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Some reactions of the platinum(II) carbene complex *cis*-dichloro(dimethylaminomethylene)(triphenylphosphine)-platinum(II) and the X-ray crystal and molecular structures of the products *trans*-(CH$_2$,P)-chloro(chloromethyl)(dimethylaminomethylene)(triphenylphosphine)platinum(II) and [1,2-bis(diphenylphosphino)ethane](dimethylaminomethylene)-(triphenylphosphine)platinum(II) bis(hexafluorophosphate)

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Abstract

The reaction of the title complex **1** with excess diazomethane results in the exclusive insertion of a methylene group into the Pt–Cl bond *trans* to the phosphine ligand, to give the chloromethyl complex **6**. The reactions of **1** with the diphosphines, $Ph_2P(CH_2)_nPPh_2$($n = 2$, dppe, $n = 3$, dppp), and with the organometallic reagents Ph_4Sn, Ph_2Hg, or $PhSnMe_3$, can also all be interpreted as proceeding via initial displacement of the chlorine *trans* to PPh_3. The chelating phosphine ligands give equilibrium mixtures of the products $[(LL)Pt(CHNMe_2)(PPh_3)]^{2+}2Cl^-$ and $[(LL)Pt(CHNMe_2)Cl]^+Cl^-$ (LL = dppe, dppp), and treatment of the mixture [(LL) = dppe] with excess aqueous KPF_6 gave $[(dppe)Pt(CHNMe_2)(PPh_3)]^{2+}2PF_6^-$ (**9b**). The insertion product $(Ph_3P)\overline{Pt(CHPhN}Me_2)Cl$ (**11**) was isolated from the reaction of **1** with $PhSnMe_3$. This complex undergoes further reaction upon standing in $CDCl_3$ solution, giving various products including benzaldehyde, *N*,*N*-dimethylbenzylamine, *cis*- and *trans*-$(Ph_3P)Pt(NHMe_2)Cl_2$, and the new carbene complex *cis*-$(Ph_3P)Pt[C(Ph)NMe_2]Cl_2$ (**17**). Mechanisms are suggested for the formation of these products. The structures of chloromethyl complex **6** and hexafluorophosphate salt **9b** have been determined by X-ray crystallography. © 2001 Published by Elsevier Science B.V.

Keywords: Platinum; Carbenes; Phosphines; Migratory insertion; Crystal structures

1. Introduction

Interest in the chemistry of transition metal carbene complexes has seen rapid growth, in particular, due to their importance in organic synthesis, either as stoichiometric reagents, or as reactive intermediates, especially in catalytic processes [1]. While a large number of platinum(II) carbene complexes has been characterized [2] there have been relatively few studies of reactivity involving the carbene moiety [3], perhaps because in many cases this is stabilized by two heteroatom substituents, and is therefore fairly unreactive. Indeed, carbene ligands of this type have recently become of interest as less dissociation labile alternatives to phosphines in complexes employed as catalysts [4]. Platinum(II) carbene complexes lacking heteroatoms have been suggested as transient intermediates in some reactions [5], and, in a few special cases, such complexes have been isolated and characterized [6]. Numerous platinum(II) carbene complexes stabilized by a single heteroatom have also been characterized [2]. The carbene moiety in such complexes would be expected to display

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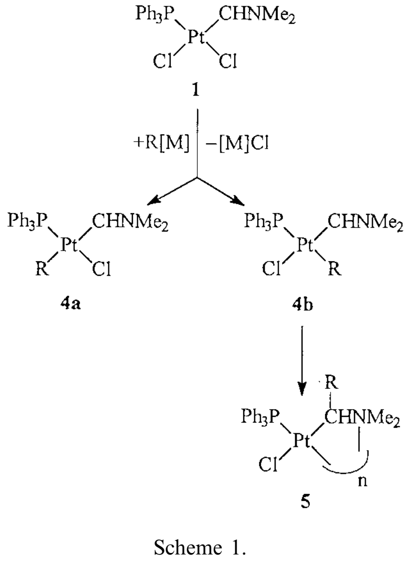
a reactivity intermediate between the reactivities of the previous two types. Indeed, both heteroatom fragments exchange [7] and, more recently, migratory insertion [8] reactions have been reported for complexes of this type.

We have investigated some reactions of *cis*-$(Ph_3P)Pt(CHNMe_2)Cl_2$ (**1**) [9], a member of the class of single heteroatom stabilized carbene complexes, with a particular interest in two aspects of its chemistry. First, there was the question of the relative *trans-effects* of the phosphine and carbene ligands in substitution reactions at the platinum center. It has been stated in the literature [10] that phosphine and carbene ligands exert similar *trans influences* in complexes of Pt(II), but there would appear to be no information on relative *trans-effects*. However, our recent finding [9b] that the reaction of **1** with dimethylamine or tripenylphosphine gives the products (**2** and **3**, respectively) of substitution of the chloride *trans* to the phosphine ligand, would indicate that the phosphine has the greater *trans-effect* if **2** and **3** are kinetic products. Second, we were interested in the possibility of observing migratory insertion reactions involving the carbene moiety. As illustrated for the general case in Scheme 1, such a process would require initial introduction of an organic group *cis* to the carbene ligand to give species **4b**, followed by migration of the organic group to give a Pt(II) α-aminoalkyl species (**5**), in which a new chiral center has been created. The chemistry of α-aminoalkylplatinum(II) complexes is almost unexplored [9b,11]. Species of this type may be of interest in the synthesis of organic compounds containing α-chiral amine functionality.



Scheme 1.

2. Reactions of carbene complex 1

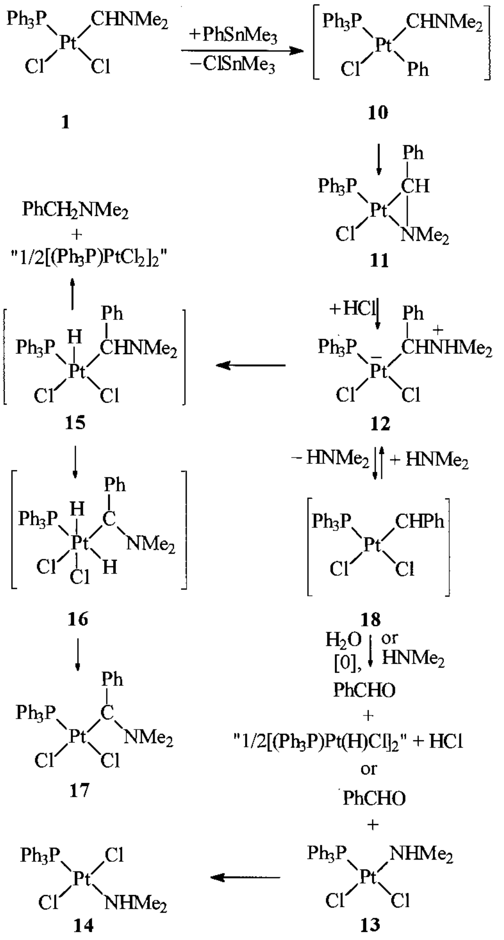
2.1. Reaction with diazomethane

In earlier work [12], we have observed that the reaction of platinum(II) chloro complexes with diazomethane gives chloromethyl derivatives by insertion only if at least one ligand of high *trans*-effect is present. In two cases [12,13], initial monoinsertion products underwent isomerization so that the chloromethyl group finished *trans* to a low *trans*-effect ligand. However, the rates of isomerization were sufficiently slow to allow characterization of the initial products. In the presence of two high *trans*-effect ligands, both mono- and bis-insertion products were obtained. We have now found that reaction of **1** with excess diazomethane gives only a single monoinsertion product, **6**. The configuration of **6**, with the newly-formed chloromethyl group *trans* to the phosphine was suggested by its ^1H-($\delta_{CH_2Cl} = 4.05$, d, $^3J_{P-H} = 4$ Hz) and ^{31}P-($\delta_P = 17.56$, $^1J_{Pt-P} = 1807$ Hz) NMR spectra, and confirmed by an X-ray crystallographic study (see below). If fast isomerization can be excluded, the formation of **6** indicates that the phosphine ligand in **1** has a higher *trans-effect* than the carbene. It is of interest to compare this result with that obtained [12] for the phosphine–isocyanide complex *cis*-$(Et_3P)Pt(CN$*tert*-$Bu)Cl_2$, which gives the bis-insertion product with excess diazomethane, and a mixture of bis(chloromethyl) product along with the mono(chloromethyl) product in which insertion has occurred *trans* to the phosphine, with a limited amount of reagent. This suggests a *trans-effect* order phosphine > isocyanide > carbene.

Complex **6**, upon standing in $CDCl_3$ solution at ambient temperature, undergoes slow (days) conversion into **1**, and other products which have not been characterized. In contrast, clean migratory insertion of the $CHClCO_2Et$ moiety, rapidly followed by further reaction, has been observed [8] upon heating solutions of the platinum(II) oxacyclopentylidene complex $[(dppe)Pt(\overline{CCH_2CH_2CH_2O})(CHClCO_2Et)][BF_4]$ and related species. Like the $CHClCO_2Et$ group, the chloromethyl group should have a relatively low migratory aptitude. Thus, in subsequent studies of the reactions of **1** (see later), we have used reagents expected to generate the phenyl analogue of **6**, because of the greater migratory aptitude of phenyl versus chloromethyl.

2.2. Reactions with bidentate ligands

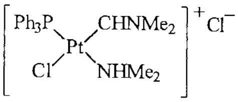
In order to obtain cationic carbene complexes of type **7** we have investigated the reactions of **1**, and of the triphenylarsine analogue **8**, with bidentate phosphine and amine ligands. Complex **1** reacts rapidly ($CDCl_3$



Scheme 2. Species enclosed in parentheses or quotation marks are postulated intermediates or products, respectively.

solution) with equimolar quantities of the bis(phosphine) ligands $Ph_2P(CH_2)_nPPh_2$($n = 2$, dppe; $n = 3$, dppp) to give the required complexes (**7a**,**b**) along with the products (**9a**,**c**) in which both chloride ligands in **1** have been displaced. In light of our earlier results, complexes **9a** and **9c** are probably formed first, via initial substitution of the chloride *trans* to PPh_3, followed by ring closure with displacement of the second chloride. Chloride exchange with PPh_3 would then give equilibrium mixtures containing **7a** and **7b**. While ^1H-NMR spectra of these mixtures are broadened, ^{31}P-NMR spectra are relatively sharp, and indicate that, at equilibrium, **7a** and **9a** are present in comparable amounts while **7b** is the predominant component in the mixture with **9c**. This difference can be rationalized by considering the steric requirements of dppe and dppp. The larger bite angle of the latter [14] would result in greater steric interaction with the neighboring PPh_3 ligand in **9c** versus that in **9a** favoring replacement of the PPh_3 by the smaller chloride ligand. As expected, the above mentioned equilibria can be displaced towards the dicationic species by removal of chloride. Thus, shaking a $CDCl_3$ solution containing **7a** and **9a** with excess aqueous KPF_6 gave the bis(hexafluorophosphate) salt, **9b**. The structure of the last has been determined by X-ray crystallography (see below). While complexes **7a** and **7b** could be recovered from the reaction mixtures by preparative thin-layer chromatography (TLC), they were obtained more readily by reaction of triphenylarsine complex **8** with dppe and dppp, respectively.

While complex **1**, as indicated in the introduction, reacts with dimethylamine to give **2**, it gives no detectable reaction upon treatment in $CDCl_3$ solution with 2,2′-bipyridine (bpy), even after heating. However, the more labile arsine analogue (**8**) reacts slowly (hours at ambient temperature) to give an equilibrium mixture containing **7c** along with unreacted **8**. Product **7c** has been recovered from such mixtures by using excess bpy to displace the equilibrium.



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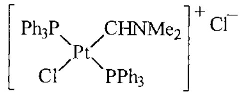

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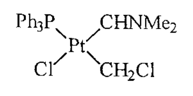

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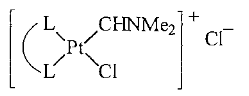

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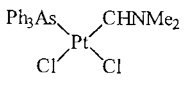

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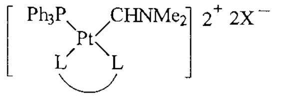
(a) $\widehat{LL}$ = dppe
(b) $\widehat{LL}$ = dppp
(c) $\widehat{LL}$ = bpy



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(a) $\widehat{LL}$ = dppe, X = Cl
(b) $\widehat{LL}$ = dppe, X = PF_6
(c) $\widehat{LL}$ = dppp, X = Cl

2.3. *Reactions with tetraphenyltin, diphenylmercury and phenyltrimethyltin*

Initial exploratory reactions were conducted in $CDCl_3$ solution at ambient temperature without precautions to exclude oxygen or adventitious water.

Complex **1** reacted slowly with Ph_4Sn to give, first, the product (**11**, Scheme 2) of addition of a phenyl group to the carbene moiety. However, before conversion of **1** was complete, further reaction of **11** proceeded as outlined in Scheme 2 to give, in succession, a product (**12**) of net HCl addition to **11** and then benzaldehyde, *cis*-$(Ph_3P)Pt(NHMe_2)Cl_2$ (**13**), and the new carbene complex *cis*-$(Ph_3P)Pt[C(Ph)NMe_2]Cl_2$ (**17**) along with additional minor products. With a small excess of Ph_4Sn, complete consumption of **1** required about one day and the reaction solution darkened on standing.

The reaction of **1** with Ph_2Hg proceeded more slowly than that with Ph_4Sn, and the only significant products detected were benzaldehyde and **13** along with a small amount of *trans*-$(Ph_3P)Pt(NHMe_2)Cl_2$ (**14**).

Complex **1** reacts more rapidly with $PhSnMe_3$ than it does with Ph_4Sn, complete consumption requiring a few hours. Although the initial product, **11**, is subject to further reaction, as outlined in Scheme 2, it can be isolated from reactions carried out initially under dry conditions. The monomeric structure of **11** is suggested for this product rather than a dimeric one, as has been found [15] for Pt(II) thioether analogues, on the basis of its ready solubility and the observation of a relatively large $^1J_{Pt-P}$ coupling of 5526 Hz [16] in the ^{31}P-NMR spectrum. As indicated in Scheme 2, formation of **11** probably involves initial exchange of the chlorine *trans* to PPh_3 in **1** for phenyl, giving the undetected intermediate **10**, and Me_3SnCl, followed by migration of the phenyl group and coordination of the resulting amine. Formation of **11** cleanly and in high yield requires that the reaction solution remain dry. In the presence of traces of water, further reaction of **11** takes place, probably as a result of the generation of HCl by reaction of the water with Me_3SnCl. Indeed ^{1}H-NMR spectra of such reaction solutions show signals ascribable to $Me_3SnOSnMe_3$ in addition to those for $PhSnMe_3$ and Me_3SnCl. Generation of HCl is also suggested by the formation of species **12** when reaction solutions containing **11** are allowed to stand. Intermediate **12** itself undergoes further reaction to give various products (Scheme 2), the relative proportions of which depend upon the conditions. However, pure **12** crystallizes from $CDCl_3$ solutions of pure **11** upon addition of acetyl chloride without protection from adventitious water.

When the reaction of carbene complex **1** with $PhSnMe_3$ is carried out in $CDCl_3$ without prior drying of the solvent or protection from the atmosphere, decomposition of the initially formed **11** is evident from the beginning, and darkening of the solution is observed. Under these conditions, the final products are again benzaldehyde, **13**, **14** and **17**. The structure of **13** is suggested by its ^{1}H- and ^{31}P-NMR spectra, but attempts to isolate it by TLC resulted in its decomposition and/or isomerization to the known [9b] *trans* isomer, **14**. Isomerization to **14** was also observed when reaction solutions containing **13** were allowed to stand.

When the above reaction was carried out under nitrogen, significant darkening of the solution was observed and *N*,*N*-dimethylbenzylamine was obtained as a final product along with a small amount of benzaldehyde, **13**, **14** and **17**.

In all reaction mixtures resulting from the formation and subsequent decomposition of **11**, at least small amounts of the new carbene complex **17** could be detected. We have been unable to find conditions that give **17** as the major product, the best yields (ca 20%), thus far obtained, resulting when the solvent is removed under vacuum as soon as the formation of **11** is complete, and the resulting gum is kept under vacuum. Pure **17** did not react further with $PhSnMe_3$, probably because of steric hindrance.

As indicated in the introduction, little work has been done on α-aminoalkylplatinum(II) derivatives. The present work and earlier results [9b] indicate that such species are relatively labile. As suggested in Scheme 2, formation of carbene product **17** from **11** through **12** may proceed via a pathway analogous to that which we have suggested previously [9b] for the conversion of *cis*-$(Ph_3P)Pt(CH_2NHMe_2)Cl_2$ into carbene complex **1**: viz. proton transfer from N (in **12**) to Pt to give Pt(IV) hydride intermediate **15**, α-H shift from the resulting $CHPhNMe_2$ moiety to give Pt(IV) carbene dihydride **16**, and finally reductive elimination of H_2 from **16** [17]. Formation of *N*,*N*-dimethylbenzylamine could be envisaged as involving reductive elimination from **15**. The finding that benzaldehyde is formed in reactions run under air or, in lower yield, under nitrogen suggests that there may be two pathways leading to this product. Both might proceed via the labile phenylcarbene complex **18**, formed by, presumably reversible, elimination of dimethylamine from **12**. Reaction of **18** with water or with atmospheric oxygen would then give benzaldehyde, along with $[(Ph_3P)Pt(H)Cl]_2$ and HCl, or, with reentry of dimethylamine, **13**, respectively. Further reaction of the platinum hydride species would then lead to darkening of the reaction solutions through the formation of $[(Ph_3P)PtCl_2]_2$ (by reaction with HCl) and deposition of platinum metal by reductive elimination of HCl. Interestingly, decomposition of the Pd(II) α-thioether complex $[BrPdCH(SPh)CH_2CH_2C_2F_5]_2$ to give, inter alia, $C_6F_5CH_2CH_2CHO$ has been suggested [18] to proceed via a palladium(II) carbene intermediate by both oxidative and hydrolytic mechanisms.

Our failure to observe any intermediates such as **11** or **12**, or product **17**, in the reaction of **1** with Ph_2Hg suggests that this reaction proceeds via a different pathway. For example, the species formed upon phenyl group migration in intermediate **10** maybe intercepted by co-product PhHgCl to give a Pt–Hg dimeric complex which undergoes rapid decomposition.

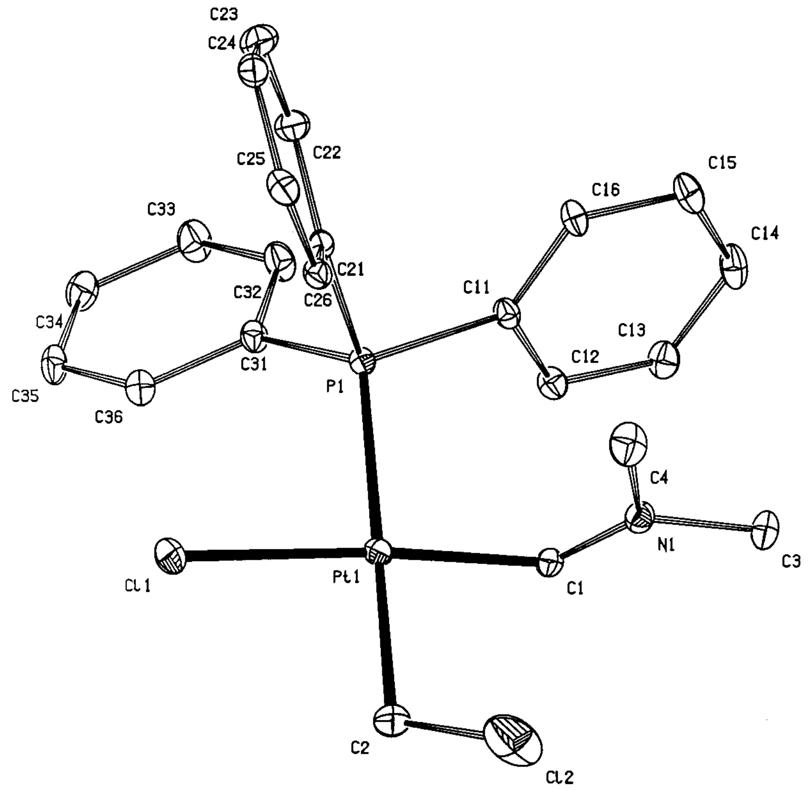

Fig. 1. View of **6** with the numbering scheme. Phenyl ring C atoms are labelled Ci1 – Ci6 (*i* = 1–3).

3. X-ray crystallographic studies

3.1. *trans-(CH_2, P)-Chloro(chloromethyl)(dimethylaminomethylene)(triphenylphosphine)–platinum (II) (**6**)*

A view of the molecule is shown in Fig. 1 and selected geometric parameters are collected in Table 1. The crystal structure of **6** consists of discrete, non-interacting molecules. The geometry about platinum is close to square planar with the chloromethyl ligand occupying the site *trans* to the phosphine. The carbene ligand is planar, and the dihedral angle between the carbene plane and the average coordination plane is 83.22(6)°, a value comparable with those found [9] for other Pt(II) carbene complexes. The carbene C1–N2 bond is typically short (1.279(9) Å), consistent with high double bond character, and the Pt1–C1 bond length is similar to the bond lengths found for other Pt(II) complexes with the dimethylaminocarbene ligand *trans* to chloride [9]. The Pt1–C2 bond length (2.079(6) Å) is similar to the Pt–C bond lengths (2.069(8) and 2.082(9) Å) reported [19] for (dppe)Pt$(CH_2Cl_2)_2$, but shorter than that (2.185(20) Å) found [20] for $[(Ph_2PCH_2PPh_2CH_2)Pt(PPh_3)(CH_2Cl)]PF_6$. In all three complexes, the chloromethyl group is *trans* to phosphine ligands.

3.2. *[1,2-Bis(diphenylphosphino)ethane]-(dimethylaminomethylene)(triphenylphosphine) platinum(II) bis(hexafluorophosphate) (**9b**)*

The crystal structure of **9b** consists of four-coordinate cations and non-interacting hexafluorophosphate anions. A view of the cation is shown in Fig. 2, and selected geometric data are collected in Table 2. The geometry of the cation is close to square planar, the main deviations being reflected in the P1–Pt1–P2 (97.85(4) Å) and P2–Pt1–P3(84.09(5) Å) angles result-

Table 1
Selected bond lengths (Å) and angles (°) for *trans*-(CH_2,*P*)-(Ph_3P)Pt($CHNMe_2$)(CH_2Cl)Cl (**6**)

Bond lengths			
Pt1–C1	1.941(5)	C2–Cl2	1.77(8)
Pt1–C2	2.079(6)	C1–N1	1.275(7)
Pt1–Cl1	2.3785(17)	C3–N1	1.469(8)
Pt1–P1	2.3249(13)	C4–N1	1.464(8)
Bond angles			
C1–Pt1–C2	88.5(2)	Pt1–C2–Cl2	117.5(4)
C1–Pt1–Cl1	174.48(14)	Pt1–C1–N1	129.6(4)
C1–Pt1–P1	92.05(14)	C1–N1–C3	123.7(5)
C2–Pt1–Cl1	86.1(2)	C1–N1–C4	122.9(6)
C2–Pt1–P1	178.1(2)	C3–N1–C4	113.4(6)
Cl1–Pt1–P1	93.37(5)		

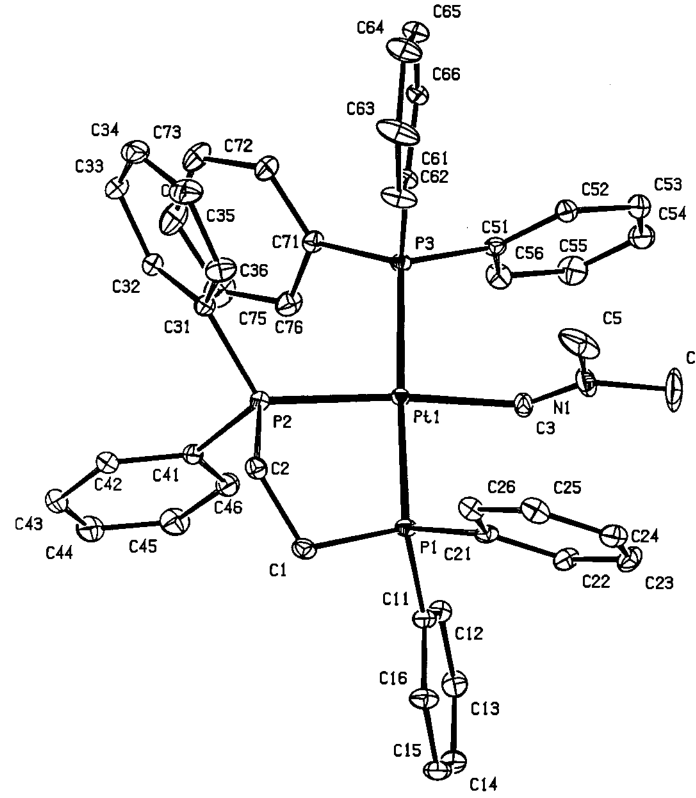

Fig. 2. View of the cation of **9b** with the numbering scheme. Phenyl ring C atoms are labelled C*i*1 – C*i*6 (*i* = 1–7).

ing from the competing steric demands of the phosphine ligands and the bite angle of dppe. The carbene ligand is planar, adopting a conformation that is close to perpendicular to the coordination plane (dihedral angle = 89.66(28)°) and in which it is 'sandwiched' between two almost parallel phenyl rings from the Ph_3P and dppe ligands. As expected, on the basis of the *trans influence* effects, the Pt1–C3 bond (2.007(5) Å), which is *trans* to a phosphine ligand, is longer than the $Pt–C_{carbene}$ bonds in other Pt(II) complexes containing the dimethylaminocarbene ligand *trans* to chloride (compound **6** above, and [9]).

4. Experimental

Unless otherwise indicated, reactions were carried out without precautions to exclude oxygen or moisture, and NMR spectra were acquired for $CDCl_3$ solutions on Varian GEMINI 200 (^1H) or UNITY 400 (^1H, ^{31}P) instruments. The solvent residual proton resonance at $\delta = 7.24$ was used as internal reference, while the phosphorus resonance of Ph_3P in $CDCl_3$($\delta = -5.31$) was used as external reference. $CDCl_3$ was dried by stirring with CaH_2 under nitrogen, followed by distillation just prior to use. Preparative thin layer chromatography (TLC) was performed on Kieselgel G(Merck). Elemental analyses were determined at Guelph Chemical Laboratories Ltd. Guelph, Ontario, Canada.

Crystal data, and details of data collection, structure solution and refinement are summarized in Table 3.

4.1. Reaction of 1 with diazomethane

Excess diazomethane (ca two equivalents) in diethyl ether [12] was added in portions to a solution of **1** (64.3 mg, 0.100 mmol) in CH_2Cl_2 (30 cm^3) while cooling in an ice-water bath. Initial reaction was rapid, as judged by the disappearance of the yellow color of the diazomethane. The final reaction solution was left in the cooling bath until the last of the yellow color had faded (ca 1.5 h). At this stage, a white precipitate of poly-

Table 2
Selected bond lengths (Å) and angles (°) for the cation, $[(dppe)Pt(PPh_3)(CHNMe_2)]^{2+}$ of **9b**

Bond lengths			
Pt1–C3	2.007(5)	C3–N1	1.279(9)
Pt1–P1	2.3164(12)	C4–N1	1.490(11)
Pt1–P2	2.3303(13)	C5–N1	1.438(15)
Pt1–P3	2.3503(12)		
Bond angles			
C3–N1–C4	122.9(11)	C3–Pt1–P3	88.06(15)
C3–N1–C5	123.5(8)	P1–Pt1–P2	84.09(5)
C4–N1–C5	113.6(9)	P1–Pt1–P3	177.38(4)
C3–Pt1–P1	88.99(15)	P2–Pt1–P3	97.85(4)
C3–Pt1–P2	174.08(15)	Pt1–C3–N1	128.9(7)

Table 3
Summary of crystal data and details of data collection, structure solution, and refinement

	6	**9b**
Crystal data		
Formula	$C_{22}H_{24}Cl_2NPPt$	$C_{47}H_{46}F_{12}NP_5Pt$
Molar mass	599.38	1202.79
Color, habit	Colorless, block	Colorless, block
Crystal size (mm)	$0.32 \times 0.38 \times 0.13$	$0.43 \times 0.32 \times 0.31$
Crystal system	Monoclinic	Monoclinic
a (Å)	10.406(2)	11.1572(14)
b (Å)	14,944(3)	29.037(3)
c (Å)	14.194(4)	14.6795(17)
α (°)	90.00	90.00
β (°)	94.97(2)	92.239(11)
γ (°)	90.00	90.00
V (Å^3)	2199.0(9)	4752.2(9)
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
F(000)	1160	2384
D_{calc} (g cm^{-3})	1.810	1.681
μ (mm^{-1})	6.704	3.203
Data acquisition [a]		
Temperature (K)	294	294
Unit cell reflections (θ range) (°)	9.90–16.05	23.10–26.58
Maximum θ for reflections (°)	26.99	26.97
hkl range of reflections	-13 to $+13$; 0–19; 0–18	-14 to $+14$; 0–36; 0–18
Decay in three standard reflections	0.5	0.5
Number of reflections measured	4960	10837
Number of unique reflections	4775	10322
R_{int}	0.012	0.009
Number of reflections with $I > 2\sigma(I)$	3617	7393
Absorption correction type	ψ scans	ψ scans
Min/max absorption corrections	0.1346, 0.4178	0.3341, 0.3716
Structure solution and refinement [b]		
Refinement on	F^2	F^2
Solution method	Patterson heavy atom	Patterson heavy atom
H-Atom treatment	Riding	Riding
Extinction correction	SHELXL 97	SHELXL 97
Extinction coefficient	0.00075(14)	0.00096(6)
Number of variables in least squares	247	598
Weights k [c]	$(0.0501P)^2 + 0.7309P$	$(0.03443P)^2 + 9.0844P$
R, R_w, goodness-of-fit	0.034, 0.081, 1.05	0.030, 0.076, 1.08
Density range in final Δ-map (eÅ^{-3})	-1.003, 2.280 adjacent to Pt1	-1.279, 0.928
Final shift/error ratio	0.001	0.001

[a] Data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å).

[b] All calculations were done on a Dell Inspiron 3200 laptop computer with the NRCVAX system of programs [21] for refinement with observed data on F or with SHELXL-97 [22] for refinement with all data on F^2.

[c] $w = 1/(\sigma^2 F_o^2 + k)$; $P = (F_o^2 + F_c^2)/3$.

methylene was present. The solvent was removed in vacuo, the residue was taken up in fresh CH_2Cl_2, and the mixture was passed through a short column of silica gel, which was then eluted with more CH_2Cl_2. Evaporation of the eluate left a white solid (63 mg) which proved (^{1}H-NMR) to be essentially a single product. Recrystallization from CH_2Cl_2–hexane (1:4) gave colorless prisms of *trans*-(C*H*$_2$,P)-chloro(chloromethyl)-(dimethylaminocarbene)(triphenylphosphine) platinum(II) **(6)**. ^{1}H-NMR $\delta = 2.80$ (s, 3H, NMe), 3.27 (brs, 3H, NMe), 4.05 (d, 2H, CH_2Cl, $^3J_{P-H} = 4.0$ Hz, $^2J_{Pt-H} = 65$ Hz), 7.2–7.8 (m, 15H, aromatic H), 10.44(brs, 1H, *CH*NMe$_2$). ^{31}P-NMR $\delta = 17.56$ ($^1J_{Pt-P} = 1807$ Hz).

4.2. Reactions of **1** and of the triphenylarsine analogue **8** with bidentate ligands

All reactions were monitored in $CDCl_3$ solution by ^{1}H- or ^{31}P-NMR spectrometry. Products were then recovered by work-up of these solutions.

4.2.1. Reactions with 1,2-bis(diphenylphosphino)ethane(dppe)

A solution (0.7 cm^3) prepared from complex **1** (5.9 mg, 10 μmol) and dppe (4.0 mg, 10 μmol) showed broad ^{1}H resonances, including a pair at $\delta = 10.15$ and 12.04 (ratio ca 1:1) corresponding to the protons attached to the carbene carbon atoms in **7a** and **9a**, respectively. The ^{31}P-NMR spectrum was better resolved, showing resonances due to **7a** (see below); at $\delta = 12.73$ ($^2J_{P-P} = 304$ and 21 Hz, $^1J_{Pt-P} = 2584$ Hz), 39.74($^2J_{P-P} = 21$Hz, $^1J_{Pt-P} = 1950$ Hz) and 45.51 ($^2J_{P-P} = 304$ Hz, $^1J_{Pt-P} = 2643$ Hz) due to **9a**, and at $\delta = -5.3$ due to free Ph_3P.

The above solution was shaken up with aqueous KPF_6(18.4 mg, 100 μmol in 1 cm^3) and the aqueous and organic layers were separated. The $CDCl_3$ layer was diluted with CH_2Cl_2, dried (Na_2SO_4), evaporated in vacuo, and the residue was recrystallized from CH_2Cl_2–hexane to give clear, well-formed prisms of [1,2-bis-(diphenylphosphino)ethane](dimethylaminomethylene)(triphenylphosphine)platinum(II) bis(hexafluorophosphate) (**9a**). Once recrystallized, this material was only slightly soluble in $CDCl_3$.

The ^{1}H-NMR spectrum of a solution prepared from triphenylarsine complex **8** (10.0 mg, 15.9 μmol) and dppe (6.4 mg, 16 μmol) indicated that displacement of the arsine was complete. The solvent was evaporated, and the residue was washed with pentane then recrystallized from CH_2Cl_2–EtOAc to give [1,2-bis(diphenylphosphino)ethane](chloro)(dimethylaminomethylene)platinum(II) chloride (**7a**), (8.8 mg. 77%), which retained some CH_2Cl_2 solvent. Anal. Found: C, 45.35; H, 4.17; N, 1.80. $C_{29}H_{31}Cl_2NP_2Pt\cdot 0.8\ CH_2Cl_2$ Calc.: C, 45.34; H, 4.16; N, 1.77%. ^{1}H-NMR $\delta = 2.52$ and 2.90 (each m, 2H, CH_2CH_2), 3.19 and 3.42 (each s, 3H, NMe_2), 7.50 and 7.59 (each m, 6H, aromatic H), 7.63 and 7.81 (each m, 4H, aromatic H) and 10.17 (br d, 1H, $^3J_{P-H} = 8$Hz, $^2J_{Pt-H} = 40$Hz, *CH*NMe$_2$). ^{31}P-NMR $\delta = 39.30$(d, $^2J_{P-P} = 7$Hz, $^1J_{Pt-P} = 3501$ Hz) and 40.69(d, $^2J_{P-P} = 7$ Hz, $^1J_{Pt-P} = 2057$ Hz).

4.2.2. Reactions with 1,3-bis(diphenylphosphino)propane (dppp)

A solution prepared from **1** (5.9 mg, 10 μmol) and dppp (4.2 mg, 10 μmol) showed mainly ^{1}H resonances due to **7b** (see below) and free Ph_3P. The ^{31}P-NMR spectrum showed, in addition to resonances corresponding to **7b** and PPh_3, weak resonances at $\delta = -16.0$ (dd, $^2J_{P-P} = 285$ and 35 Hz), -14.2(dd, $^2J_{P-P} = 35$ and 22 Hz) and 9.3(dd, $^2J_{P-P} = 285$ and 22 Hz) due to **9c** (Pt satellites were not detected. **7b**:**9c** ca 9:1 based on peak heights).

Reaction of arsine complex **8** (7.0 mg, 11 μmol) with dppp (4.6 mg, 11 μmol) was rapid and complete. Evaporation of the solvent, washing of the residue with pentane, and crystallization from CH_2Cl_2 by layering with hexane gave [1,3-bis(diphenylphospino)-propane](chloro)(dimethylaminomethylene)platinum(II) chloride (**9c**), (8.0 mg, 98%) containing some water of crystallization. Anal. Found: C, 48.20; H, 4.44; N, 1.80. $C_{30}H_{33}Cl_2NP_2Pt\cdot 0.5H_2O$ Calc.: C, 48.40; H, 4.60; N, 1.88%. ^{1}H-NMR $\delta = 2.00$, 3.05 and 3.57 (each br m, 2H, $CH_2CH_2CH_2$), 2.82 and 3.72 (each s, 3H, NMe_2), 7.40 (m, 12H, aromatic H), 7.75(m, 8H, aromatic H) and 9.41(apparent t, br, 1H, $^3J_{P-H} = 7$ Hz, $^2J_{Pt-H} = 40$ Hz, *CH*NMe$_2$). ^{31}P-NMR $\delta = -7.06$(d, $^2J_{P-P} = 31$ Hz, $^1J_{Pt-P} = 3499$ Hz) and -6.69(d, $^2J_{P-P} = 31$ Hz, $^1J_{Pt-P} = 1955$ Hz).

4.2.3. Reactions with 2,2′-bipyridine(bpy)

No reaction was observed in a solution containing equimolar quantities of **1** and bpy, even after heating at 55°C for 3 h.

Reaction of arsine complex **8** (5.0 mg, 8.0 μmol) and bpy(1.3 mg, 8.0 μmol) proceeded slowly at ambient temperature, requiring several hours to reach equilibrium. After 24 h, product **7c** and starting complex **8** were present in a ratio of 4:1. No change in this ratio was observed after heating the solution at 55°C for a further 2 h. For the preparation of **7c**, complex **8** (10 mg, 16 μmol) was reacted with excess bpy (7.5 mg, 48 μmol). When **8** could no longer be detected by ^{1}H-NMR spectrometry the solution was transferred to a vial and excess pentane was added to give a precipitate. This was collected and recrystallized from CH_2Cl_2/pentane to give (2.2’-bipyridine)(chloro)(dimethylaminomethylene)platinum(II) chloride **7c**; 6.8 mg, 89%) containing some water of crystallization. Anal. Found: C, 31.30; H, 3.16; N, 8.16. $C_{13}H_{15}Cl_2N_3Pt\cdot H_2O$ Calc.: C, 31.39; H, 3.44; N, 8.45%. ^{1}H-NMR $\delta = 3.96$ and 4.02(each s, 3H, NMe_2), 7.75, 7.90, 8.20 and 8.26 (each t, $J_{obs} = 7.2$ Hz, 1H), 8.38 and 8.47 (each d, $J_{obs} = 8.0$ Hz, 1H), 9.29 (d, br at base, $J_{obs} = 6.4$ Hz), 9.66 (d, $J_{obs} = 6.4$ Hz, $^3J_{Pt-H} = 56$ Hz) and 10.98(s, 1H, *CH*NMe$_2$). The bpy proton signals (7.75–9.66 ppm) all showed additional unresolved coupling.

*4.3. Reactions of **1** with organotin and organomercury derivatives*

4.3.1. Reaction with tetraphenyltin

A solution of **1** (8.2 mg, 14 μmol) and Ph_4Sn (6.8 mg, 16 μmol) in $CDCl_3$ (0.7 cm^3) was allowed to stand at ambient temperature. After 2 h, ca 20% of **1** had reacted to give **11**. After 1 day all of **1** had reacted and the major product present was **12**, which was accompanied by significant amounts of benzaldehyde (*CH*O at $\delta = 10.03$, s) and **13** along with some of the new carbene complex, **17**. Benzaldehyde and **13** were the major products after 2 days, and after 5 days, only benzaldehyde, **13**, **17**, and a trace of **14** were detectable.

4.3.2. Reaction with diphenylmercury

The only significant products detected upon reaction of **1** (6.4 mg, 11 μmol) with Ph_2Hg (4.3 mg, 12 μmol) in $CDCl_3$ (0.7 cm^3) were benzaldehyde and **13** [^{1}H-NMR $\delta = 2.55$ (dd, $^3J_{H-H} = 6$ Hz, $^4J_{P-H} = 3$ Hz, $^3J_{Pt-H} = 36$ Hz, NMe_2), 3.84 (br, NH) and 7.2 – 7.8 (aromatic H). ^{31}P-NMR $\delta = 12.24$($^1J_{Pt-P} = 4291$ Hz)]. An attempt to isolate **13** by preparative TLC (eluant MeOH–CH_2Cl_2, 1:49) resulted in partial isomerisation to **14** (NMe_2 at $\delta_H = 2.74$; $\delta_P = 3.90$, $^1J_{Pt-P} = 3524$ Hz) [9b].

4.3.3. Reaction with phenyltrimethyltin

Reaction of **1** (5.6 mg, 9.6 μmol) with $PhSnMe_3$ (2.9 mg, 12 μmol) initially gave **11** (ca 1/3 conversion after 30 min.). After a few hours, when **11** was the major platinum complex present, small amounts of **12**, benzaldehyde and **13** could be detected. Further reaction proceeded less cleanly than had been observed with Ph_4Sn or Ph_2Hg, but on standing for 2 days the quantity of **11** present in the mixture decreased significantly, **12** disappeared, and benzaldehyde, **13**, **14** and carbene complex **17** built up, along with additional minor products.

When the above reaction was repeated in dry $CDCl_3$ and in an NMR tube capped under nitrogen, clean conversion of **1** into **11** was observed to take place over a few hours. After about one day, resonances corresponding to benzaldehyde, *N*,*N*-dimethylbenzylamine (s at $\delta = 2.6$ and 3.45), **13**, **14** and carbene complex **17** could be detected. These resonances grew slowly when the solution was left to stand, but initial product **11** was still present after several days.

Similar initial clean conversion of **1** into **11** was observed under air when dry $CDCl_3$ was used, with the addition of one or two small pellets of CaH_2.

*4.3.4. Preparation of chloro[(α-dimethylamino)benzyl]-(triphenylphosphine)platinum(II) (**11**)*

Complex **1** (22.4 mg, 38.4 μmol) and $PhSnMe_3$ (11.9 mg, 49.3 μmol) were dissolved in dry $CDCl_3$ (1.4 cm^3) in a dry NMR tube under N_2. The tube was capped and the reaction was allowed to proceed until conversion of **1** into **11** was complete (< 2 h). The tube was then opened to air and the reaction solution was washed with water (3 × 2 cm^3) to remove Me_3SnCl and briefly dried (Na_2SO_4). The resulting solution was concentrated in vacuo almost to dryness, and the resulting gummy residue was triturated with pentane to precipitate a white solid. This was washed with fresh pentane and dried in vacuo to give an essentially clean sample of **11** (22.3 mg, 92.6%). Recrystallization from CH_2Cl_2–pentane, or CH_2Cl_2–diethylether gave **11** containing one molar equivalent of water. Anal. Found: C, 50.40; H, 4.40; N, 2.08. $C_{27}H_{27}ClNPPt \cdot H_2O$. Calc.: C, 50.27; H, 4.53; N, 2.17%. ^{1}H-NMR $\delta = 2.63$ (d, $^4J_{P\text{–}H} = 5.6$ Hz, $^3J_{Pt\text{–}H} = 18$ Hz, 3H, NMe), 3.10(d, $^4J_{P\text{–}H} = 4.8$ Hz, $^3J_{Pt\text{–}H} = 24$ Hz, 3H, NMe), 4.19 (d, $^3J_{P\text{–}H} = 5.6$ Hz, $^2J_{Pt\text{–}H} = 80$ Hz, 1H, *CH*Ph), 6.9 − 7.2(m, 3H, CHPh), 7.25(br, 11H, aromatic H) and 7.49(br, 6H, aromatic H). ^{31}P-NMR $\delta = 23.67(^1J_{Pt\text{–}P} = 5526$ Hz).

*4.3.5. Dichloro[(α-dimethylammonio)benzyl]-(triphenylphosphine)platinum(II) (**12**)*

Excess acetyl chloride (three to four equivalents) was added to a solution of **11** (15.5 mg, 24.0 μmol) in $CDCl_3$ (1 cm^3). Monitoring by ^{1}H-NMR spectrometry showed consumption of **11** and formation of **12** along with additional minor products. During this time, a white, crystalline solid began to deposit. The sample was left in the refrigerator overnight, the crystals were recovered and washed with $CDCl_3$ to give **12** (9.7 mg, 61%). Recrystallization from CH_2Cl_2–$CHCl_3$ gave material containing $CHCl_3$. Anal. Found: C, 45.14; H, 3.87; N, 1.96. $C_{27}H_{29}Cl_2NPPt \cdot 0.6CHCl_3$ Calc.: C, 45.10; H, 3.92; N, 1.91%. ^{1}H-NMR (CD_2Cl_2) $\delta = 2.24$.(d, $^3J_{H\text{–}H} = 5.6$ Hz, 3H, NMe), 3.23(d, $^3J_{H\text{–}H} = 5.2$ Hz, 3H, NMe), 3.29 (t, $^3J_{H\text{–}H} = {}^3J_{P\text{–}H} = 7.8$ Hz, 1H, *CH*Ph), 7.15(br m, 3H, CH*Ph*), 7.38(m, 7H, aromatic H), 7.50 (m, 10H, aromatic H) and 8.75(br, 1H, NH). A 2D COSY spectrum showed that the resonance at $\delta = 8.75$ was coupled to those at $\delta = 2.24$, 3.23 and 3.29. ^{31}P-NMR ($CDCl_3$) $\delta = 13.13$ ($^1J_{Pt\text{–}P} = 4710$ Hz).

On standing, solution **12** decomposed to give mainly benzaldehyde and **14** along with a trace of **13**.

*4.3.6. Dichloro[(α-dimethylamino)benzylidene]-(triphenylphosphine)platinum(II) (**17**)*

Carbene complex **1** (16.0 mg, 27.3 μmol) and $PhSnMe_3$ (9.9 mg, 41 μmol) in dry $CDCl_3$ (1 cm^3) were allowed to sit until conversion of **1** into **11** was complete. The solution was transferred to a round-bottomed flask, the solvent was removed in vacuo, and the residue was left under vacuum (ca 1 torr) overnight. The resulting dark, gummy material was then subjected to preparative TLC (eluant MeOH–CH_2Cl_2, 1:49) to give a fraction containing **17**. Recrystallization from CH_2Cl_2–benzene gave pure **17** (4.2 mg, 23%) containing some water. Anal. Found: C, 48.71; H, 4.04; N, 2.02 $C_{27}H_{26}Cl_2NPPt \cdot 0.25H_2O$ Calc.: C, 48.69; H, 4.01; N, 2.10%. ^{1}H-NMR $\delta = 2.98$(s, $^4J_{Pt\text{–}H} = 7$ Hz, 3H, NMe), 4.14(s, $^4J_{Pt\text{–}H} = 9$ Hz, 3H, NMe), 6.53(d, $^3J_{H\text{–}H} = 7.6$ Hz, 2H, C–*Ph o* − H), 7.14 (t, $^3J_{H\text{–}H} = 7.6$ Hz, 2H, C − *Ph m* − H), 7.25 (t, $^3J_{H\text{–}H} = 7.6$ Hz, 1H, C − *Ph p* − H) 7.33(br, 6H, aromatic H) and 7.42(br, 9H, aromatic H). ^{31}P-NMR $\delta = 7.77(^1J_{Pt\text{–}P} = 4194$ Hz).

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