Addition Reactions on Co-ordinated Olefinic Ligands. Part 8.[1,2] Platinum(II) Complexes of 1,1-Dimethylallene and their Reaction with Amines. Molecular Structure of the Zwitterionic Derivative Dichloro-[1-(*NN*-diethylammoniomethyl)-2-methylprop-1-enyl](triphenylphosphine)platinum(II)

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Some new platinum(II) complexes of 1,1-dimethylallene (dma) of general formula *cis*-$[PtCl_2(dma)L]$ ($L = PPh_3$, $AsPh_3$, $H_2NC_6H_4Me$-*p*, or SMe_2O) have been prepared. They react with aliphatic and aromatic amines to give zwitterionic alkenyl derivatives of the type *cis*-$[PtCl_2(Me_2C{=}CCH_2NR^1R^2R^3)L]$, which on treatment with hydrogen chloride afford the ammonium salts $[NR^1R^2R^3(CH_2CH{=}CMe_2)]Cl$. The structure of the alkenyl complexes has been confirmed by *X*-ray diffraction analysis in the case of the title complex. Crystals are triclinic, space group $P\bar{1}$, with $Z = 4$ in a unit cell of dimensions $a = 11.130(3)$, $b = 18.887(5)$, $c = 14.370(5)$ Å, $\alpha = 108.8(3)$, $\beta = 90.1(2)$, $\gamma = 95.1(2)°$. The structure has been solved by Patterson and Fourier methods and refined by block-diagonal least-squares to $R = 0.10$ for 3 630 observed reflections. The σ-bonded alkenyl group is perpendicular to the metal co-ordination plane. A short intramolecular contact between the nitrogen and a chlorine atom suggest the existence of a hydrogen bond.

THE addition of nucleophiles to co-ordinated mono-olefins and dienes, leading to alkyl metal derivatives, has been the object of several recent investigations.[1,3,4] Most of the interest in this field arose because these reactions, besides their potential synthetic value, are useful models of important catalytic processes. A growing interest has focused on the co-ordination chemistry of the allenes,[5] due mainly to the role played by the metal activation in their catalytic polymerisation and oligomerisation reactions. Scarce attention however has been devoted to the subject of nucleophilic addition on co-ordinated 1,2-dienes.

TABLE 1

Selected data for the dimethylallene and allene complexes

Complex	Yield (%)	M.p. (θ_c/°C)	I.r.[a] ν(Pt–Cl)(cm^{-1})	^{1}H N.m.r. (δ/p.p.m.)[b]
cis-$[PtCl_2(Me_2C{=}C{=}CH_2)(PPh_3)]$	93	decomp. >160	300, 325	1.73 (bs,[c] Me), 1.98 (bs,[c] Me), 2.58 (m, 1 H, 62), 3.78 (m, 1 H, 72), 7.26—7.77 (m, PPh_3)
cis-$[PtCl_2(Me_2C{=}C{=}CH_2)(AsPh_3)]$	91	decomp. >170	305, 325	1.75 (bs,[c] Me), 2.02 (bs,[c] Me), 2.82 (m, 1 H, 60), 3.77 (m, 1 H, 66), 7.27—7.73 (m, $AsPh_3$)
cis-$[PtCl_2(Me_2C{=}C{=}CH_2)(H_2NC_6H_4Me$-*p*$)]$	89	162—163 (decomp.)	310, 335	1.87 (bs,[c] Me), 1.91 (s, aryl Me), 2.30 (bs,[c] Me), 3.88 (m, 2 H, 68), 6.00 (NH_2) 7.07 (C_6H_4)
cis-$[PtCl_2(Me_2C{=}C{=}CH_2)(SMe_2O)]$	86	decomp. >120	310, 325,[d] 340[d]	2.05 (bs,[c] CMe), 2.26 (bs,[c] CMe), 3.45 (s, SMe, 21), 3.57 (s, SMe, 20), 3.98 (m, $C{=}CH_2$, 60)
cis-$[PtCl_2(CH_2{=}C{=}CH_2)(PPh_3)]$	78	decomp. >115	300, 330	2.56 (m, 1 H, 58), 4.0 (m, 1 H, 70), 5.43 (m, 2 H, 80), 7.30—7.96 (m, PPh_3)

[a] In Nujol mulls. [b] In $CDCl_3$; s = singlet, bs = broad singlet, m = multiplet. Values in parentheses are coupling constants $J(^{195}Pt–H)$ in Hz revealed by satellite peaks. [c] J(Pt–H) <8 Hz. [d] One of the two bands can be assigned to ν(Pt–S).

As a part of our studies on the reactivity of co-ordinated olefins[1,3] we report the preparation of some new complexes of general formula *cis*-$[PtCl_2(dma)L]$ ($L = PPh_3$, $AsPh_3$, $H_2NC_6H_4Me$-*p*, or SMe_2O; dma = 1,1-dimethylallene), the reaction of *cis*-$[PtCl_2(dma)(PPh_3)]$ with aliphatic and aromatic amines, and the molecular and crystal structure of an addition product.

RESULTS AND DISCUSSION

1,1-*Dimethylallene Complexes*.—Complexes of the type *cis*-$[PtCl_2(allene)L]$ have not been previously described in the literature. We have prepared the complexes reported in Table 1 by displacement of co-ordinated ethylene in *cis*-$[PtCl_2(C_2H_4)L]$.[6] The reaction is fast and almost quantitative. Immediate evolution of gas is observed after addition of an equimolar amount of dma to a chloroform solution of *cis*-$[PtCl_2(C_2H_4)L]$. In addition to the dma complexes we also prepared the allene complex *cis*-$[PtCl_2(C_3H_4)(PPh_3)]$, which is rather unstable and decomposes readily in solution. The dma complexes are air-stable crystalline solids, which can be handled and stored without special precautions.

The *cis* configuration has been assigned to the complexes on the basis of the preparation method, and it is confirmed by the presence of two strong Pt–Cl stretching bands in the i.r. spectra. As in other dma complexes of transition metals,[5] the allene co-ordinates through the less-substituted double bond, and is evidenced by the

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[1] Part 7, A. De Renzi, G. Paiaro, A. Panunzi, and V. Romano, *Chimica e Industria*, 1973, **55**, 248.

[2] A. De Renzi, G. Paiaro, and A. Panunzi, presented in part at VIIth Italian Meeting of Inorganic Chemistry, Pesaro, September 1974.

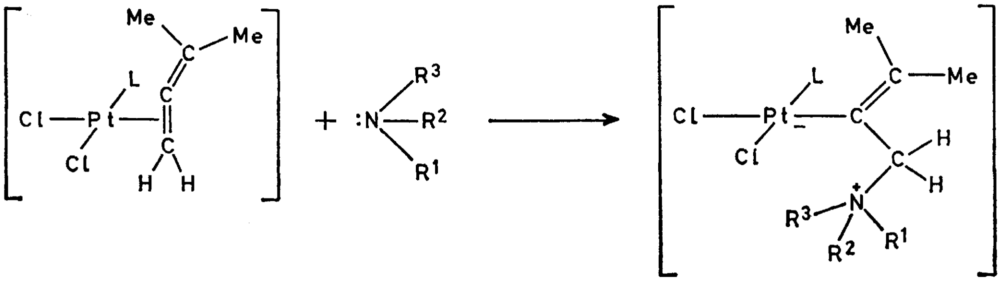
[3] E. Benedetti, A. De Renzi, G. Paiaro, A. Panunzi, and C. Pedone, *Gazzetta*, 1972, **102**, 744 and refs. therein.

[4] R. N. Haszeldine, R. V. Parish, and D. W. Robbins, *J.C.S. Dalton*, 1976, 2355 and refs. therein.

[5] F. L. Bowden and R. Giles, *Co-ordination Chem. Rev.*, 1976, **20**, 81 and refs. therein.

[6] A. De Renzi, G. Paiaro, and A. Panunzi, *Gazzetta*, 1972, **102**, 413; R. Kramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

high coupling constant ^2J(Pt–H) of the methylene protons in the ^1H n.m.r. spectra of the complexes and the correspondingly low coupling constant ^4J(Pt–H) of the methyl protons (see Table 1).



SCHEME 1

The ^1H n.m.r. spectra of some alleneplatinum(II) complexes that have been described in the literature show, at room temperature, free rotation about the platinum–allene bond.[5,7] In contrast, in the case of *cis*-[$PtCl_2(dma)(PPh_3)$] and *cis*-[$PtCl_2(dma)(AsPh_3)$] the ^1H n.m.r. spectra, recorded up to 80 °C, exhibit two distinct resonances for the two methylene protons of dma, indicating restricted rotation about the platinum–allene bond. In the case of the *p*-toluidine and dimethyl sulphoxide complexes the two methylene protons have almost the same chemical shift; however, in the latter complex the hindered rotation is still present as shown by the non-equivalence of the two methyl groups of the sulphoxide.

TABLE 2

Selected data for the complexes $[\overset{-}{Pt}Cl_2(Me_2C{=}CCH_2\overset{+}{N}R^1R^2R^3)L]$

Amine ($NR^1R^2R^3$)	L	Yield (%)	M.p.^{a} (θ_c/°C)	I.r.^{b} (cm^{-1}) ν(Pt–Cl)	Analysis (%) ^{c}	
					N	Cl
NMe_2H	PPh_3	87	188	250, 290	2.10 (2.20)	11.3 (11.05)
	$AsPh_3$	84	168	250, 295	2.20 (2.05)	10.8 (10.35)
	$H_2NC_6H_4Me$-*p*	82	156—157	250, 300	5.40 (5.75)	15.05 (14.6)
	SMe_2O	84	140—160	250, 305	3.25 (3.05)	15.75 (15.5)
NEt_2H	PPh_3	90	194—196	255, 280	2.00 (2.10)	10.9 (10.6)
NMe_3	PPh_3	95	168—170	255, 282	2.00 (2.15)	11.3 (10.8)
$NBu^n{}_2H$	PPh_3	89	181	265, 290	2.05 (1.95)	10.0 (9.75)
C_5H_5N	PPh_3	88	147—148	255, 290	2.20 (2.05)	10.7 (10.5)
NMePhH	PPh_3	92	152—153	255, 280	2.20 (2.00)	10.35 (10.1)
$H_2NC_6H_4Me$-*p*	PPh_3	82	156—157	250, 278	2.05 (2.00)	10.35 (10.1)
$NPhH_2$	PPh_3	92	184—185	250, 273	2.25 (2.05)	10.75 (10.3)
$H_2NC_6H_4Cl$-*p*	PPh_3	86	166—167	<250, 275	2.00 (1.95)	14.95 (14.7)
$H_2NC_6H_4Cl$-*m*	PPh_3	83	187—188	<250, 268	1.95 (1.95)	15.1 (14.7)
$H_2NC_6H_4Cl$-*o*	PPh_3	73	142—143	250, 280	1.90 (1.95)	15.0 (14.7)

^{a} With decomposition. ^{b} Nujol mulls. ^{c} Calculated values are given in parentheses.

Addition of Amines to dma Complexes.—The reaction of several amines with the complex *cis*-[$PtCl_2(dma)(PPh_3)$] and the reaction of dimethylamine with the other dma complexes were examined at room temperature in dichloromethane solution. Regardless of the nature of the *cis* ligand L, of the steric hindrance, or of the basicity of the amine, addition of the amine was observed in each case. The amine nitrogen atom was found to bind to the terminal carbon atom of the allene ligand, with formation of a alkenylplatinum(II) derivative. The reaction that occurred for all the amines except primary aliphatic amines (see below) is illustrated by Scheme 1.

The reaction products (see Table 2) were obtained in good yields as colourless, air-stable, crystalline solids. They were characterised by elemental analysis and i.r. and ^1H n.m.r. spectroscopy, and through the identification of the products of their protolytic cleavage. Furthermore, in order to remove any uncertainty * about the structure of the addition products, we carried out a single-crystal *X*-ray diffraction analysis of *cis*-$[\overset{-}{Pt}Cl_2(Me_2C{=}CCH_2\overset{+}{N}Et_2H)(PPh_3)]$, gaining definitive evidence of the assigned structure (see below).

The i.r. spectra of the addition products show two absorption bands of medium intensity in the range 250—300 cm^{-1} that can be assigned to ν(Pt–Cl). The bands are shifted to lower frequencies compared with those of the starting η complexes (300—340 cm^{-1}), consistent with the *trans*-bond-weakening effect induced by the σ-bonded alkenyl group.[9] The ^1H n.m.r. data for the alkenyl derivatives are reported in Table 3. In each case the spectra show that the two methylene protons of the dma moiety are not equivalent, and neither are the two *N*-methyl groups in all the dimethylammonio-derivatives. This

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* For example, in the aminomercuration of dma the nitrogen atom has been reported to attack at the C(2) atom of the allene and the product to rearrange giving the 3-amino-derivative only on demercuration.[8]

[7] K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometallic Chem.*, 1970, **21**, 467.

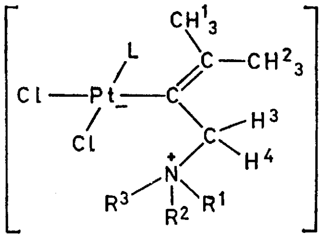
[8] H. Hodjat-Kachani, J. J. Perie, and A. Lattes, *Chem. Letters* (*Japan*), 1976, 405.

[9] B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc.* (*A*), 1971, 2667; H. D. Empsall, B. L. Shaw, and A. J. Stringer, *J. Organometallic Chem.*, 1975, **96**, 461.

indicates asymmetry in the chemical environment of the quoted protons and thus a restricted rotation about the Pt–C σ bond. The most favourable conformation is expected to be that in which the plane of the alkenyl group is almost at right angles to the metal co-ordination plane. The crystal structure of the diethylammonio-derivative showed that this type of conformation is present in the solid state (see Figure). The ^{1}H n.m.r. spectrum of the complex *cis*-$[\overset{-}{Pt}Cl_2(Me_2C{=}CCH_2\overset{+}{N}Me_2H)(PPh_3)]$ was recorded up to 85 °C, and even at this temperature the hindered rotation about the Pt–C σ bond was retained, no appreciable variation being observed in the linewidths or in the resonance frequencies of the two *N*-methyl groups.* Such a restricted rotation about the Pt–C σ bond has been observed at room temperature for complexes of the type *trans*-$[PtX(alkenyl)(PMe_2Ph)_2]$.[9] We note that, in the case of our alkenyl complexes, the *cis*-geometry of the ligands would make enantiomeric any two rotamers mutually related by opposite rotation angles between the plane of the alkenyl group and the metal co-ordination plane. Therefore, if the barrier to rotation about the Pt–C σ bond allowed a small racemization rate it would be possible in principle to resolve the alkenyl derivatives into enantiomers. This possibility of course also exists for the starting dma complexes, if the rotation about the platinum–allene bond is sufficiently slow.

TABLE 3

Hydrogen-1 n.m.r. data (p.p.m.)[a] for the complexes $[\overset{-}{Pt}Cl_2(Me_2C{=}CCH_2\overset{+}{N}R^1R^2R^3)L]$ in $CDCl_3$ solution



Amine ($NR^1R^2R^3$)	L	δ (H^1)[b]	δ (H^2)[b]	δ (H^3)[c]	δ (H^4)[c]	J (H^3–H^4)	J (^{195}Pt–H^1)	J (^{195}Pt–H^2)	Other resonances
NMe_2H	PPh_3	1.30	1.87	3.0—3.8[d]			11.5	14	2.67 (d, NMe), 2.93 (d, NMe)
	$AsPh_3$	1.25	1.98	2.8—3.8[d]			<10	<12	2.72 (d, NMe), 2.93 (d, NMe)
	SMe_2O	1.75	2.26	3.0—4.3[d]			12	14	2.80 (d, NMe), 3.03 (d, NMe), 3.37 (s, SMe,)[e] 3.58 (s, SMe)[e]
NEt_2H	PPh_3	1.34	1.93	*f*	*f*		*f*	13.5	1.27 (t, Me), 1.47 (t, Me), 2.5—3.5 (NCH_2)[d]
C_5H_5N[g]	PPh_3	1.43	2.00	3.80 (d)	4.73 (d)	13.5	<14	<14	
NMePhH	PPh_3	1.25	1.92	3.27 (d)	4.10 (d)	13	11[h]	13.5[h]	3.08 (bs, NMe)
$H_2NC_6H_4Me$-*p*[g]	PPh_3	0.36	1.76	3.50 (d)	4.35 (d)	13	11	13	2.24 (s, aryl Me)
$NPhH_2$[g]	PPh_3	0.35	1.81	3.60 (d)	4.53 (d)	13	11	13	
$H_2NC_6H_4Cl$-*p*[g]	PPh_3	0.42	1.82	3.57(d)	4.46 (d)	13	11	13	
$H_2NC_6H_4Cl$-*m*[g]	PPh_3	0.38	1.87	3.57 (d)	4.56 (d)	13	11.5	13.5	
$H_2NC_6H_4Cl$-*o*[g]	PPh_3	0.35	1.81	3.76 (d)	4.37 (d)	13	11	13	

[a] d = Doublet, t = triplet. [b] δ(H^1) and δ(H^2) were tentatively assigned to the methyl groups directed towards and away from the metal respectively. [c] H^3 and H^4 are the protons absorbing to high and low field respectively, without any configurational meaning. [d] Complex multiplet partially overlapped by other signals. [e] ^{195}Pt satellite peaks are present: ^3J(^{195}Pt–H) 31 and 28 Hz for the two methyl groups. [f] Not detectable because overlapped by other signals. [g] Spectrum recorded on the crude reaction solution (in $CDCl_3$), owing to poor solubility of the crystallised complex. [h] Coupling constants detectable only within 2—3 min of the dissolution of the solid complex.

Further support for the structures assigned to the addition products was obtained from the reaction of the alkenyl derivatives with hydrogen chloride. Cleavage of the Pt–C bond occurred readily, either when the solid complexes were treated with gaseous HCl or when HCl was bubbled through a chloroform solution or suspension of the complexes. In each case the organic moiety was recovered in good yield by addition of triphenylphosphine and extraction with water of the resulting ammonium chloride (see Scheme 2). The ammonium salts were identified through their ^{1}H n.m.r. spectra (see Table 4). In one case (see Experimental section) the hydrochloride was identified also by comparison with an authentic sample.

The identification of the ammonium salts reported in Table 4, together with the crystal structure of the diethylammonio-derivative (see Figure), showed that the amine addition is regiospecific, and orientated on the terminal carbon atom of the allene. Although it is not possible at present to assess the influence of electronic factors on the direction of addition to a co-ordinated allene,† we point out that in a related instance steric factors predominate over electronic effects. In fact, in the ammine addition to co-ordinated 3-methylbut-1-ene (a mono-olefin having the same carbon skeleton as dimethylallene), although purely electronic factors would pro-

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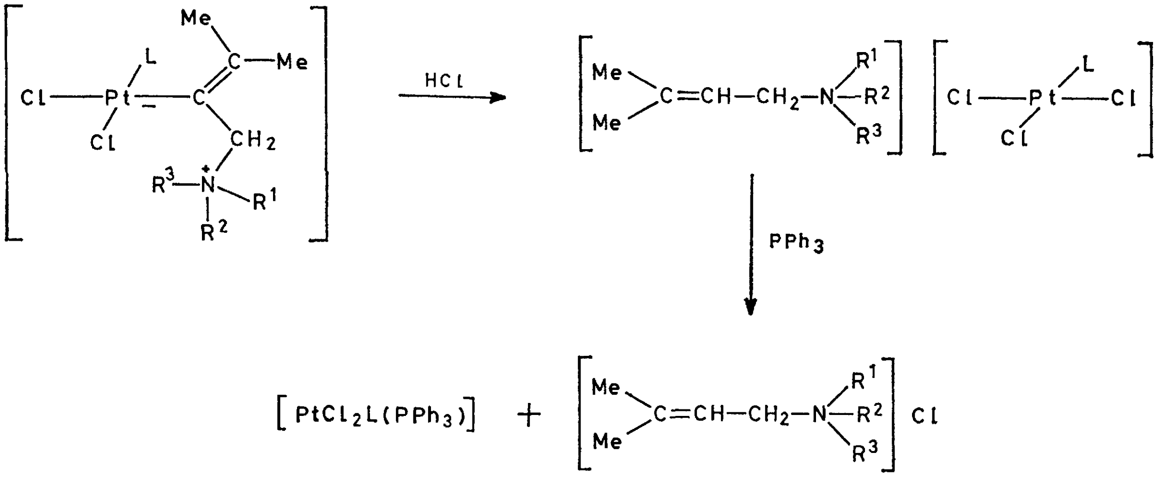
* At *ca.* 80 °C (CD_3NO_2 solution) the coupling between the N–CH_3 and N–H protons disappears, owing to fast exchange of the N–H proton. The coupling is not reversibly restored on decreasing the temperature, pointing to intermolecular proton exchange between the zwitterionic complex and the free amine generated by slight decomposition of the complex. Loss of the coupling is observed also at room temperature, by adding a small amount (*ca.* 10%) of NMe_2H to the n.m.r. sample.

† The effect of electronic factors has not been clarified even for unco-ordinated allenes.[10]

[10] A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, 1964, 1.

mote a Markownicov attack a completely anti-Markownicov addition was observed.[1]

A remarkable feature of the nucleophilic attack on dma is that, unlike co-ordinated mono-olefins,[1] the allene undergoes ready addition of aromatic as well as aliphatic amines, according to Scheme 1. Even weakly basic chloroanilines are suitable reagents for the nucleophilic addition.



SCHEME 2

Addition of Primary Aliphatic Amines.—The reaction of primary aliphatic amines with the complex *cis*-$[\mathrm{PtCl_2(dma)(PPh_3)}]$ did not lead to the isolation of pure, crystalline, alkenyl derivatives like those reported in Table 2. Generally, the elimination of the solvent afforded an amorphous residue, and attempts to obtain a crystalline solid from this material were unsuccessful. The ^{1}H n.m.r. spectra of the crude products were rather complex and of scarce utility for characterization purposes; however, evidence for amine addition was obtained through protolysis of the solid residues. The results were dependent on the bulkiness of the amine. The attack of $\mathrm{NMeH_2}$, and to a smaller extent of $\mathrm{NEtH_2}$, resulted in double alkylation of the nitrogen atom, giving tertiary ammonium salts, whereas for higher amines only the secondary ammonium salts were obtained in appreciable amounts. Thus, after addition of $\mathrm{NMeH_2}$ to the complex *cis*-$[\mathrm{PtCl_2(dma)(PPh_3)}]$ and protolysis of the crude product, the main compound identified was the hydrochloride $[\mathrm{NMe(CH_2CH{=}CMe_2)_2H}]\mathrm{Cl}$, together with small amounts of $[\mathrm{NMe(CH_2CH{=}CMe_2)H_2}]\mathrm{Cl}$. Conversely, the addition of $\mathrm{NEtH_2}$ afforded mainly (*ca.* 80%) the secondary ammonium salt $[\mathrm{NEt(CH_2CH{=}CMe_2)H_2}]\mathrm{Cl}$, with a minor amount (*ca.* 20%) of the tertiary ammonium salt $[\mathrm{NEt(CH_2CH{=}CMe_2)_2H}]\mathrm{Cl}$. Higher amines, such as isopropylamine and benzylamine, afforded almost exclusively the secondary ammonium salts. We suggest that, as in the case of amine addition to co-ordinated ethylene,[11] the double alkylation occurs by the following steps: (*a*) addition of the amine to the dma η complex; (*b*) acid-base equilibrium between free and bonded amine; and (*c*) addition of the resulting deprotonated nitrogen to a further molecule of co-ordinated dma and formation of a binuclear species.[11]

TABLE 4

Hydrogen-1 n.m.r.[a] data for the ammonium salts $[\mathrm{NR^1R^2R^3(CH^3{}_2CH^4{=}CMe^1Me^2)}]\mathrm{Cl}$ obtained on protolysis of $[\overset{-}{\mathrm{Pt}}\mathrm{Cl_2(Me_2C{=}CCH_2}\overset{+}{\mathrm{N}}\mathrm{R^1R^2R^3)L}]$

Amine $(\mathrm{NR^1R^2R^3})$	δ (H^1)	δ (H^2)	δ (H^3)	δ (H^4) [b]	Other resonances
$\mathrm{NMe_2H}$	1.75 (s)	1.83 (s)	3.74 (d)	5.34 (t)	2.85 (s, $\mathrm{NMe_2}$)
$\mathrm{NMe_3}$	1.77 (s)	1.86 (s)	3.86 (d)	5.43 (t)	3.05 (s, $\mathrm{NMe_3}$)
$\mathrm{NEt_2H}$	1.82 (s)	1.88 (s)	3.80 (d)	5.37 (t)	1.35 (t, Me), 3.25 (q, $\mathrm{NCH_2}$)
$\mathrm{C_5H_5N}$	1.90 (s)	1.90 (s)	5.28 (m) [c]	5.63 (m) [c]	8.0—9.0 (aromatic)
NMePhH	1.52 (s)	1.73 (s)	4.20 (d)	5.23 (t)	3.30 (s, NMe), 7.60 (aryl)
$\mathrm{H_2NC_6H_4Me}$-*p*	1.56 (s)	1.81 (s)	4.08 (d)	5.38 (t)	2.42 (s, aryl Me), 7.42 (aryl)
$\mathrm{NPhH_2}$	1.53 (s)	1.78 (s)	4.10 (d)	5.38 (d)	7.60 (aryl)
$\mathrm{H_2NC_6H_4Cl}$-*p*	1.50 (s)	1.77 (s)	4.06 (d)	5.33 (t)	7.53 (aryl)
$\mathrm{H_2NC_6H_4Cl}$-*m*	1.48 (s)	1.77 (s)	4.07 (d)	5.33 (t)	7.60 (aryl)
$\mathrm{H_2NC_6H_4Cl}$-*o*	1.48 (s)	1.78 (s)	4.14 (d)	5.38 (t)	7.52 (aryl)
$\mathrm{NMeH_2}$ [d]	1.73 (s)	1.83 (s)	3.73 (d)	5.33 (t)	2.76 (s, NMe)
$\mathrm{NEtH_2}$ [e]	1.63 (s)	1.70 (s)	3.20 (d)	5.25 (t)	1.08 (t, Me), 2.63 (q, $\mathrm{NCH_2}$)
$\mathrm{NPr^iH_2}$	1.73 (s)	1.80 (s)	3.67 (d)	5.28 (t)	1.32 (d, Pr^i)
$\mathrm{N(CH_2Ph)H_2}$	1.73 (s)	1.85 (s)	3.73 (d)	5.36 (t)	4.26 (s, $\mathrm{NCH_2}$), 7.58 (aryl)

[a] In $\mathrm{D_2O}$ solution; chemical shifts (δ/p.p.m.) relative to dss (sodium 2,2-dimethyl-2-silapentanesulphonate) as internal standard. q = Quartet. [b] Triplets broadened by long range coupling with the methyl groups. [c] Values referred to the centres of gravity of the multiplets. [d] Data for the tertiary ammonium salt $[\mathrm{NMe(CH_2CH{=}CMe_2)_2H}]\mathrm{Cl}$. [e] Data for the free base in $\mathrm{CDCl_3}$ solution.

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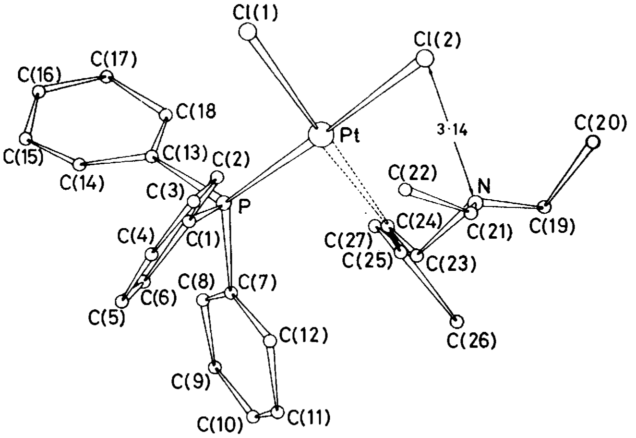
[11] A. De Renzi, G. Paiaro, A. Panunzi, and L. Paolillo, *Gazzetta*, 1972, **102**, 281.

Molecular Structure of the Complex $cis\text{-}[\bar{\text{Pt}}\text{Cl}_2(\text{Me}_2\text{C}{=}\text{CCH}_2\overset{+}{\text{N}}\text{Et}_2\text{H})(\text{PPh}_3)]$.—Single crystals of the complex were examined by *X*-ray diffraction. A molecular model of the complex is shown in the Figure. The asymmetric unit contains two independent molecules, which differ by small variations of the internal parameters. The largest difference is in the orientation of the aromatic rings around the C–P bond. The internal rotation angles Pt–P–C(13)–C(18) (see Figure) are −32 and −12° for the two molecules. The complex shows the usual square-planar arrangement of the ligands around the platinum atom with the two chlorine atoms in *cis* positions and the phosphorus atom and the σ-bonded C(24) atom of the alkenyl group occupying the other two corners of the co-ordination square. The Pt–Cl and Pt–P distances (means: * Pt–Cl 2.40 ± 0.01, Pt–P 2.21 ± 0.01 Å) and the various ligand–platinum–ligand angles, typical of an almost undistorted square-planar configuration, are within experimental error comparable with similar bond lengths and angles reported in the literature.[12] The geometrical parameters involving the light atoms, even those affected by larger errors, are still in agreement with the expected geometry. The C–C distances and C–C–C angles in the aromatic rings have mean values of 1.42 ± 0.16 Å and 120 ± 8°; the mean P–C bond length is 1.84 ± 0.04 Å. The distances Pt–C(24) (2.00 ± 0.10 Å) and Pt–C(25) (3.07 ± 0.01 Å) show that the unsaturated organic moiety is σ bonded to the platinum atom.[3] The plane containing the C(23),C(24),C(25),C(26),C(27), and Pt atoms is almost perpendicular to the co-ordination plane (81 ± 1°), the maximum deviation from this plane being 0.04 Å. The rotation angle Pt–C(24)–C(23)–N is 67 ± 4°, resulting in a short intramolecular contact between N and Cl(2) that can be considered as a hydrogen bond, in agreement with a hydrogen-bond distance of the type Cl · · · H–N in an analogous group.[3]



Molecular structure of $cis\text{-}[\bar{\text{Pt}}\text{Cl}_2(\text{Me}_2\text{C}{=}\text{CCH}_2\overset{+}{\text{N}}\text{Et}_2\text{H})(\text{PPh}_3)]$

TABLE 5

Fractional co-ordinates (× 10^4) *

Atom	*x*	*y*	*z*
(*a*) Molecule A			
Pt(1)	4 494(2)	7 772(1)	4 439(1)
Cl(1)	3 259(13)	8 252(8)	5 822(10)
Cl(2)	6 234(13)	8 345(8)	−5 542(10)
P(1)	2 826(12)	7 336(8)	3 466(10)
C(1)	2 220(48)	8 110(30)	3 155(39)
C(2)	2 729(48)	8 898(30)	3 793(40)
C(3)	2 316(61)	9 482(38)	3 448(50)
C(4)	1 579(66)	9 295(41)	2 673(54)
C(5)	1 086(61)	8 550(38)	2 029(51)
C(6)	1 476(57)	7 930(35)	2 300(46)
C(7)	2 948(48)	6 638(30)	2 203(39)
C(8)	2 466(58)	5 851(37)	2 090(48)
C(9)	2 655(62)	5 296(39)	1 159(51)
C(10)	3 317(65)	5 571(41)	502(54)
C(11)	3 712(78)	6 358(49)	579(64)
C(12)	3 572(61)	6 866(38)	1 582(30)
C(13)	1 570(44)	6 877(28)	4 034(36)
C(14)	357(58)	6 832(37)	3 883(48)
C(15)	−629(71)	6 470(45)	3 989(59)
C(16)	−305(80)	6 189(51)	4 889(67)
C(17)	838(67)	6 168(43)	5 130(55)
C(18)	1 854(57)	6 517(36)	4 641(47)
N(1)	7 052(36)	8 641(23)	3 602(30)
C(19)	8 157(70)	8 384(45)	3 573(58)
C(20)	8 987(62)	8 916(39)	4 491(52)
C(21)	6 994(52)	9 410(33)	3 441(43)
C(22)	5 895(81)	9 776(51)	3 733(67)
C(23)	6 066(48)	8 071(30)	2 821(40)
C(24)	5 599(43)	7 383(27)	3 229(35)
C(25)	5 838(58)	6 695(36)	2 866(48)
C(26)	6 774(54)	6 473(34)	1 950(45)
C(27)	5 388(63)	6 067(40)	3 225(52)
(*b*) Molecule B			
Pt(2)	3 416(2)	2 134(1)	527(2)
Cl(3)	1 969(14)	1 507(9)	−842(11)
Cl(4)	4 980(15)	1 663(10)	−537(10)
P(2)	1 939(13)	2 546(8)	1 504(10)
C(28)	2 444(49)	3 240(31)	2 700(40)
C(29)	2 921(50)	3 049(32)	3 480(41)
C(30)	3 489(59)	3 557(37)	4 385(48)
C(31)	3 322(49)	4 301(31)	4 484(40)
C(32)	2 839(65)	4 578(42)	3 890(54)
C(33)	2 349(59)	4 012(37)	2 882(48)
C(34)	1 010(41)	3 023(26)	968(34)
C(35)	1 292(51)	3 248(32)	169(42)
C(36)	583(58)	3 619(36)	−204(48)
C(37)	−533(60)	3 748(38)	173(50)
C(38)	−1 050(72)	3 485(45)	995(60)
C(39)	−138(76)	3 204(48)	1 441(63)
C(40)	1 021(39)	1 802(25)	1 828(32)
C(41)	275(66)	1 966(41)	2 716(54)
C(42)	−435(52)	1 334(33)	2 880(43)
C(43)	−541(63)	633(39)	2 252(52)
C(44)	100(51)	425(32)	1 427(42)
C(45)	941(44)	1 031(28)	1 136(37)
N(2)	5 572(39)	1 374(25)	1 455(32)
C(46)	5 502(55)	678(35)	1 731(46)
C(47)	4 156(71)	300(45)	1 363(58)
C(48)	6 976(60)	1 723(38)	1 493(49)
C(49)	7 532(81)	1 083(51)	519(67)
C(50)	4 954(54)	1 976(34)	2 025(44)
C(51)	4 541(51)	2 603(32)	1 601(42)
C(52)	2 586(50)	3 333(31)	2 002(41)
C(53)	4 972(61)	3 930(38)	1 653(51)
C(54)	6 237(90)	3 610(57)	2 938(75)

* Standard deviations (in parentheses) are in units of the last significant figure.

EXPERIMENTAL

General Procedures and Materials.—All the reagents and solvents were reagent-grade chemicals and, unless otherwise stated, were used without further purification and/or exclusion of air. Melting points are uncorrected. Elemental analyses were by the Alfred Bernhardt Laboratory, Elbach,

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* The deviation associated with any mean value indicates the range of the individual values.

[12] G. G. Messmer, E. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.

West Germany. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer, ^{1}H n.m.r. spectra on Varian T-60 A, equipped with a variable-temperature accessory, and Varian XL-100 spectrometers. Published procedures [6] were used for the preparation of the starting complexes *cis*-$[\mathrm{PtCl_2(C_2H_4)L}]$ (L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{MeC_6H_4NH_2}$-*p*, or $\mathrm{SMe_2O}$).

Preparation of the 2—3-η-1,1-*Dimethylallene Complexes*.—To a stirred solution of the corresponding ethylene complex, in the minimum amount of chloroform or dichloromethane, an equimolar amount of 1,1-dimethylallene (dma) was added dropwise at room temperature. Rapid evolution of gas was observed. The solution was stirred for 10 min, then the resulting dma complex was crystallised by addition of n-heptane (yields are reported in Table 1 for the colourless prisms or needles).

Preparation of the Allene Complex.—To a solution of *cis*-$[\mathrm{PtCl_2(C_2H_4)(PPh_3)}]$ (1.10 g, 2 mmol), in the minimum amount of anhydrous dichloromethane, was added a large excess (0.4 g, 10 mmol) of allene through a reflux condenser cooled by solid $\mathrm{CO_2}$. The mixture was stirred at 0 °C for 5 min, then n-hexane (30 cm^3) was added, giving 0.88 g of a white powder. Elemental analysis and i.r. and ^{1}H n.m.r. spectra of the complex were consistent with the formula *cis*-$[\mathrm{PtCl_2(C_3H_4)(PPh_3)}]$. This complex decomposes in solution at room temperature, and on recrystallisation affords in part a different material which is no longer soluble in chloroform or dichloromethane. Addition reactions of amines with this complex gave unsatisfactory and scarcely reproducible results.

General Procedure for the Reaction with Amines.—To a solution of 0.3 g of the dma complex in dichloromethane (8 cm^3) was added an equimolar amount of the appropriate amine (through a gas syringe in the case of gaseous amines) and the mixture was kept at room temperature for a few minutes. When the amine was trimethylamine or *p*-toluidine a white solid crystallised spontaneously; in other cases the product was crystallised by adding n-hexane (yields are reported in Table 2). In most cases (see footnotes to Table 3) the crystallised product was nearly insoluble in dichloromethane or chloroform, and the ^{1}H n.m.r. spectra had to be recorded on the crude reaction solution (in $\mathrm{CDCl_3}$). The reaction of primary aliphatic amines gave amorphous white products which could not be satisfactorily purified. When the amine was *o*-chloroaniline, in order to obtain the product in good yields, the dma complex had to be suspended in a small amount of solvent (0.4 g in 2 cm^3 of $\mathrm{CH_2Cl_2}$). Crystallisation of the addition product occurred simultaneously with the dissolution of the starting dma complex and was completed by adding a small amount of n-hexane.

General Procedure for Protolysis of the Alkenyl Derivatives.—Procedures (*a*) or (*b*) were used. They are both suitable, the former giving slightly better yields in most cases.

(*a*) The finely powdered alkenyl complex (200 mg) was treated with gaseous HCl (1 atm) * at 50 °C for a few minutes. If the original complex still remained as a white powder a small amount of HCl was condensed into the reaction vessel and allowed to evaporate whilst the mixture was stirred. When the solid changed to an orange-yellow oil the vessel was evacuated and an equimolar amount of triphenylphosphine, dissolved in a small amount of dichloromethane, was added. Within a few minutes the solution became colourless. It was evaporated *in vacuo* and the resulting white residue was extracted with water and the extract filtered. Evaporation of the water gave the crude ammonium salt.

(*b*) Gaseous HCl was bubbled through a solution (or suspension) of the alkenyl complex (200 mg) in chloroform (5 cm^3), until the solid had completely dissolved and the solution became orange-yellow. The solvent was removed *in vacuo* and the residue was processed as described above. The crude ammonium salts from (*a*) or (*b*) were sufficiently pure to allow their identification through their ^{1}H n.m.r. spectra in $\mathrm{D_2O}$ solution (see Table 4), and were therefore not submitted to further purification. The yields of the whole process were in the range 60—85%, determined by integration of the n.m.r. signals after addition of an internal weighted standard (generally Bu^{t}OH) to the crude ammonium salt. The hydrochloride obtained on protolysis of *cis*-$[\overset{-}{\mathrm{Pt}}\mathrm{Cl_2(Me_2C{=}CCH_2}\overset{+}{\mathrm{N}}\mathrm{Et_2H)(PPh_3)}]$ was also compared with an authentic sample of 1-(diethylamino)-3-methylbut-2-ene hydrochloride, synthesised by a described procedure.[13] The two samples were identical.

Crystal–structure Determination of cis-$[\mathrm{PtCl_2(Me_2C{=}CCH_2NEt_2H)(PPh_3)}]$.—The data were collected using a single-crystal Siemens diffractometer, equipped with a PDP-8/I digital computer. Of the total of 4 350 recorded independent intensities, 3 630 had $I \geqslant 2.5\,\sigma(I)$ and were used in subsequent calculations. Lorentz, polarisation, and absorbtion corrections were applied.

Crystal data. $\mathrm{C_{27}H_{34}Cl_2NPPt}$, $M = 669.0$, Triclinic, space group $P\bar{1}$, $a = 11.130(3)$, $b = 18.887(5)$, $c = 14.370(5)$ Å, $\alpha = 108,8(3)$, $\beta = 90.1(2)$, $\gamma = 98.1(2)^\circ$, $U = 2\,827.9$ Å^3, $D_c = 1.57$ g cm^{-3}, $Z = 4$, $D_m = 1.55$ g cm^{-3} (flotation), λ (Mo-K_α) = 0.710 7 Å, μ(Mo-K_α) = 54.79 cm^{-1}. $F(000) = 1\,320$.

Structure solution and refinement. The Pt and Cl atoms were located from a Patterson synthesis, and all the remaining atoms (excluding hydrogens) by successive difference-Fourier syntheses. The structure was refined by block-diagonal least squares, with anisotropic thermal parameters for Pt, Cl, and P and isotropic thermal parameters for the lighter atoms, to R 0.10. Fractional co-ordinates are listed in Table 5. A list of structure factors and thermal parameters is available as Supplementary Publication No. SUP 22288 (20 pp.).†

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* Throughout this paper: 1 atm = 101 325 Pa.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[13] I. N. Nazarov, V. N. Rakcheeva, and L. I. Shmonina, *Zhur. obshchei Khim.*, 1952, **22**, 611.