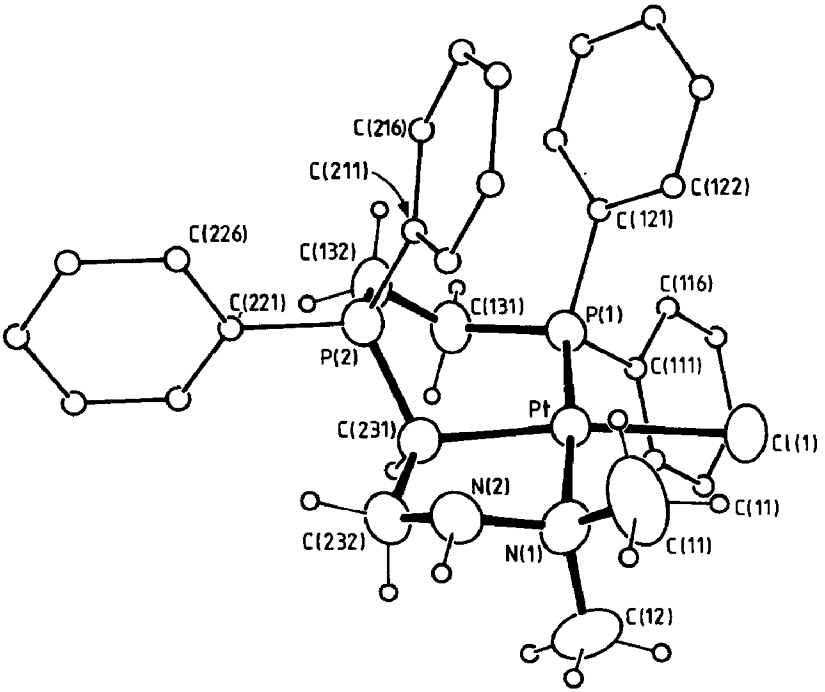


Fig. 1. Crystal structure of $[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]^+$ (**1a**).

phosphorus atom remained coordinated to platinum, with $\delta = 3.7$ ppm and $^1J(PtP)$ of 3530 Hz (see data in Table 2). In view of the great stability of this complex and the $^{31}P\text{-}\{^1H\}$ and proton NMR data (see later) we formulated the chloride salt as **1a** containing a novel tridentate ylide ligand. We then determined the crystal structure of the chloride salt **1a**, crystals of which suitable for X-ray crystallographic structure determination were grown by diffusion of ethanol into a dichloromethane solution.

The molecular structure of the cation in **1a** is shown in Fig. 1 with selected bond lengths and angles in Table 3, and Table 4 gives the atomic coordinates. The complex contains a tridentate ligand with two fused multi-atom rings joined along a Pt–C bond. Both the five-membered PtNNCC and six-membered PtPCCPC rings deviate from planarity, presumably to accommodate the preferred tetrahedral geometries of carbon and phosphorus. The internal angles of the phosphorus atoms of the six-membered ring deviate very little from the nature tetrahedral angle (105° vs. 108°), whilst those at carbon deviate slightly more (115° vs. 108°). The internal angles at carbon in the five-membered ring are 108.7(5) and 110.9(7)°, the angles at nitrogen being close to the tetrahedral geometry too. A chloride ligand completes the approximately square-planar geometry around platinum. The bond lengths to the metal are not abnormal [8,9]. We can find no further examples of a square-planar PtClPCN moiety having been structurally characterised, nor any examples of such fused ring systems. The structure of **1a** clearly indicates that a novel reaction has occurred between *N*,*N*-dimethylhydrazine and *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$, resulting in formation of the fused bicyclic product (see below).

The proton NMR spectrum for **1a** is complicated. However, we have determined the ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra and also ^1H spectra with selective decoupling of the two *P*-nuclei in turn, i.e. the $^1H\text{-}\{^{31}P_A\}$ and $^1H\text{-}\{^{31}P_B\}$ spectra and these, in

Table 3

Selected interatomic distances (pm) and angles (°) for compound **1a** with estimated standard deviations in parentheses

Cl(1)–Pt(1)	236.4(4)	P(1)–Pt(1)	222.4(4)
P(2)–Pt(1)	314.1(5)	C(231)–Pt(1)	205.2(9)
N(1)–Pt(1)	214.5(9)		
C(111)–P(1)	180.0(6)	C(121)–P(1)	181.2(6)
C(131)–P(1)	181.5(10)		
C(132)–P(2)	182.9(10)	C(211)–P(2)	178.2(6)
C(221)–P(2)	178.5(6)	C(231)–P(2)	176.9(9)
C(132)–C(131)	153.3(13)	C(232)–C(231)	154.0(12)
N(2)–C(232)	142.0(11)		
C(11)–N(1)	145.8(13)	C(12)–N(1)	148.4(13)
N(2)–N(1)	148.0(10)		
P(1)–Pt(1)–Cl(1)	92.4(2)	P(2)–Pt(1)–Cl(1)	155.3(1)
P(2)–Pt(1)–P(1)	75.3(2)	C(231)–Pt(1)–Cl(1)	172.4(2)
C(231)–Pt(1)–P(1)	93.7(3)	C(231)–2Pt(1)–P(2)	31.9(2)
N(1)–Pt(1)–Cl(1)	91.3(3)	N(1)–Pt(1)–P(1)	176.3(2)
N(1)–Pt(1)–P(2)	101.2(3)	N(1)–Pt(1)–C(231)	82.6(4)
C(111)–P(1)–Pt(1)	115.1(3)	C(121)–P(1)–Pt(1)	115.3(3)
C(121)–P(1)–C(111)	104.9(4)	C(131)–P(1)–Pt(1)	111.4(3)
C(131)–P(1)–C(111)	103.5(4)	C(131)–P(1)–C(121)	105.4(4)
C(132)–P(2)–Pt(1)	95.8(4)	C(211)–P(2)–Pt(1)	86.7(3)
C(211)–P(2)–C(132)	112.2(4)	C(221)–P(2)–Pt(1)	148.4(2)
C(221)–P(2)–C(132)	104.6(4)	C(221)–P(2)–C(211)	106.9(4)
C(231)–P(2)–Pt(1)	37.8(2)	C(231)–P(2)–C(132)	105.1(5)
C(231)–P(2)–C(211)	115.4(4)	C(231)–P(2)–C(221)	112.2(4)
C(132)–C(131)–P(1)	115.5(7)	C(131)–C(132)–P(2)	116.1(6)
P(2)–C(231)–Pt(1)	110.3(4)	C(232)–C(231)–Pt(1)	108.7(6)
C(232)–C(231)–P(2)	117.7(6)		
C(11)–N(1)–Pt(1)	114.8(7)	C(12)–N(1)–Pt(1)	110.2(7)
C(12)–N(1)–C(11)	109.4(10)	N(2)–N(1)–Pt(1)	105.7(5)
N(2)–N(1)–C(11)	105.5(8)	N(2)–N(1)–C(12)	111.0(8)
N(1)–N(2)–C(232)	109.8(7)		

conjunction with the crystal structure, enabled the resonances to be assigned. The data obtained and the assignments are given in Table 5.

Two sharp singlets of relative intensity 3 were observed for the $\mathrm{N(C}H_3)_2$ protons, at 2.73 and 3.04 ppm, and the $\mathrm{N}H$ proton signal appeared as a singlet (intensity 1), with no couplings to any other protons or to phosphorus being observed. The four $\mathrm{PC}H_2\mathrm{C}H_2\mathrm{P}$ protons of the six-membered ring showed three multiplets in the intensity ration 1 : 2 : 1 at 2.52, 2.69 and 3.39 ppm, but unambiguous assignment of each hydrogen was not possible from the observed spectra. Two multiplet resonances of relative intensity 1, at 3.18 and 4.86 ppm, were assigned to the $\mathrm{NC}H_2\mathrm{CH}$ protons of the five-membered ring, the resonance at 4.86 ppm showing coupling to ^{195}Pt [^2J(PtH) = 42.0 Hz]. The $\mathrm{NCH_2C}H$ proton gave rise to an apparent triplet at 3.92 ppm with satellites due to coupling to ^{195}Pt [^2J(PtH) = 97.7 Hz].

Table 4

Non-hydrogen atom co-ordinates ($\times 10^4$) for compound **1a**

	x	y	z
Pt(1)	899.2(1)	261.8(3)	−300.4(1)
Cl(1)	899(1)	−1504(2)	235(1)
Cl(2)	3501(1)	3552(2)	1584(1)
P(1)	1918(1)	392(2)	634(1)
P(2)	1185(1)	3007(2)	−322(1)
C(111)	2318(2)	−1019(4)	863(3)
C(112)	2038(2)	−1909(4)	300(3)
C(113)	2342(2)	−3007(4)	469(3)
C(114)	2926(2)	−3216(4)	1200(3)
C(115)	3206(2)	−2326(4)	1764(3)
C(116)	2902(2)	−1228(4)	1595(3)
C(121)	2244(2)	949(5)	1534(2)
C(122)	1955(2)	633(5)	1741(2)
C(123)	2188(2)	1057(5)	2426(2)
C(124)	2710(2)	1797(5)	2903(2)
C(125)	2999(2)	2114(5)	2696(2)
C(126)	2766(2)	1690(5)	2012(2)
C(131)	2201(3)	1422(7)	387(4)
C(132)	1996(3)	2762(7)	253(5)
C(211)	1069(3)	3335(6)	248(3)
C(212)	488(3)	3138(6)	−62(3)
C(213)	376(3)	3418(6)	362(3)
C(214)	846(3)	3896(6)	1094(3)
C(215)	1427(3)	4094(6)	1404(3)
C(216)	1538(3)	3813(6)	981(3)
C(221)	980(3)	4355(4)	−861(3)
C(222)	981(3)	4297(4)	−1405(3)
C(223)	853(3)	5343(4)	−1814(3)
C(224)	723(3)	6449(4)	−1680(3)
C(225)	722(3)	6508(4)	−1136(3)
C(226)	850(3)	5461(4)	−727(3)
C(231)	803(3)	1689(7)	−903(4)
C(232)	120(3)	1814(8)	−1664(4)
N(1)	−85(3)	248(6)	−1228(4)
C(11)	−395(5)	110(12)	−1006(7)
C(12)	−296(5)	−727(10)	−1781(5)
N(2)	−262(3)	1477(6)	−1581(3)

Both the *cis*-dibromide $[PtBr_2(PPh_2CH{=}CH_2)_2]$ and the *cis*-di-iodide $[PtI_2(PPh_2CH{=}CH_2)_2]$ reacted with *N*,*N*-dimethylhydrazine to give analogous products, $[XPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]X$, X = Br (**1b**) or X = I (**1c**), in high yield. Preparative details in the Experimental, and elemental analytical data and ^{31}P-$\{^1H\}$ NMR data are given in Tables 1 and 2, respectively. The NMR data are similar to those for the chloro-complex (**1a**). We also prepared the bromo- (**1b**) and iodo-complexes (**1c**) from the chloro-complex (**1a**) by treatment with LiBr or NaI, respectively, in acetone solution (see Experimental). Treatment of the chloro-complex (**1a**) with NH_4PF_6 gave the PF_6 salt (**1d**), see Experimental and Tables 1 and 2 for characterizing data.

Table 5

^{1}H NMR data for $\{[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Cl\}$ [a]

δ	Relative Intensity	Multiplicity [b]				$J(P_AH)$	$J(P_BH)$	$J(PtH)$	Assignment
		^1H	$^1H\{^{31}P\}$	$^1H\{P_A\}$	$^1H\{P_B\}$				
2.73	3	d	s	s	d	2.9		~18	N-CH_3
3.04	3	d	s	s	d	2.7		~18	N-CH_3
3.51	1	s	s	s	s				N-H
3.18	1	m	d,t	m	d,t		24.0	42.0	HN-CH_2-CH
4.86	1	t,br	t,br	t,br	t,br	< 2			
3.92	1	d,t	t	t	d,t		8.7	97.7	P_B-CH-CH_2
2.52	1	m	d,t	m	m	10.5	26.2		P_ACH_2-CH_2-P_B
2.69	2	m	t	m	t,br	< 2			
3.39	1	m,br	m	m	m	7.0	5.8		
7.4–8.4			m						Phenyls

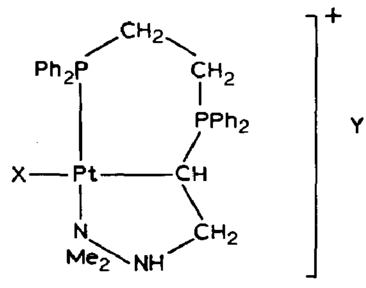
[a] Recorded at 400 MHz in CD_2Cl_2 at 24° C. Chemical shifts (δ) in ppm and coupling constants (J) in hertz. P_A is the phosphorus bound to platinum. [b] s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

Table 6

^{1}H and ^{1}H-$\{^{31}P\}$ NMR data [a] for the complexes **2** and **3**

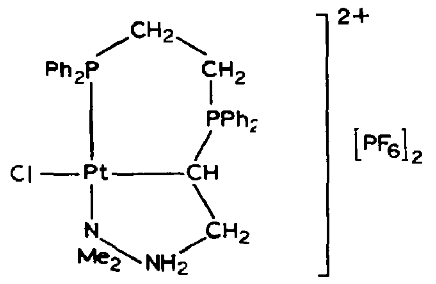
	δMe	$^2J(PtH)$	$^3J(PH)$	$\delta P_B(CH)$	$^2J(P_BH)$	$\delta(NCH_2)$	$^3J(P_BH)$	$^2J(CHH)$	$^3J(CH\ CH_2)$	δNH_2
2	2.70	15	3.0	3.17	1.5	2.85	15		+3.6	1.82
								−13.5		
	2.85	19	2.7			3.23	13.8		+6.4	
3 [b]	3.02	~15	~2			[c]				[c]
	3.46	~15	~2							

[a] Measured at 400 MHz or 100 Mhz in CD_2Cl_2, δ-values (±0.01 ppm) to high frequency of TMS. J-values ±0.1 Hz. [b] $\delta(PtH) = -6.85$ ppm, $^1J(PtH) = 1020$, $^2J(PH) = 21.6$, $^3J(PH) = 3.6$ Hz. [c] Too broad to observe, see Discussion.



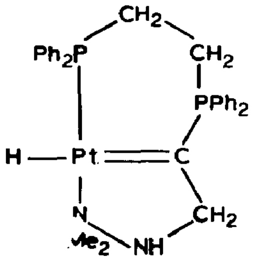
(**1a**) X = Cl , Y = Cl
(**1b**) X = Br , Y = Br
(**1c**) X = I , Y = I
(**1d**) X = Cl , Y = PF_6

Treatment of an aqueous solution of the platinum-ylide chloride salt (**1a**) with an excess of concentrated HCl, followed by addition of NH_4PF_6, gave the protonated complex **2** in 36% yield. This complex was characterised by NMR spectroscopy. The $^{31}P\text{-}\{^{1}H\}$ NMR spectrum showed that the ligand framework was unchanged (Table 2). The $^{1}H\text{-}\{^{31}P\}$ NMR spectrum showed several resonances which were broad but when the CD_2Cl_2 solution was shaken with D_2O these resonances sharpened and, with further line narrowing, nearly all the fine detail could be resolved, although the platinum satellites about the ylide proton were lost. The spectrum showed the four methylene protons of the six-membered ring as an ABCD pattern with two protons centred at $\delta = \sim 2.5$ and the other two at ~ 2.75 ppm (at 400 MHz). The methylene–methine protons of the five-membered ring gave an 'AMX' pattern at 400 MHz. A two-dimensional $(^{1}H\text{–}^{1}H)\{^{31}P\}$ COSY NMR spectrum allowed us to interpret this pattern since the two values of vicinal coupling $^{3}J(HH)$ will be positive and the geminal $^{2}J(HH)$ would be expected to be negative [10]. We do indeed find that one coupling constant is opposite in sign to the other two and this enabled us to assign the resonance at $\delta = 3.17$ ppm as that of the methine proton. The COSY NMR spectrum also showed that the two methyl groups were coupled together, albeit weakly, with $^{4}J(HH)$ less than 1 Hz. In the ^{1}H NMR spectrum all the hydrogens attached to carbon showed coupling to one or both phosphorus nuclei (data in Table 6).



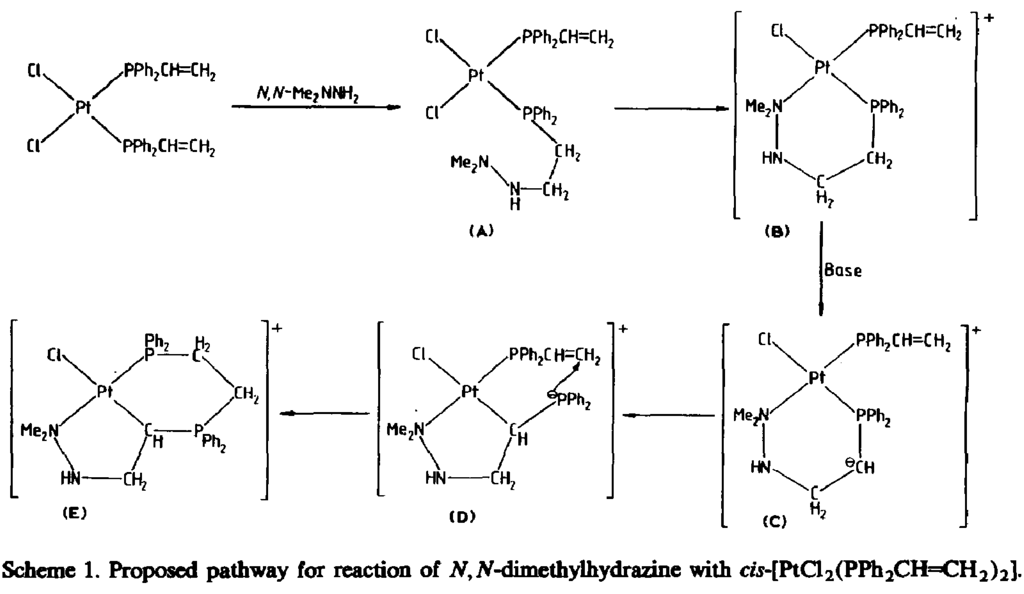
(**2**)

We also attempted to replace the chloride ligand in **1a** by hydride. Treatment of an aqueous solution of the chloro-platinum-ylide salt with an aqueous solution of sodium borohydride gave an immediate white precipitate. This product was labile and not obtained quite pure. However, the complex was electrically neutral and the ^{31}P-{^{1}H} NMR spectrum showed that the ligand framework of the tridentate ligand was retained (data in Table 2), although $J(P_AP_B)$ was too small to be resolved. The ^{1}H NMR spectrum showed a hydride resonance at $\delta = -6.85$ ppm with $^{1}J(PtH) =$ 1020 Hz and $^{2}J(PH) = 21.6$ Hz and $^{3}J(PH) = 3.6$ Hz. The *N*-methyls showed singlets at $\delta = 3.02$ and 3.46 ppm, each with $^{3}J(PtH)$ of ca. 15 Hz and $^{4}J(PH)$ of ca. 2 Hz, but the remaining hydrogens gave broad and frequently overlapping resonances which we could not assign. We tentatively formulate this neutral hydride complex as **3** with a tridentate carbene ligand.



(3)

Whereas treatment of *cis*-[$PtCl_2(PPh_2CH{=}CH_2)_2$] with Me_2NNH_2 in hot benzene gives the complex **1a**, none of this complex is formed when ethanol is used as solvent. When a suspension of *cis*-[$PtCl_2(PPh_2CH{=}CH_2)_2$] in ethanol was treated with an excess of Me_2NNH_2 it dissolved within a few minutes at 20 °C to give a mixture of phosphorus-containing species [^{31}P-{^{1}H} evidence]. After 16 hours, essentially a single product had formed, with equivalent *P*-nuclei both strongly coupled to platinum. We formulate this as the dication [Pt{$PPh_2CH_2CH_2NHNMe_2$}$_2$]$^{2+}$. This species was formed rapidly in hot ethanol from the same two reactants (after 30 min at 80 °C) and isolated as the PF_6 salt in 71% yield. The salt



Scheme 1. Proposed pathway for reaction of *N*,*N*-dimethylhydrazine with *cis*-[$PtCl_2(PPh_2CH{=}CH_2)_2$].

was not obtained analytically pure but gave the following NMR data (in CD_2Cl_2): $\delta P = 29.6$ ppm, $^1J(PtP) = 3313$ Hz. From the ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra the following data were obtained (the multiplicities s,d,t, b = broad, h = hidden, refer to the $^1H\text{-}\{^{31}P\}$ NMR spectra). δ 2.62dt ppm (2H), $J(PH) = 15$, $J(HH) = 16$, 4.6 and 4.6; δ 2.79h ppm (2H); δ 2.82s ppm (12H) (methyls); δ 3.30ddd ppm (2H), $J(PH) = 7$, $J(HH)$ 18, 12.0, 5.5; δ 3.646b ppm (2H), $J(PH) = 30$; δ 6.60b ppm (2H), $^2J(PtH) = 50$ Hz (N*H*).

In none of these syntheses in ethanol was even a trace of the tridentate ylide complex **1a** observed to be formed ($^{31}P\text{-}\{^1H\}$ NMR evidence). We suggest that in the ionizing solvent ethanol, Me_2NNH_2 first displaces chloride ion(s) and eventually, by intramolecular Michael additions, the dication **3** is formed. In poorly ionizing benzene as solvent we suggest that Me_2NNH_2 attacks a vinyl group of *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ directly giving species **A** in Scheme 1. Coordination of NMe_2, with displacement of Cl^-, then gives **B** which with base (i.e. Me_2NNH_2) loses H^+ to give **C**, which immediately rearranges to give **D** containing an uncoordinated PPh_2 group. This PPh_2 group then attacks the remaining vinyl group in an intramolecular Michael addition and, after picking up a proton, the Cation **E** is formed and is readily isolated as its chloride salt (**1a**).

Experimental

The general techniques and apparatus were as described previously [11].

Preparation of $\{[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Cl\}$ (1a)

A solution of Me_2NNH_2 (0.5 cm^3) and *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ (0.114 g, 0.165 mmol) in dry degassed benzene was refluxed under nitrogen for 1 h. The resulting colourless solution was allowed to cool and set aside for 24 h to give white microcrystals of the product. Yield 0.12 g (95%).

The bromide (**1b**) and iodide (**1c**) analogues were prepared similarly in 88% and 62% yields, respectively, from the bromo- and chloro-*bis*(diphenylvinylphosphine) complexes, although they both required reaction times of ca. 4 h.

Preparation of $[BrPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Br$ (1b) by metathesis

$\{[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Cl\}$ (0.2 g, 0.27 mmol) and LiBr (0.23 g, 2.7 mmol), were added to a mixture of acetone (10 cm^3) and dichloromethane (10 cm^3) and the suspension stirred for 4 h. The resulting colourless solution was taken to dryness in vacuo to leave an oily residue, which was taken up in dichloromethane (20 cm^3). The resulting suspension was filtered and the filtrate evaporated to dryness in vacuo. The white residue was then triturated with diethyl ether (10 cm^3) to give the product as cream microcrystals. Yield 0.1976 g (87%).

The iodide analogue (**1c**) was prepared similarly, by metathesis with NaI, in 87% yield.

Preparation of $[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]PF_6$ (1d)

NH_4PF_6 (0.1 g, 0.61 mmol) was added to a suspension of $\{[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Cl\}$ (0.15 g, 0.2 mmol) in acetone (20 cm^3), and the mixture was stirred for 30 min, giving a colourless solution. This was evaporated to dryness in vacuo and the residue extracted with dichloromethane. The extract was filtered and evaporated to dryness in vacuo, and the residue triturated with diethyl ether (10 cm^3) to give the product as white microcrystals. Yield 0.163 g (95%).

Preparation of [HPt(NMe$_2$NHCH$_2$CPPh$_2$CH$_2$CH$_2$PPh$_2$)]Cl (3)

A solution of NaBH$_4$ (0.025 g, 0.66 mmol) in aqueous 1 *M* NaOH solution (2 cm^3) was added to a solution of **1a** in water (3 cm^3). The product separated immediately as a white solid, and was filtered off, washed with water, and dried. Yield 0.020 g. The product was labile, and was characterized by NMR spectroscopy only (see Discussion).

Single crystal X-ray diffraction study

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using a standard procedure described elsewhere [12]. The data set was corrected for absorption empirically once the structure had been determined [13].

The structure was determined by standard heavy-atom methods and refined by full-matrix least-squares using the SHELX program system [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl groups were treated as rigid bodies and were refined with idealised hexagonal symmetry. All hydrogen atoms were included in calculated positions and assigned to an overall isotropic parameter (apart from the one attached to N(2) which was located in a Fourier difference synthesis but was not refined). The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in order to obtain satisfactory agreement analyses. Final non-hydrogen atomic co-ordinates are given in Table 4. A complete table of bond lengths and angles, and lists of hydrogen coordinates, thermal parameters, and structure factors are available from the author.

Crystal data for compound (1a). $C_{30}H_{34}Cl_2N_2P_2Pt$, $M = 750.55$, monoclinic, *a* 3171.1(8), *b* 1090.8(2), *c* 2558.8(5) pm, $\beta = 136.63(1)$, *U* 6.078(3) nm^3, $Z = 8$, space group *C*2/*c*, D_c 1.79 Mg m^{-3}, μ 72.73 cm^{-1}, $F(000) = 464$.

Data collection. Scan widths 1.8° + α-doublet splitting, scans speeds 2.0–29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 3249 Data collected, 3088 with $I > 2.0\sigma(I)$ considered observed, *T* 290 K.

Structure refinement. Number of parameters 255, $g = 0.0002$, $R = 0.0250$, $R_w = 0.0270$.

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