Transition Metal–Carbon Bonds. Part 49.[1] The Action of Amines on *cis*-[PtCl$_2$(PPr$^n{}_3$)(C$_3$H$_4$)]: Crystal Structures of the Complexes [PtCl(PPr$^n{}_3$){C(=CH$_2$)CH$_2$NHBu^t}] (Four-membered Ring) and [Pt$_2$Cl$_2$(PPr$^n{}_3$)$_2${C(=CH$_2$)CH$_2$NHMe}$_2$] (Eight-membered Ring) †

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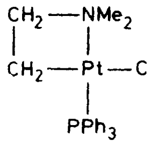
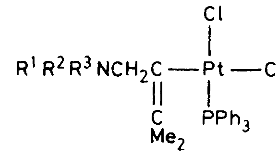
Addition of NR$_3$(R = Me or Et) to the allene complex *cis*-[PtCl$_2$(PPr$^n{}_3$)(C$_3$H$_4$)] rapidly gives the zwitterionic alkenyl complexes [PtCl$_2$(PPr$^n{}_3$){C(=CH$_2$)CH$_2$NR$_3$}]. Addition of NH$_2$Bu^t to the allene complex at or below −20° C gives an analogous complex, *viz.* [PtCl$_2$(PPr$^n{}_3$){C(=CH$_2$)CH$_2$NH$_2$Bu^t}], but this with base, *i.e.* an excess of NH$_2$Bu^t or preferably Na[OPr^i], immediately cyclizes to give [PtCl(PPr$^n{}_3$){C(=CH$_2$)CH$_2$NHBu^t}] (5) the crystal structure of which has been determined and shown to contain a four-membered ring. Treatment of the allene complex with an excess of methylamine gives [Pt$_2$Cl$_2$(PPr$^n{}_3$)$_2${C(=CH$_2$)CH$_2$NHMe}$_2$] (6a) the crystal structure of which has also been determined and shown to contain an eight-membered ring. Benzylamine gives an analogous complex. Proton, ^{31}P, and ^{195}Pt n.m.r. data are given and discussed, as are i.r. data. Crystals of (5) are monoclinic, space group *C*2/*c*, with *a* = 19.653(3), *b* = 11.538(2), *c* = 18.785(2) Å, β = 107.10(1)°, and *Z* = 8; *R* = 0.036 for 2 300 independent reflections. The complex (6a) is monoclinic, space group *P*2$_1$/*n*, with *a* = 11.315(3), *b* = 13.782(2), *c* = 11.385(3) Å, β = 100.76(2)°, and *Z* = 2; *R* = 0.032 for 2 083 independent reflections.

STUDIES of attack by nucleophiles on olefins co-ordinated to platinum(II) go back over 70 years.[2-7] In such reactions the nucleophile and the platinum atom effectively add across the double bond in a *trans* fashion, *i.e.* the nucleophilic attack is *exo*.[4] With the closely related palladium(II) complexes addition or elimination of nucleophiles normally also occurs specifically in a *trans* fashion, although the oxidative hydrolysis of ethylene (Wacker process) is usually considered to be a *cis* addition.[8] In the past few years there have been several studies of the attack by amines on olefin–platinum(II) complexes. Early work was mainly with chelating diolefins to give chelated aminoalkylmono-olefin–platinum(II) complexes which were readily isolated.[9] Products from amine attack on co-ordinated mono-olefins are less stable [10] and, for example, Al-Najjar and Green [11] have measured the stabilities of a series of zwitterionic adducts of the type *trans*-$\overset{+}{\text{am}}$CH$_2\overset{-}{\text{C}}$H$_2$PtCl$_2$(am), where am = a primary, secondary, or tertiary amine, with respect to dissociation to free amine and the ethylene complex *trans*-[PtCl$_2$(C$_2$H$_4$)(am)]. It has also been reported [12] that attack of dimethylamine on *cis*-[PtCl$_2$(C$_2$H$_4$)(PPh$_3$)] gives complex (1) containing a four-membered ring; other complexes containing four-membered rings but with ligands other than phosphines have since been reported.[13] The 1,1-dimethylallene complex *cis*-[PtCl$_2$(PPh$_3$)(CH$_2$=C=CMe$_2$)] is attacked by primary, secondary, or tertiary amines (am) to give adducts of the type (2),[14] but further attack by nitrogen on platinum to give a ring complex (*e.g.* a four-membered ring) was not observed. In a more recent paper [15] it has been reported that the action of poorly basic aromatic primary amines, *e.g.* 4-nitroaniline, on *cis*-[PtCl$_2$(PPh$_3$)(CH$_2$=C=CMe$_2$)] gives only an enamine complex (3).

We have now studied the products formed by attack of some aliphatic amines on the allene complex *cis*-[PtCl$_2$(PPr$^n{}_3$)(CH$_2$=C=CH$_2$)]. This allene complex is stable in solution [1] in contrast with *cis*-[PtCl$_2$(PPh$_3$)(CH$_2$=C=CH$_2$)] which was reported to be unstable in solution.[14] We hoped to study the regiospecificity of the amine attack on the co-ordinated allene and also the possibility of ring formation through further co-ordination of the amine to the platinum to give either a four-membered ring (mononuclear complex) or an eight-membered ring (binuclear complex). There was also the further possibility of reactions of the second double bond including prototopic shifts, addition reactions, *etc.*


(1)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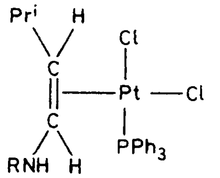
(3) R = aryl

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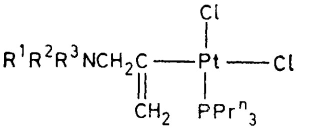
† Chloro(1-methylene-2-t-butylaminoethyl-*C'N*)(tri-n-propylphosphine)platinum(II) and *trans*-*bis*-μ-(1-methylene-2-methylaminoethyl-*C'N*)-bis[chloro(tri-n-propylphosphine)platinum(II)] respectively.

RESULTS AND DISCUSSION

Addition of trimethyl- or triethyl-amine to a dichloromethane solution of the allene complex *cis*-[$PtCl_2(PPr^n_3)(C_3H_4)$] rapidly gave the zwitterionic alkenyl complexes (4a) and (4b) respectively in good yield. These adducts are stable in the solid state but decompose after a few hours in solution at room temperature. Microanalytical and i.r. data are given in Table 1 and ^{31}P, ^{195}Pt, and ^{1}H n.m.r. data in Tables 2 and 3 respectively. There was no evidence for attack of the amine on the central carbon atom of the allene, *i.e.* attack occurred regiospecifically on the terminal (methylene) carbon. The complexes are thus analogous to those formed by nucleophilic attack of secondary or tertiary amines on the 1,1-dimethylallene complex *cis*-[$PtCl_2(PPh_3)(CH_2{=}C{=}CMe_2)$], *viz.* type (2). For our products (4a) and (4b) the low values of ν(Pt–Cl) in the i.r. spectra (Table 1) indicate retention of the *cis*-dichloro-configuration and this is confirmed by the high value of ^{1}J(PtP) (>4 300 Hz, Table 2). An alkyl group *cis* to a phosphine produces a large increase in ^{1}J(PtP) relative to most other ligands.[16] In the ^{1}H n.m.r. spectrum of (4a) the methylene protons of the alkenyl moiety are isochronous down to −60 °C, implying free rotation about the platinum–carbon bond. This contrasts with the dimethylallene adducts (2) where hindered rotation was indicated by inequivalence of the methylene protons even at +85 °C.[14] The two vinylic protons of (4a) or (4b) have large disparate values of ^{3}J(PtH); the larger coupling (*ca.* 120 Hz) is clearly the *trans* coupling and the smaller (*ca.* 60 Hz) the *cis* coupling.[17,18]



(4a) $R^1 = R^2 = R^3 = Me$
(4b) $R^1 = R^2 = R^3 = Et$
(4c) $R^1 = Bu^t$, $R^2 = R^3 = H$
(4d) $R^1 = Me$, $R^2 = R^3 = H$

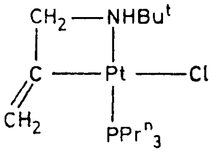
TABLE 1

Analytical (%: calculated values in parentheses) and i.r. (cm⁻¹) data

Complex	Analyses C	Analyses H	Analyses N	M.p. (θ_c/°C) [a]	ν(C=C)	ν(N–H)	ν(Pt–Cl)
cis-[$PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NMe_3\}$]	34.0 (34.3)	6.35 (6.50)	2.70 (2.65)	120—130	1 575		254, 277
cis-[$PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NEt_3\}$]	38.25 (38.1)	7.00 (7.10)	2.40 (2.45)	105—110	1 550		260, 287
cis-[$PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NH_2Bu^t\}$]	35.45 (35.65)	6.65 (6.75)	2.35 (2.60)	145—148	1 587	2 420 2 625	255, 275
[$PtCl(PPr^n_3)\{C(=CH_2)CH_2NHBu^t\}$] [b]	38.3 (38.2)	6.90 (7.00)	2.80 (2.80)	141—145	1 600	3 200	260
[$Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NHMe\}_2$] [c]	33.7 (33.9)	6.25 (6.35)	3.00 (3.05)	198—203	1 582	3 180	280
[$Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NH(CH_2Ph)\}_2$] [d]	42.5 (42.5)	6.05 (6.20)	2.60 (2.60)	170 [e]	1 582	3 180	[f]

[a] With decomposition. [b] Molecular weight, *M* 508 (503). [c] *M* 908 (922). [d] *M* 1 082 (1 074). [e] Decomposed without melting. [f] Not identified in spectrum.

The previous workers attempted to add primary amines to *cis*-[$PtCl_2(PPh_3)(CH_2{=}C{=}CMe_2)$] but were unable to characterize the products.[14] We have identified the products formed by treating *cis*-[$PtCl_2(PPr^n_3)(C_3H_4)$] with t-butyl-, methyl-, or benzyl-amine. Addition of NH_2Bu^t (1 mol per platinum atom) to a dichloromethane solution of the allene complex at room temperature gave a mixture consisting of unchanged allene complex and two products, A and B, characterized by ^{31}P n.m.r. spectroscopy. However, addition of 1 mol of NH_2Bu^t to *cis*-[$PtCl_2(PPr^n_3)(C_3H_4)$] at −20 °C gave a single product (adduct) A, identified as the zwitterion (4c) (characterizing data in the Tables). Treatment of this adduct with an excess of NH_2Bu^t gave incomplete conversion of this zwitterion (4c) into the previously observed second species B, identified from its ^{31}P n.m.r. parameters. However, addition of 1 mol of sodium propan-2-oxide to the adduct (4c) caused complete conversion into B which is conveniently prepared from the allene complex *cis*-[$PtCl_2(PPr^n_3)(C_3H_4)$] by addition of 1 mol NH_2Bu^t followed by 1 mol Na[OPr^i] at *ca.* −20 °C. This product is mononuclear (Table 1) and on the basis of microanalytical and n.m.r. data (Tables) was tentatively formulated as the four-membered ring chelate (5). This formulation has been confirmed by a single-crystal structural determination, see below. In the zwitterionic adduct (4c) the chlorine *trans* to phosphorus will be labile and the amine nitrogen readily displaces it in the presence of base which removes an



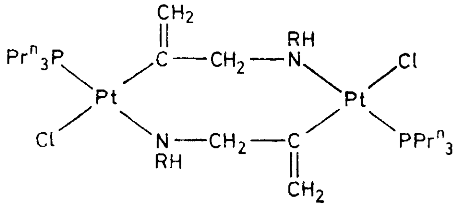
(5)

NH_2 proton. Analysis of the ^1H n.m.r. spectrum of (5) was facilitated by the addition of D_2O which replaces the NH proton with deuterium over several hours. The ^{13}C n.m.r. spectrum of the cyclized product (5) is consistent with the assigned structure. The ^{13}C n.m.r. parameters (δ/p.p.m., *J*/Hz) are as follows:

$C{=}CH_2$	δ 116.0	^2J(PC)	2	^1J(PtC)	838
$C{=}CH_2$	δ 105.3	^3J(PC)	3	^2J(PtC)	83
NCH_2	δ 64.0	^3J(PC)	4	^2J(PtC)	104
$C(CH_3)_3$	δ 56.6	^3J(PC)	<1	^2J(PtC)	12
$C(CH_3)_3$	δ 27.9	^4J(PC)	1	^3J(PtC)	16
PCH_2	δ 25.7	^1J(PC)	37	^2J(PtC)	46
PCH_2CH_2	δ 18.3	^2J(PC)	1	^3J(PtC)	35
$PCH_2CH_2CH_3$	δ 15.7	^3J(PC)	15	^4J(PtC)	0

Thus complex (5) is related to (1), formed by treatment of *cis*-$[PtCl_2(C_2H_4)(PPh_3)]$ with dimethylamine.[12] As mentioned above, it has recently been shown that such cyclization is not unique to phosphine complexes [13] but as yet no crystal structure has been reported for this type of complex.

In view of the tendency for t-butylamine and dimethylamine to give four-membered ring chelates (5) and (1) respectively, we studied the action of the much less sterically demanding amine, methylamine, on the allene complex *cis*-$[PtCl_2(PPr^n_3)(C_3H_4)]$. With 1 mol of methylamine per platinum, mixtures were formed, but treatment of a dichloromethane solution of the allene complex with an excess of methylamine at −30 °C gave an immediate precipitate of $[NH_3Me]Cl$ and a colourless crystalline complex, formulated on the basis of microanalytical and molecular-weight measurements (in solution) as a binuclear species $[Pt_2Cl_2(PPr^n_3)_2(C_8H_{16}N_2)]$. It seemed most likely that a zwitterionic intermediate (4d) in the presence of a base (*i.e.* NH_2Me) attacked a similar molecule such that the nitrogen of one molecule displaced the chlorine *trans* to tri-n-propylphosphine in a second molecule, giving eventually the binuclear complex (6a) containing an eight-membered ring. Whilst some of the ^1H n.m.r. parameters for the eight-membered ring complex (6a) are similar to those of the four-membered ring complex (5a) (Table 3), most of the ^1H chemical shifts are significantly different and the value of ^1J(PtP) is lower. These differences are presumably consequent on the differences in steric strain and hybridization between the four- and the eight-membered rings.



(6a) R = Me
(6b) R = CH_2Ph

Another parameter which might be expected to show the effect of ring strain is the ^{195}Pt chemical shift. We,[19,20] and others,[21] have found that in platinum and rhodium complexes the effect of a four-membered ring is to shift the metal resonance to high frequency, and here we find that the ^{195}Pt shift of (5) is 409 p.p.m. higher than that of (6a) (see Table 2). It is interesting to note that the reported ^{195}Pt chemical shift of the ^{15}N isotopomer of (1) [12] (635 p.p.m. on our scale) is midway between

TABLE 2

Phosphorus-31 and ^{195}Pt n.m.r. parameters

Complex	δ(^{31}P) [a]	^1J(PtP)/Hz	δ(^{195}Pt) [b]
cis-$[PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NMe_3\}]$ [c]	−3.0	4 307	
cis-$[PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NEt_3\}]$ [d]	−4.4	4 334	642
cis-$[PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NH_2Bu^t\}]$ [d]	−0.9	4 512	
$[PtCl(PPr^n_3)\{C(=CH_2)CH_2NHBu^t\}]$ [e]	−3.5	4 153	829
$[Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NHMe\}_2]$ [d]	−4.0	3 774	420
$[Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NH(CH_2Ph)\}_2]$ [d]	−4.7	3 833	

[a] In p.p.m. to high frequency of H_3PO_4. [b] In p.p.m. to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. [c] In CD_2Cl_2. [d] In $CDCl_3$. [e] In $(CD_3)_2CO$.

TABLE 3

Hydrogen-1 n.m.r. parameters [a]

	C=CH₂		CCH₂N		NH	NR	Coupling constants (*J*/Hz)												
Complex	δ(H^1)	δ(H^2)	δ(H^3)	δ(H^4)	δ(H^5)	δ(H^6)	H^1H^2	H^1H^3	H^1H^4	H^2H^3	H^2H^4	H^3H^4	H^3H^5	H^4H^5	PtH^1	PtH^2	PtH^3	PtH^4	PtH^5
cis-$[PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NMe_3\}]$ [b]	6.02	5.55	3.72			3.40	2.1	<1		0					116.7	63.0	58.8		
cis-$[PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NEt_3\}]$ [c]	6.05	5.60	3.71			3.73 1.39	1.9	<1		0					121.0	63.7	54.5		
cis-$[PtCl_2(PPr^n_3)\{C(=CH_2)CH_2NH_2Bu^t\}]$ [c]	5.98	5.16	3.61		7.98	1.51	1.2	*ca.* 1		0				5	126	62.2	50.4		<5
$[PtCl(PPr^n_3)\{C(=CH_2)CH_2NHBu^t\}]$ [d]	4.74	4.43	4.71	4.46	3.8	1.34	<1	1.8	1.8	2.2	2.2	15	7.5	6.9	173.7	90.4	72	*e*	*e*
$[Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NHMe\}_2]$ [c,f]	5.84	5.08	4.10	3.15	4.50	2.77	1.5	0	1.5	0	1.5	12.0	11.9	*ca.* 1	128.7	69.1	84.7 [g]	64 [g]	*e*

[a] Phosphine resonances have been omitted. [b] In CD_2Cl_2. [c] In $CDCl_3$. [d] In $(CD_3)_2CO$. [e] Coupling not identified in spectrum. [f] J(PtH⁶) 30.1; J(PH¹) *ca.* 0.5; J(PH²) *ca.* 0; J(PH³) *ca.* 1; J(PH⁴) 10; J(PH⁵) *ca.* 5; J(PH⁶) 2.9 Hz. For the other complexes all couplings to ^{31}P were <1 Hz. [g] Only one set of ^{195}Pt satellites identified.

the two.* This may reflect a greater degree of ring strain in complex (5), which contains an sp^2-hybridized carbon atom, than in (1) where the carbon is sp^3. [The fact that the phosphines in (1) and (5) are different should have little effect on the value of δ(Pt).[22]]

In view of these differences in n.m.r. parameters there was some doubt about our formulation and therefore the crystal structure of the eight-membered ring complex (6a) was determined and is discussed below. Although the binuclear nature of (6a) was established beyond doubt by osmometric measurements in solution (Table 1), and by single-crystal *X*-ray diffraction, its mass spectrum showed no peaks higher than *m/e* 463, corresponding to a mononuclear species $[PtCl(PPr^n_3)(C_4H_8N)]$. Since the formulation of the product obtained by treating *cis*-$[PtCl_2(C_2H_4)(PPh_3)]$ with dimethylamine as a mononuclear species (1) with a four-membered ring was dependent on the molecular-weight determination, solely by mass spectrometry,[12] we have repeated the preparation. We find that the molecular weight of the product in chloroform solution as determined osmometrically also shows it to be mononuclear and we therefore agree with the formulation as a four-membered ring chelate (1).

We have also treated *cis*-$[PtCl_2(PPr^n_3)(C_3H_4)]$ with benzylamine. The product $[Pt_2Cl_2(PPr^n_3)(C_{20}H_{24}N_2)]$ is formulated as an eight-membered-ring chelate complex (6b) on the basis of microanalytical, molecular-weight, and ^1H and ^{31}P n.m.r. data (Tables). Overlapping of the methylene resonances precluded a full analysis of the ^1H n.m.r. spectrum, although the vinylic protons were readily identified at δ 5.69 and 4.22. Treatment of *cis*-$[PtCl_2(PPr^n_3)(C_3H_4)]$ with dimethylamine, however, gave a mixture of products which were very soluble and which we could not separate.

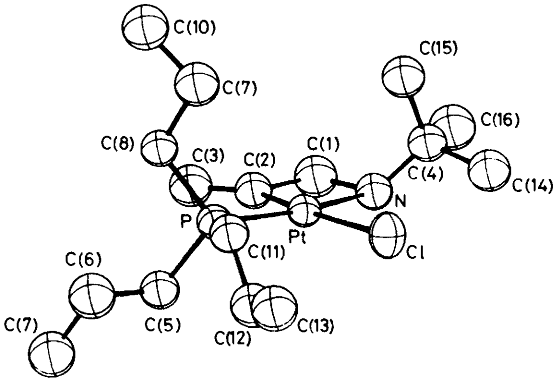


FIGURE 1 Molecular structure of $[PtCl(PPr^n_3)\{C(=CH_2)CH_2NHBu^t\}]$ (5)

Crystal Structures of $[PtCl(PPr^n_3)\{C(=CH_2)CH_2NHBu^t\}]$ (5) *and* $[Pt_2Cl_2(PPr^n_3)_2(C_8H_{16}N_2)]$ (6a).—The structures of (5) and (6a) were determined by *X*-ray diffraction, and are shown with the atom numbering in Figures 1 and 2. The t-butylamine derivative (5) is confirmed to be mononuclear with a four-membered ring, while the binuclear methylamine derivative (6a) has a centrosymmetric eight-membered ring of chair conformation. Selected bond lengths and angles are given in Table 4. While the Pt–P and Pt–Cl bond lengths show close agreement between the two structures, the Pt–N and Pt–C bonds appear significantly different. Since these are the bonds involved in the four- and eight-membered rings, these differences may be associated with strain in the small ring, although it is not obvious why an elongation of the Pt–N bond and a compression of the Pt–C bond should occur in the small ring. Alternatively, the lengthening of the Pt–N bond may be due to non-bonded repulsion between the metal and the

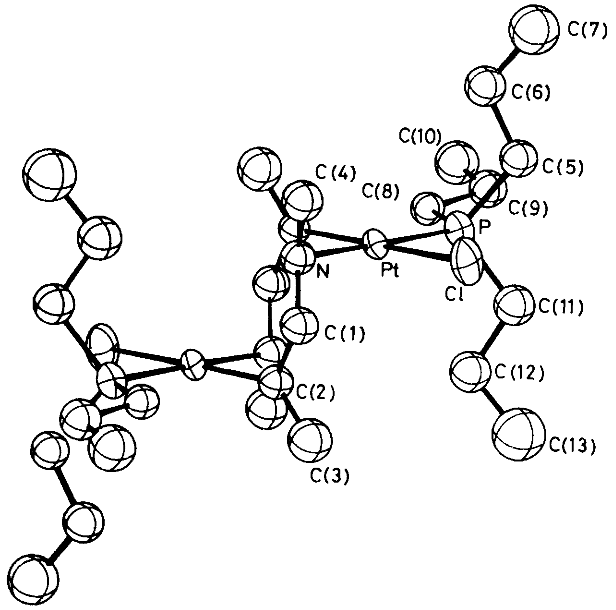


FIGURE 2 Molecular structure of $[Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NHMe\}_2]$ (6a)

TABLE 4

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

	t-Butylamine derivative	Methylamine derivative
Pt–N	2.179(9)	2.132(6)
Pt–C(2)	1.975(11)	2.011(8)
Pt–P	2.217(3)	2.220(2)
Pt–Cl	2.406(3)	2.400(2)
N–C(1)	1.494(15)	1.488(12)
C(1)–C(2)	1.553(17)	1.496(11)
N–C(4)	1.475(13)	1.488(12)
C(2)–C(3)	1.336(16)	1.322(14)
P–C(5)	1.831(10)	1.833(9)
P–C(8)	1.817(9)	1.832(8)
P–C(11)	1.828(13)	1.836(11)
P–Pt–Cl	95.6(1)	89.3(1)
P–Pt–C(2)	96.6(3)	95.1(2)
N–Pt–Cl	98.8(2)	89.7(2)
N–Pt–C(2)	69.0(4)	85.9(3)
Pt–N–C(1)	91.5(7)	114.1(5)
N–C(1)–C(2)	101.4(9)	111.5(6)
C(1)–C(2)–Pt	97.9(7)	120.7(5)

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* We obtained a value of 659 p.p.m. for complex (1) in $CDCl_3$ solution.

t-butyl group, with Pt–C bond shortening by a similar amount in compensation.

The difference in behaviour of dimethyl- or t-butyl-amine, on the one hand, which give four-membered ring chelates, and methyl- or benzyl-amine, on the other, which give eight-membered ring binuclear chelates, can be considered as an example of the Thorpe–Ingold effect.[23] Thorpe and Ingold found that a *gem*-dimethyl group was particularly effective in promoting small carbocyclic ring formation and Ingold [24] in 1921 pointed out that all naturally occurring three- and four-membered rings which were known at that time carried a *gem*-dimethyl group, *i.e.* the effect manifests itself in nature. Other sterically demanding groups such as t-butyl also have a pronounced effect on the tendency to ring close. The Thorpe–Ingold effect has been reviewed.[23] It also seems likely that with a t-butylamine adduct of type (4c) the nitrogen would be very sterically hindered and attack on the platinum of a second molecule would be difficult, whereas with the methylamine analogue (4d), for which steric hindrance would be less, attack on a second platinum to give (6a) can occur.

EXPERIMENTAL

The general techniques used were the same as in other recent papers from this laboratory.[25] The ^{1}H, ^{31}P-{^{1}H}, and ^{13}C-{^{1}H} n.m.r. spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock. Except where stated otherwise, measurements were made at ambient temperature (*ca.* 296 K). Platinum-195 chemical shifts were determined on a JEOL FX90Q spectrometer.

The Trimethylamine Adduct (4a).—Trimethylamine (0.015 3 g, 0.260 mmol) in dichloromethane (0.15 cm^3) was added to a solution of *cis*-[PtCl$_2$(PPr$^n_3$)(C$_3$H$_4$)] (0.121 g, 0.260 mmol) in dichloromethane (5 cm^3). Removal of most of the solvent under reduced pressure gave the required product as white plates (0.124 g, 91%). The triethylamine adduct (4b) was prepared similarly. Yield 87%.

The t-Butylamine Adduct (4c).—t-Butylamine (0.026 g, 0.356 mmol) was added to a solution of the allene complex (0.166 g, 0.356 mmol) in dichloromethane (5 cm^3) at −20 °C. The solvent was removed under reduced pressure and the residual yellow oil was extracted with diethyl ether. The insoluble residue was recrystallized from dichloromethane–diethyl ether to give the required product as white prisms (0.062 g, 32%).

[PtCl(PPr$^n_3$){C(=CH$_2$)CH$_2$NHBu^t}] (5).—t-Butylamine (0.024 g, 0.329 mmol) was added to a solution of the allene complex (0.150 g, 0.322 mmol) in dichloromethane (5 cm^3) at *ca.* −78 °C followed by a solution of sodium propan-2-oxide (0.32 mmol) in propan-2-ol (*ca.* 3 cm^3). The solvent was removed under reduced pressure and the residual brown oil washed with water. The residue was dried (vacuum), washed with pentane, and recrystallized from diethyl ether at *ca.* −25 °C. The required product was obtained as white prisms (0.093 g, 57%).

[Pt$_2$Cl$_2$(PPr$^n_3$)$_2$(C$_8$H$_{16}$N$_2$)] (6a).—Methylamine (*ca.* 0.4 g, *ca.* 1.3 mmol) was added to a solution of the allene complex (0.112 g, 0.24 mmol) in dichloromethane (5 cm^3) at −30 °C. This gave an immediate precipitate of methylamine hydrochloride. The solvent was removed under reduced pressure and the resultant residue washed with water, dried (under vacuum), and recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) at *ca.* −30 °C. This gave the required product as colourless prisms (0.093 g, 84%). The complex [Pt$_2$Cl$_2$(PPr$^n_3$)$_2$(C$_{20}$H$_{24}$N$_2$)] (6b) was prepared similarly as colourless *prisms*. Yield 64%.

Crystal Data.—(*a*) *t-Butylamine derivative.* C$_{16}$H$_{35}$ClNPPt, M = 502.98, Monoclinic, a = 19.653(3), b = 11.538(2), c = 18.785(2) Å, β = 107.10(1)°, U = 4 071(1) Å^3, D_m = 1.629, Z = 8, D_c = 1.641 g cm^{-3}, F(000) = 1 984, space group $C2/c$, Mo-K_α radiation, graphite monochromatized, λ = 0.710 69 Å, μ(Mo-K_α) = 71.67 cm^{-1}.

(*b*) *Methylamine derivative.* C$_{26}$H$_{58}$Cl$_2$N$_2$P$_2$Pt$_2$, M = 921.8, Monoclinic, a = 11.315(3), b = 13.782(2), c = 11.385(3) Å, β = 100.76(2)°, U = 1 744.2(6) Å^3, Z = 2, D_c = 1.755 g cm^{-3}, F(000) = 896, space group $P2_1/n$, λ = 0.710 69 Å, μ(Mo-K_α) = 83.58 cm^{-1}.

TABLE 5

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) t-Butylamine derivative (5)			
Pt	0.104 20(2)	0.067 64(3)	0.312 49(2)
P	0.160 02(14)	−0.079 72(21)	0.278 48(15)
Cl	0.132 66(15)	0.206 73(25)	0.230 19(16)
N	0.045 4(4)	0.180 8(7)	0.366 2(4)
C(1)	0.034 6(7)	0.084 4(10)	0.414 9(7)
C(2)	0.068 5(5)	−0.019 2(9)	0.384 8(5)
C(3)	0.066 0(6)	−0.126 1(10)	0.411 2(6)
C(4)	0.073 4(5)	0.288 5(10)	0.406 6(5)
C(5)	0.098 7(5)	−0.196 4(9)	0.235 0(5)
C(6)	0.133 4(7)	−0.307 5(12)	0.218 3(7)
C(7)	0.076 7(8)	−0.398 0(12)	0.182 7(8)
C(8)	0.225 5(6)	−0.147 2(9)	0.356 5(5)
C(9)	0.280 8(7)	−0.060 2(10)	0.403 1(7)
C(10)	0.333 4(7)	−0.127 5(12)	0.466 7(7)
C(11)	0.213 5(5)	−0.048 9(9)	0.215 8(6)
C(12)	0.169 4(6)	−0.031 6(11)	0.133 2(7)
C(13)	0.215 7(7)	0.011 3(12)	0.086 8(7)
C(14)	0.071 3(6)	0.383 9(11)	0.348 3(7)
C(15)	0.153 4(6)	0.272 8(11)	0.455 4(7)
C(16)	0.027 8(7)	0.324 8(12)	0.458 2(7)
(*b*) Methylamine derivative (6a)			
Pt	0.033 57(2)	0.112 92(2)	0.124 05(3)
P	−0.023 64(20)	0.267 22(15)	0.111 66(20)
Cl	0.235 16(20)	0.164 04(17)	0.204 79(22)
N	−0.090 9(6)	0.034 6(5)	−0.141 1(6)
C(1)	−0.183 2(8)	0.060 1(6)	−0.068 8(8)
C(2)	−0.131 6(7)	0.059 3(6)	0.062 1(7)
C(3)	−0.197 5(9)	0.018 9(8)	0.133 2(10)
C(4)	−0.132 0(9)	0.062 8(7)	−0.268 4(9)
C(5)	0.011 4(8)	0.328 7(7)	0.256 7(8)
C(6)	−0.064 6(10)	0.293 1(8)	0.347 3(10)
C(7)	−0.020 6(13)	0.336 1(10)	0.473 2(13)
C(8)	−0.183 6(7)	0.292 4(6)	0.057 7(7)
C(9)	−0.219 9(9)	0.400 1(7)	0.064 8(9)
C(10)	−0.358 2(10)	0.409 6(8)	0.034 4(11)
C(11)	0.057 8(9)	0.338 5(7)	0.016 1(9)
C(12)	0.051 4(9)	0.286 6(8)	−0.106 6(9)
C(13)	0.119 7(14)	0.348 4(12)	−0.185 0(14)

Structure Determination.—Cell dimensions for each compound were determined by least-squares treatment of the diffractometer setting angles of 15 reflections with 35 < 2θ < 40°. Intensities of all independent reflections with 4 < 2θ < 45° were measured in the ω—2θ scan mode using scan speeds ranging according to intensity between 3.9 and 29.3° min^{-1}. The structure analyses used only those reflections having $I > 3\sigma(I)$, *i.e.* 2 300 for (*a*) and 2 083 for (*b*), while 404 for (*a*) and 219 for (*b*) were below this threshold and were excluded as ‘ unobserved.’ They were corrected for Lorentz, polarization, and transmission factors; the A^* values were 4.11—6.86 for (*a*) and 2.88—10.24 for (*b*).

After solution of the structures by Patterson and electron-density syntheses, full-matrix least-squares refinement with anisotropic temperature factors for Pt, P, and Cl and isotropic temperature factors for other non-hydrogen atoms converged at $R = 0.036$, $R' = 0.055$ for (*a*) and $R = 0.032$, $R' = 0.049$ for (*b*).

Atomic scattering factors were taken from ref. 26 and weights were derived from the modified variances $\sigma^2(I) = \sigma_c^2(I) + (0.03I)^2$, σ_c being the variance obtained from counting statistics. The atomic co-ordinates with their estimated standard deviations are given in Table 5. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22961 (30 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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