Isoprene Platinum(II) Complexes from *cis*-Dichlorobis(triphenylphosphine)platinum(II) and Isopropenylacetylene. Crystal and Molecular Structures of *trans*-Chloro(1-isopropenylvinyl)bis(triphenylphosphine)platinum(II)–Benzene (1/1) and *trans*-(Isopropenylethynyl)(1-isopropenylvinyl)bis(triphenylphosphine)platinum(II)

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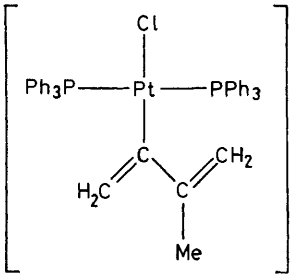
When *cis*-$[PtCl_2(PPh_3)_2]$ is warmed in ethanol with hydrazine hydrate in the presence of isopropenylacetylene three main products are obtained: *trans*-$[PtCl(CH_2{=}C{-}CMe{=}CH_2)(PPh_3)_2]$ (1), *trans*-$[Pt(CH_2{=}C{-}CMe{=}CH_2)(C{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2]$ (2), and $[Pt(CH{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2]$ (3). Formation of (1), (2), or (3) is dependent on the reaction time and reagent concentrations. For comparison, the behaviour of phenylacetylene under similar conditions has been examined and *trans*-$[Pt(C{\equiv}CPh)(CH_2{=}CPh)(PPh_3)_2]$ has also been obtained. The structures of (1) and (2) have been determined by single-crystal *X*-ray diffractometry: (1), monoclinic, $a = 15.521(3)$, $b = 18.738(8)$, $c = 16.872(5)$ Å, $\beta = 125.07(2)°$, $Z = 4$, space group *Cc*, $R = 0.056$; (2), orthorhombic, $a = 18.94(1)$, $b = 19.57(1)$, $c = 10.42(1)$ Å, $Z = 4$, space group $P2_12_12_1$, $R = 0.050$. In both complexes the co-ordination around Pt is *trans* planar and the organic ligands are σ-bonded to platinum. The metal–ligand distances are: in (1) Pt–C 2.07(1), Pt–P 2.296(9), 2.299(14), and Pt–Cl 2.408(3) Å; in (2), Pt–C(isopropenylvinyl) 2.09(2), Pt–C(isopropenylethynyl) 1.99(1), and Pt–P 2.287(5), 2.284(4) Å.

MANY alkene and alkyne platinum complexes are known.[1,2] However, as far as we know, the only example of a complex in which an alkene and an alkyne are co-ordinated to the same metal atom is the chloro(cyclo-octa-1,5-diene)(hexafluorobut-2-yne)iridium(I) dimer.[3] In this complex the two unsaturated hydrocarbons are both π-bonded to iridium, and no cases where both the alkene and alkyne ligands are σ-bonded to a metal are known.

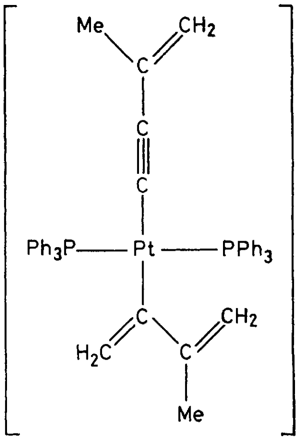
During research on the behaviour of isopropenylacetylene as a ligand in platinum complexes we studied the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ and hydrazine hydrate in the presence of isopropenylacetylene. It is known that this complex under these reaction conditions gives, with alkenes or alkynes, complexes of the type $[PtL(PPh_3)_2]$ (L = alkene or alkyne),[4-6] and that, in the absence of unsaturated hydrocarbons, one of the possible reaction products is $[PtClH(PPh_3)_2]$.[7] By *X*-ray single-crystal analysis it is now found that platinum complexes containing both σ-bonded alkene and alkyne ligands are formed in these reactions.

RESULTS AND DISCUSSION

In reactions between *cis*-$[PtCl_2(PPh_3)_2]$, hydrazine hydrate, and isopropenylacetylene, by varying the concentrations of reagents and the reaction time (see Experimental section), we isolated three complexes: *trans*-$[PtCl(CH_2{=}C{-}CMe{=}CH_2)(PPh_3)_2]$ (1), *trans*-$[Pt(CH_2{=}C{-}CMe{=}CH_2)(C{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2]$ (2), and $[Pt(CH{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2]$ (3). In complex (3), which could be expected on the basis of the previous results,[4-8] the isopropenylacetylene is bonded to platinum through the triple bond. In fact (3) exhibits an i.r. spectrum with no bands in the 2 100 cm^{-1} region, where the C≡C stretching vibrations of free asymmetric triple bonds are expected, but two bands do occur at 1 720 and 1 680 cm^{-1} in the region for C≡C stretching frequencies of bridging acetylenes bonded to platinum.



(1)



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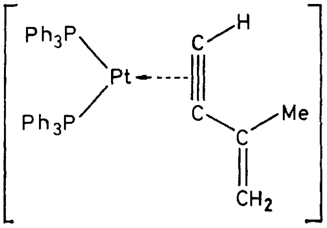

(3)

For (1) and (2) the *X*-ray analysis indicates the structures shown, revealing the presence in both complexes

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[1] U. Belluco, B. Crociani, R. Pietropaolo, and P. Uguagliati, *Inorg. Chim. Acta Rev.*, 1969, 19.

[2] T. R. Jack and J. Powell, *J. Organometallic Chem.*, 1973, **53**, 215.

[3] D. A. Clarke, R. D. W. Kemmit, D. R. Russell, and P. A. Tucker, *J. Organometallic Chem.*, 1975, **93**, C37.

[4] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 1957, 208.

[5] J. Chatt, B. L. Shaw, and A. A. Williams, *J. Chem. Soc.*, 1962, 3269.

[6] J. L. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, 1959, **8**, 2591.

[7] M. Keubler, R. Ugo, S. Cenini, and F. Conti, *J.C.S. Dalton*, 1975, 1081.

[8] A. Furlani, P. Carusi, and M. V. Russo, *J. Organometallic Chem.*, 1974, **67**, 315.

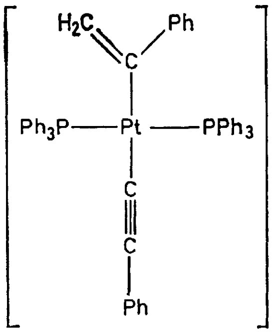
of an isoprene molecule σ-bonded to platinum through C^2. Owing to the impossibility of locating the hydrogen atoms, the chemical nature of this molecule, not easily inferable from the bond lengths only, was established by comparison of the n.m.r. spectrum of complex (2) and that of *trans*-[Pt(C≡C–CMe=CH$_2$)$_2$(PPh$_3$)$_2$].[9]

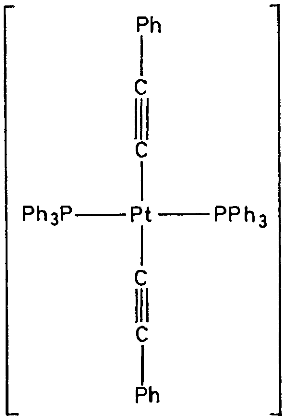
Formation of (1) and (2) could be interpreted in the light of the observations of Keubler *et al.*[7] on the reduction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] by hydrazine and those of Clark and his co-workers [10–12] on the insertion reactions of alkenes and alkynes into the Pt–H bond. The first step of the reaction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with a small excess of hydrazine is the formation of an unstable cationic complex which decomposes by evolution of nitrogen giving *trans*-[PtClH(PPh$_3$)$_2$]. We assumed that, in the presence of isopropenylacetylene, an insertion reaction (1) into the Pt–H bond occurs giving complex (1). Complex (2) originates in a subsequent reaction step (2), in which hydrazine behaves as a base and facilitates the elimination of HCl.

$$\textit{trans}\text{-}[\mathrm{PtClH(PPh_3)_2}] + \mathrm{CH{\equiv}C{-}CMe{=}CH_2} \longrightarrow \textit{trans}\text{-}[\mathrm{PtCl(CH_2{=}C{-}CMe{=}CH_2)(PPh_3)_2}] \quad (1)$$

$$\textit{trans}\text{-}[\mathrm{PtCl(CH_2{=}C{-}CMe{=}CH_2)(PPh_3)_2}] + \mathrm{CH{\equiv}C{-}CMe{=}CH_2} \xrightarrow{\mathrm{N_2H_4}} \textit{trans}\text{-}[\mathrm{Pt(CH_2{=}C{-}CMe{=}CH_2)(C{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2}] + \mathrm{N_2H_5Cl} \quad (2)$$

In order to confirm these reaction mechanisms we carried out some reactions starting from the probable intermediates and studied the behaviour of phenylacetylene under similar reaction conditions. When *trans*-[PtClH(PPh$_3$)$_2$] was warmed with isopropenylacetylene without hydrazine (1) was obtained, thus confirming that formation of (1) occurs through insertion of the isopropenylacetylene into the Pt–H bond. Complex (2) was obtained when the same reaction was carried out in the presence of hydrazine or when (1) was heated with isopropenylacetylene and hydrazine, as in equation (2), showing that hydrazine facilitates the elimination of HCl and formation of (2). In these reactions sometimes *trans*-[Pt(C≡C–CMe=CH$_2$)$_2$(PPh$_3$)$_2$] was also identified in the reaction mixtures.


(4)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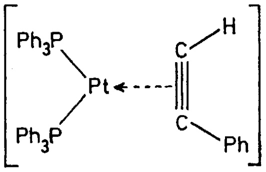
(6)

When *cis*-[PtCl$_2$(PPh$_3$)$_2$] and hydrazine were heated under reflux with phenylacetylene under the reaction conditions reported in the Experimental section a mixture of three products was obtained: *trans*-[Pt(C≡CPh)(CH$_2$=CPh)(PPh$_3$)$_2$] (4), *trans*-[Pt(C≡CPh)$_2$(PPh$_3$)$_2$] (5), and [Pt(CH≡CPh)(PPh$_3$)$_2$] (6). Also in this case we observed that the yields of the three products depended on the reaction time and the concentrations of reagents. The three products can be separated by chromatography on a silica-gel column and recognized in the eluted fractions by their u.v. spectra. Complex (4) exhibits a u.v. spectrum with a maximum at the same position as complex (2), and is eluted in the first fraction. Its i.r. spectrum shows the same group of bands as that observed in the spectra of (1) and (2) and in the i.r. spectrum of *trans*-[PtCl(CH$_2$=CPh)(PPh$_3$)$_2$] (7) [13] for the C=C vibrations. We synthesized (7) from (6) and HCl as proposed by Mann *et al.*,[13] because we failed to obtain it in the reactions of *cis*-[PtCl$_2$(PPh$_3$)$_2$], hydrazine, and phenylacetylene. Complex (7) is characterized by an n.m.r. spectrum showing two signals in the region of vinylic protons at τ 4.32 and 5.21, assigned to the two hydrogens of the CH$_2$ group.[13] In the n.m.r. spectra of complexes *trans*-[PtX(CH=CHR)(PPh$_3$)$_2$] only one signal at τ 3.95 was observed,[13] the second signal being probably obscured by other resonances. The n.m.r. spectrum of complex (4) shows two signals in the region of vinylic protons at τ 4.2 and 5.35 (in CDCl$_3$; SiMe$_4$ as internal standard) indicating that the 1-phenylvinyl ligand is bonded to platinum through C^1. This is also confirmed by the *X*-ray structure analysis of (4).[14] Owing to the

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[9] A. Chiesi Villa, A. Gaetani Manfredotti, and C. Guastini, *Cryst. Struct. Comm.*, 1976, **5**, 139.

[10] H. C. Clark and C. S. Wong, *J. Organometallic Chem.*, 1975, **92**, C31.

[11] M. H. Chisholm and H. C. Clark, *Accounts Chem. Res.*, 1973, **6**, 202.

[12] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.

[13] B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc.* (*A*), 1971, 2667.

[14] A. Chiesi Villa, A. Gaetani Manfredotti, C. Guastini, and M. V. Russo, unpublished work.

low solubility of (4) in $CDCl_3$ we could not observe the satellites produced by coupling with ^{195}Pt.

We also obtained (4) from (7), phenylacetylene, and hydrazine. However, when *trans*-$[PtClH(PPh_3)_2]$ was warmed with phenylacetylene in the presence of hydrazine, (6) was obtained and not (7). The same reaction in the absence of hydrazine gave (7), by insertion of phenylacetylene into the Pt–H bond as in equation (1).

Finally, the intermediate $[PtClH(PPh_3)_2]$ in the presence of hydrazine and acetylenes can react by the following two routes: (*a*) insertion of the acetylene into the Pt–H bond giving alkenylplatinum complexes, $[PtCl(alkenyl)(PPh_3)_2]$, and subsequently $[Pt(alkynyl)(alkenyl)(PPh_3)_2]$ by elimination of HCl facilitated by hydrazine; and (*b*) elimination of HCl (see Keubler *et al.*[7]) according to (3) followed by addition of acetylene

$$trans\text{-}[PtClH(PPh_3)_2] + N_2H_4 \longrightarrow [Pt(PPh_3)_2] + N_2H_5Cl \quad (3)$$

to the unstable $[Pt(PPh_3)_2]$ giving complexes of the type $[Pt(HC{\equiv}CR)(PPh_3)_2]$. The two mechanisms are evidently influenced by the nature of the alkyne, the concentrations of the reactants, and the reaction time.

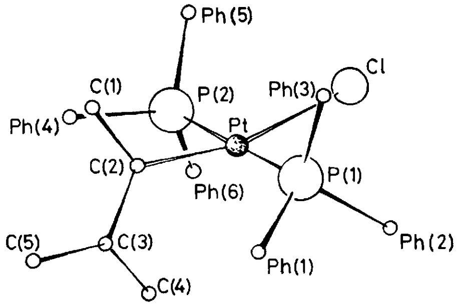

FIGURE 1 Clinographic projection of a unit of complex (1)

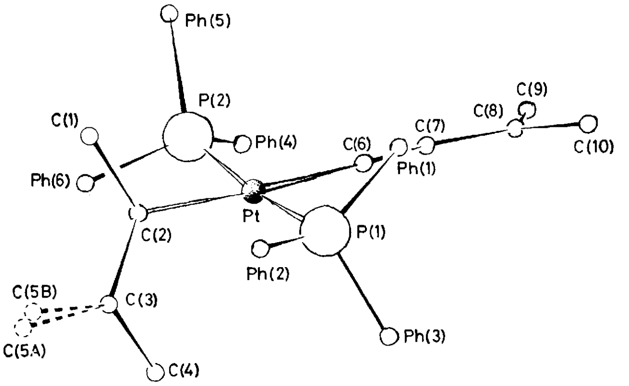

FIGURE 2 Clinographic projection of a unit of complex (2)

These reaction mechanisms could not be postulated on the basis of u.v. and i.r. information only because these data were not sufficient to assign a structure to some of the reaction products. Thus an *X*-ray crystal-structure analysis was carried out for (1) and (2). This showed a *trans*-planar configuration of the ligands around the metal in both complexes in agreement with the spectral evidence. As can be seen from Figures 1 and 2, both complexes are monomeric with two triphenylphosphine molecules co-ordinated *trans* to platinum. The other two co-ordination sites are occupied by a chlorine atom and a σ-bonded carbon atom from isoprene in (1), and by two σ-bonded carbon atoms from isoprene and isopropenylethynyl in (2). Co-ordination is nearly square planar (Table 5). The isoprene ligand is nearly perpendicular to the co-ordination plane in both complexes [dihedral angles 88 and 76° in (1) and (2) respectively], while the isopropenylethynyl ligand in (2) is nearly coplanar with the co-ordination plane (dihedral angle 165°).

The Pt–Cl distance [2.408(3) Å] is comparable with those found in square-planar platinum(II) complexes where σ-donor ligands, *trans* to chlorine, exert a high *trans* influence.[15] The Pt–C(2) bond lengths, which are not significantly different in the two complexes [2.07(1) and 2.09(2) Å for (1) and (2) respectively], are in agreement with those observed for Pt–C(sp^2) σ bonds, *e.g.* 2.03(2) Å in *trans*-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$,[16] 2.059(7) Å in *trans*-$[Pt(CO_2Et)_2(PPh_3)_2]$,[17] 2.079(13) Å in *trans*-$[PtMe(MeCNMe_2)(PMe_2Ph)_2][PF_6]$,[18] and 2.058(7) Å in *trans*-$[Pt(CNMe)_2\{C(NHMe)(SEt)\}_2][PF_6]$.[19] The Pt–C(6) distance [1.99(1) Å] agrees well with those found in other complexes.[9,16] The values of the Pt–C–C angles are in agreement with the σ character of the Pt–C bonds [Pt–C(2)–C(1) and Pt–C(2)–C(3), 126.4(1.2) and 117.9(9)° in (1), 119(1) and 117(2)° in (2); Pt–C(6)–C(7) 179(1)°]. Accordingly platinum lies nearly on the ligand planes (Table 5).

The geometry of the isopropenylethynyl group, which is planar, is as expected. The isoprene ligands are planar in both complexes. Unfortunately the accuracy of the data is not sufficient for a reliable discussion of bond distances and angles in this molecule. Nevertheless, the correspondence between the bond distances in the two complexes does not seem accidental (Tables 3 and 4). In particular the Pt–C(2) interaction is responsible for removing the symmetry of the π charge in the ligand.

The Pt–P distances [2.296(9) and 2.299(14) Å in (1), 2.287(5) and 2.284(4) Å in (2)] fall in the range (2.27—2.32 Å) observed in *trans*-$[Pt^{II}(PPh_3)_2]$ complexes.[20] The geometry of the triphenylphosphine groups is as expected.

EXPERIMENTAL

The complexes *cis*-$[PtCl_2(PPh_3)_2]$ and *trans*-$[PtClH(PPh_3)_2]$ were prepared by literature methods.[21,22] Isopropenylacetylene and phenylacetylene (Fluka) were

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[15] Lj. Manojlović-Muir and K. W. Muir, *Inorg. Chim. Acta*, 1974, **10**, 47 and refs. therein.

[16] C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometallic Chem.*, 1973, **60**, C70.

[17] P. L. Bellon, M. Manassero, F. Porta, and M. Sansoni, *J. Organometallic Chem.*, 1974, **80**, 139.

[18] R. F. Stepaniak and N. C. Payne, *Inorg. Chem.*, 1974, **13**, 797.

[19] W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 1973, **12**, 540.

[20] K. W. Muir, *Mol. Struct. Diffr. Methods*, 1973, **1**, 606.

[21] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

[22] J. C. Bailar and M. Itatani, *Inorg. Chem.*, 1965, **4**, 1618.

distilled under reduced pressure before use. Absolute ethanol and hydrazine hydrate (*ca.* 100%; E. Merck) were used as received.

Spectra were recorded on Perkin-Elmer model 800 and 521 (i.r.), Beckmann DK 2A (u.v.), and Jeol NM-C-6O-HL (n.m.r.) instruments. Melting points were determined on a Köfler apparatus. *X*-Ray intensity data were collected on a Siemens single-crystal computer-controlled diffractometer by use of niobium-filtered Mo-K_α radiation and the ω–2θ scan technique.

Preparations.— trans-*Chloro*(1-*isopropenylvinyl*)*bis*(*triphenylphosphine*)*platinum*(II), (1). *Method* (*i*). Hydrazine hydrate (0.36 g, 7.2 mmol) was added dropwise to a suspension of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.20 g, 0.25 mmol) in absolute ethanol (10 cm^3) until a clear yellow solution was obtained. Isopropenylacetylene (1 cm^3, 10.6 mmol) was then added and the mixture was heated under reflux for *ca.* 5 min. On cooling (1) (0.16 g, 0.19 mmol, 78%) separated as white crystals which were recrystallized from chloroform–ethanol, benzene–ethanol, or benzene, m.p. 211—213 °C. Elemental analyses were carried out on the product recrystallized from benzene before and after elimination of the crystallization solvent *in vacuo* (Found: C, 62.4; H, 4.9. $\mathrm{C_{41}H_{37}ClP_2Pt{\cdot}C_6H_6}$ requires C, 62.8; H, 4.8. Found: C, 59.9; H, 4.6; Cl, 4.1. $\mathrm{C_{41}H_{37}ClP_2Pt}$ requires C, 59.9; H, 4.5; Cl, 4.3%). I.r. (Nujol mull): 1 605w, 1 590w, 1 578w, and 1 555m $\nu(\mathrm{C{=}C})$; 880s and 860s $\delta(\mathrm{{=}CH_2})$; and 284s cm^{-1} $\nu(\mathrm{Pt{-}Cl})$. No characteristic u.v. absorption bands were observed in chloroform or benzene.

Method (*ii*). Isopropenylacetylene (0.5 cm^3, 5.3 mmol) was added to a suspension of *trans*-$[\mathrm{PtClH(PPh_3)_2}]$ (0.10 g, 0.13 mmol) in absolute ethanol (10 cm^3). The reaction mixture was then heated under reflux for *ca.* 15 min. White crystals of (1) separated on cooling (0.06 g, 0.07 mmol, 55%).

trans-(*Isopropenylethynyl*)(1-*isopropenylvinyl*)*bis*(*triphenylphosphine*)*platinum*(II), (2). *Method* (*i*). Hydrazine hydrate (0.50 g, 10.0 mmol) was added dropwise to a suspension of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.40 g, 0.50 mmol) in absolute ethanol (40—50 cm^3). When a clear solution was obtained, isopropenylacetylene (2 cm^3, 21.2 mmol) was added and the mixture was heated under reflux for *ca.* 90 min. On cooling at 0 °C for 1—2 d, yellow crystals of (2) separated (0.19 g, 0.22 mmol, 44%) which were recrystallized from chloroform– or benzene–ethanol, m.p. 158—160 °C (Found: C, 65.0; H, 5.0. $\mathrm{C_{46}H_{42}P_2Pt}$ requires C, 64.9; H, 4.9%). I.r. (Nujol mull): 2 100s and 2 075m $\nu(\mathrm{C{\equiv}C})$; 1 600m, 1 590m, and 1 570w $\nu(\mathrm{C{=}C})$; and 892s and 875s cm^{-1} $\delta(\mathrm{{=}CH_2})$. U.v. in chloroform: $\lambda_{\mathrm{max.}}$ 320 nm.

Method (*ii*). To a suspension of *trans*-$[\mathrm{PtClH(PPh_3)_2}]$ (0.32 g, 0.42 mmol) in absolute ethanol (50 cm^3) were added hydrazine hydrate (0.30 g, 6.0 mmol) and isopropenylacetylene (2 cm^3, 21.2 mmol) and the mixture was heated under reflux for *ca.* 60 min. Complex (2) was obtained on cooling as above (0.13 g, 0.15 mmol, 36%).

Method (*iii*). A mixture of (1) (0.25 g, 0.30 mmol), isopropenylacetylene (2 cm^3, 21.2 mmol), absolute ethanol (30 cm^3), and 15 drops of hydrazine hydrate (0.35 g, 7.0 mmol), heated under reflux for *ca.* 90 min, gave on cooling a crude product which was chromatographed on a silica-gel column (benzene as eluant) giving (2) (0.05 g, 0.06 mmol, 19%) and *trans*-$[\mathrm{Pt(C{\equiv}C{-}CMe{=}CH_2)_2(PPh_3)_2}]$ (0.06 g, 0.07 mmol, 23%).

(*Isopropenylacetylene*)*bis*(*triphenylphosphine*)*platinum*(0), (3). The complex *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.20 g, 0.25 mmol) was dissolved in absolute ethanol (4 cm^3) by dropwise addition of hydrazine hydrate (0.36 g, 7.2 mmol). Isopropenylacetylene (2 cm^3, 21.2 mmol) was added to the solution. From the mixture, heated under reflux for *ca.* 20 min, (3) separated as a white crystalline solid on standing at low temperature (0.12 g, 0.15 mmol, 60%), m.p. 133—135 °C (Found: C, 62.6; H, 4.6. $\mathrm{C_{41}H_{36}P_2Pt}$ requires C, 62.7; H, 4.6%). I.r. (Nujol mull): 1 720m and 1 680m $\nu(\mathrm{C{\equiv}C})$; 895m cm^{-1} $\delta(\mathrm{{=}CH_2})$. No characteristic u.v. absorption bands were observed in $\mathrm{CHCl_3}$ or $\mathrm{C_6H_6}$.

trans-(*Phenylethynyl*)(1-*phenylvinyl*)*bis*(*triphenylphosphine*)*platinum*(II), (4). *Method* (*i*). The complex *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.40 g, 0.50 mmol) was dissolved in absolute ethanol (50 cm^3) by dropwise addition of hydrazine hydrate (0.50 g, 10.0 mmol). Phenylacetylene (1 cm^3, 9.1 mmol) was then added and the reaction mixture was heated under reflux for *ca.* 20 min. After cooling, a crude product separated which was a mixture of (4), $[\mathrm{Pt(C{\equiv}CPh)_2(PPh_3)_2}]$ (5), and $[\mathrm{Pt(CH{\equiv}CPh)(PPh_3)_2}]$ (6). The precipitate was dissolved in benzene and chromatographed on a silica-gel column (Kieselgel, 70—230 mesh; E. Merck) using benzene as eluant. The eluted fractions, exhibiting an absorption spectrum with a maximum at 322 nm, were evaporated to a small volume and pure (4) was separated as yellowish crystals (0.15 g, 0.16 mmol, 32%) and recrystallized from chloroform, m.p. 163—165 °C (Found: C, 63.8; H, 4.4. $\mathrm{C_{52}H_{42}P_2Pt{\cdot}0.5CHCl_3}$ requires C, 64.5; H, 4.4%), *M* (mass spectrum) 923. I.r. (Nujol mull): 2 110s $\nu(\mathrm{C{\equiv}C})$; 1 590s, 1 570w, and 1 555w $\nu(\mathrm{C{=}C})$, 865(sh), and 855m cm^{-1} $\delta(\mathrm{{=}CH_2})$: U.v. in chloroform: $\lambda_{\mathrm{max.}}$ 322 nm.

Method (*ii*). The complex $[\mathrm{PtCl(CH_2{=}CPh)(PPh_3)_2}]$ (7) (0.40 g, 0.47 mmol), prepared according to ref. 13, was suspended in absolute ethanol (50 cm^3). Hydrazine hydrate (0.35 g, 7.0 mmol) and phenylacetylene (2 cm^3, 18.2 mmol) were added and the mixture was heated under reflux with stirring for *ca.* 30 min. On cooling at 0 °C for *ca.* 1 d, pale yellow crystals of (4) separated (0.32 g, 0.34 mmol, 72%).

Reactions of trans-$[\mathrm{PtClH(PPh_3)_2}]$ *with Phenylacetylene.*—(*i*). To a suspension of the complex (0.18 g, 0.24 mmol) in absolute ethanol (20 cm^3) were added hydrazine hydrate (0.35 g, 7.0 mmol) and phenylacetylene (1 cm^3, 9.1 mmol). The solution was heated under reflux for *ca.* 5 min. On cooling, yellow crystals of $[\mathrm{Pt(CH{\equiv}CPh)(PPh_3)_2}]$ (6) separated immediately (0.19 g, 0.23 mmol, 97%).

(*ii*). The complex (0.18 g, 0.24 mmol), absolute ethanol (20 cm^3), and phenylacetylene (2 cm^3, 18.2 mmol) were heated under reflux for *ca.* 5 min. On cooling, white crystals of (7) were obtained (0.14 g, 0.16 mmol, 68%).

X-*Ray Crystallography.*—*Crystal data.* (1) $\mathrm{C_{41}H_{37}ClP_2}$-$\mathrm{Pt{\cdot}C_6H_6}$, $M = 900.3$, Monoclinic, $a = 15.521(3)$, $b = 18.738(8)$, $c = 16.872(5)$ Å, $\beta = 125.07(2)°$, $U = 4\,016$ Å^3, $D_{\mathrm{m}} = 1.47$ (flotation), $Z = 4$, $D_{\mathrm{c}} = 1.49$ g cm^{-3}, $F(000) = 1\,800$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 38.5 cm^{-1}. Space group $C2/c$ or Cc, the last being confirmed by structural analysis. (2) $\mathrm{C_{46}H_{42}P_2Pt}$, $M = 851.9$, Orthorhombic, $a = 18.94(1)$, $b = 19.57(1)$, $c = 10.42(1)$ Å, $U = 3\,862$ Å^3, $D_{\mathrm{m}} = 1.44$ (flotation), $Z = 4$, $D_{\mathrm{c}} = 1.46$ g cm^{-3}, $F(000) = 1\,704$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 39.4 cm^{-1}. Space group $P2_12_12_1$.

Cell dimensions were determined from rotation and Weissenberg photographs and refined from diffractometer measurements.

Intensity-data collection. The crystals used for data collection had dimensions $0.15 \times 0.35 \times 0.34$ and $0.21 \times$

0.12 × 0.16 mm for (1) and (2) respectively. They were mounted with the [100] axis along the ϕ axis of the diffractometer. The intensities were measured using the moving-*counter*–moving-crystal scan technique with a drive speed related to the number of counts on the peaks (lowest scan speed, 2.5° min^{-1}). A standard reflection, monitored every 20 reflections, did not change noticeably during data collection. The intensities were measured in the interval $5 < 2\theta < 58°$ for (1) and $5 < 2\theta < 54°$ for (2) using the five-points procedure. For (1), 4 834 independent reflections were measured, of which 3 888 having $I > 2\sigma(I)$ were considered observed and used in the analysis; for (2) the number of independent reflections was 5 665, 2 790 of which $[I > 2\sigma(I)]$ were included in the analysis. Corrections were applied for Lorentz and polarization factors but not for absorption in view of the rather low absorbance of the samples ($\mu\bar{r} < 0.5$ for the two samples).

TABLE 1

Final atomic fractional co-ordinates (×10^4) for *trans*-[PtCl(CH$_2$=C–CMe=CH$_2$)(PPh$_3$)$_2$]·C$_6$H$_6$ (1) with standard deviations in parentheses

	x/a	y/b	z/c
Pt	0	856(1)	2 500
Cl	−7(8)	2 141(1)	2 518(7)
P(1)	1 515(4)	845(3)	2 559(6)
P(1)	−1 495(7)	848(3)	2 478(8)
C(1)	827(19)	−517(14)	3 875(18)
C(2)	214(8)	−214(6)	2 868(8)
C(3)	−252(11)	−720(7)	2 108(10)
C(4)	−746(16)	−424(11)	1 212(15)
C(5)	−127(17)	−1 505(9)	2 331(13)
C(11)	1 888(7)	17(5)	2 247(7)
C(12)	2 344(7)	−535(5)	2 924(7)
C(13)	2 638(7)	−1 167(5)	2 702(7)
C(14)	2 476(7)	−1 246(5)	1 803(7)
C(15)	2 019(7)	−694(5)	1 126(7)
C(16)	1 725(7)	−63(5)	1 349(7)
C(21)	1 348(7)	1 463(5)	1 625(6)
C(22)	342(7)	1 551(5)	777(6)
C(23)	196(7)	1 972(5)	27(6)
C(24)	1 057(7)	2 305(5)	125(6)
C(25)	2 063(7)	2 216(5)	972(6)
C(26)	2 209(7)	1 795(5)	1 723(6)
C(31)	2 658(8)	1 121(5)	3 712(7)
C(32)	2 560(8)	1 493(5)	4 372(7)
C(33)	3 459(8)	1 699(5)	5 264(7)
C(34)	4 455(8)	1 533(5)	5 495(7)
C(35)	4 552(8)	1 162(5)	4 834(7)
C(36)	3 654(8)	956(5)	3 942(7)
C(41)	−1 919(7)	15(4)	2 706(6)
C(42)	−2 401(7)	−494(4)	1 969(6)
C(43)	−2 707(7)	−1 150(4)	2 125(6)
C(44)	−2 530(7)	−1 296(4)	3 018(6)
C(45)	−2 047(7)	−787(4)	3 755(6)
C(46)	−1 742(7)	−132(4)	3 599(6)
C(51)	−1 491(7)	1 456(5)	3 305(6)
C(52)	−531(7)	1 596(5)	4 183(6)
C(53)	−501(7)	2 020(5)	4 878(6)
C(54)	−1 430(7)	2 303(5)	4 695(6)
C(55)	−2 389(7)	2 163(5)	3 817(6)
C(56)	−2 420(7)	1 739(5)	3 122(6)
C(61)	−2 687(7)	1 091(4)	1 281(6)
C(62)	−2 543(7)	1 545(4)	710(6)
C(63)	−3 404(7)	1 752(4)	−203(6)
C(64)	−4 410(7)	1 507(4)	−546(6)
C(65)	−4 554(7)	1 054(4)	24(6)
C(66)	−3 693(7)	846(4)	938(6)
C(71)	5 809(12)	166(7)	3 629(9)
C(72)	5 131(12)	−190(7)	2 754(9)
C(73)	4 486(12)	197(7)	1 901(9)
C(74)	4 521(12)	942(7)	1 922(9)
C(75)	5 199(12)	1 298(7)	2 797(9)
C(76)	5 843(12)	910(7)	3 650(9)

Structure determination and refinement. The structures were solved by conventional Patterson and Fourier methods. Some difficulties were found in the analysis of complex (1) as the two $C2/c$ and Cc space groups seemed equally probable. The centrosymmetric space group implied a statistical distribution of the organic ligand over two positions about the C_2 axis running through Pt and Cl. The non-centrosymmetric space group did not require this assumption. As it was not possible to test by direct experiment for centrosymmetry, two refinements for both structures were tried using block-diagonal least squares. Only the centrosymmetric model could be refined in this way; the non-centrosymmetric one did not converge. The refinement was stopped at R 0.054, using anisotropic thermal parameters for all the undisordered atoms. A difference-Fourier synthesis calculated at R 0.065 revealed

TABLE 2

Final atomic fractional co-ordinates (×10^4) for *trans*-[Pt(CH$_2$=C–CMe=CH$_2$)(C≡C–CMe=CH$_2$)(PPh$_3$)$_2$] (2) with standard deviations in parentheses

	x/a	y/b	z/c
Pt	586(1)	1 414(1)	462(1)
P(1)	1 583(2)	1 859(2)	−451(5)
P(2)	−328(2)	912(2)	1 536(4)
C(1)	679(12)	30(9)	−949(20)
C(2)	463(7)	751(10)	−1 097(15)
C(3)	149(8)	1 027(13)	−2 219(21)
C(4)	−30(12)	1 686(17)	−2 313(28)
C(6)	773(6)	1 993(7)	1 993(14)
C(7)	892(7)	2 352(7)	2 900(17)
C(8)	1 044(10)	2 807(8)	3 970(18)
C(9)	571(13)	2 899(9)	4 951(17)
C(10)	1 754(11)	3 119(12)	4 003(27)
C(11)	2 332(8)	1 807(7)	590(18)
C(12)	2 364(8)	1 237(9)	1 444(16)
C(13)	2 941(10)	1 156(11)	2 264(19)
C(14)	3 474(10)	1 648(12)	2 261(20)
C(15)	3 472(8)	2 178(10)	1 473(21)
C(16)	2 893(9)	2 301(8)	647(21)
C(21)	1 938(6)	1 421(8)	−1 936(13)
C(22)	1 683(8)	1 630(8)	−3 144(16)
C(23)	1 925(9)	1 329(10)	−4 189(15)
C(24)	2 446(9)	796(9)	−4 121(15)
C(25)	2 688(8)	601(8)	−2 968(20)
C(26)	2 467(7)	938(7)	−1 825(17)
C(31)	1 516(8)	2 765(8)	−952(15)
C(32)	2 018(7)	3 041(7)	−1 798(14)
C(33)	1 934(9)	3 691(10)	−2 216(20)
C(34)	1 382(13)	4 115(10)	−1 731(25)
C(35)	883(12)	3 831(9)	−863(27)
C(36)	949(8)	3 137(7)	−426(23)
C(41)	−760(5)	1 422(8)	2 712(13)
C(42)	−927(8)	2 115(8)	2 468(15)
C(43)	−1 295(8)	2 497(9)	3 297(17)
C(44)	−1 524(9)	2 271(9)	4 486(21)
C(45)	−1 389(9)	1 543(11)	4 801(17)
C(46)	−1 018(9)	1 159(9)	3 904(18)
C(51)	54(8)	175(7)	2 436(15)
C(52)	−86(8)	−473(7)	2 064(17)
C(53)	233(9)	−1 000(9)	2 800(21)
C(54)	682(8)	−859(9)	3 777(18)
C(55)	822(8)	−185(8)	4 056(14)
C(56)	499(9)	294(8)	3 386(17)
C(61)	−1 101(6)	616(7)	685(13)
C(62)	−1 274(8)	918(9)	−474(22)
C(63)	−1 937(9)	756(10)	−1 123(20)
C(64)	−2 360(9)	267(10)	−626(21)
C(65)	−2 175(8)	−42(9)	374(27)
C(66)	−1 545(10)	105(9)	1 196(24)
C(5A)	−124(32)	613(32)	−3 266(61)
C(5B)	290(30)	522(30)	−3 448(60)

TABLE 3

Comparison of bond distances (Å) and angles (°) obtained in different refinements for the benzene solvate of (1)

Space group Refinement	$C2/c$ Full matrix	Cc Full matrix
Pt–P(1)	2.300(4)	2.296(9)
Pt–P(2)		2.299(14)
Pt–Cl	2.410(3)	2.408(3)
Pt–C(2)	2.06(1)	2.07(1)
C(1)–C(2)	1.44(1)	1.50(3)
C(2)–C(3)	1.42(2)	1.41(2)
C(3)–C(4)	1.31(2)	1.36(2)
C(3)–C(5)	1.60(2)	1.50(2)
P(1)–C(11)	1.826(5)	1.84(1)
P(1)–C(21)	1.814(6)	1.85(1)
P(1)–C(31)	1.830(5)	1.80(1)
P(2)–C(41)		1.82(1)
P(2)–C(51)		1.80(1)
P(2)–C(61)		1.85(1)
Cl–Pt–P(1)	90.4(1)	91.2(4)
Cl–Pt–P(2)		89.7(4)
P(1)–Pt–P(2)	179.2(1)	178.4(3)
Cl–Pt–C(2)	166.8(3)	165.1(4)
C(2)–Pt–P(1)	89.6(4)	89.7(4)
C(2)–Pt–P(2)	89.6(4)	89.1(4)
Pt–C(2)–C(1)	122.8(7)	126.4(1.2)
Pt–C(2)–C(3)	118.4(8)	117.9(9)
C(1)–C(2)–C(3)	118.8(1.0)	115.7(1.4)
C(2)–C(3)–C(4)	117.9(1.1)	113.7(1.3)
C(2)–C(3)–C(5)	109.6(1.1)	120.3(1.2)
C(4)–C(3)–C(5)	132.5(1.1)	125.9(1.5)
Pt–P(1)–C(11)	118.5(2)	118.6(5)
Pt–P(1)–C(21)	112.1(2)	108.6(5)
Pt–P(1)–C(31)	112.9(2)	113.2(6)
Pt–P(2)–C(41)		119.1(6)
Pt–P(2)–C(51)		115.5(6)
Pt–P(2)–C(61)		112.5(7)
C(11)–P(1)–C(21)	102.6(3)	101.4(6)
C(11)–P(1)–C(31)	103.6(3)	106.0(6)
C(21)–P(1)–C(31)	105.9(3)	108.1(6)
C(41)–P(2)–C(51)		102.7(8)
C(41)–P(2)–C(61)		100.7(7)
C(51)–P(2)–C(61)		104.3(7)

TABLE 4

Bond distances (Å) and angles (°) in complex (2)

Pt–P(1)	2.287(5)	C(7)–C(8)	1.46(2)
Pt–P(2)	2.284(4)	C(8)–C(9)	1.37(3)
Pt–C(2)	2.09(2)	C(8)–C(10)	1.48(3)
Pt–C(6)	1.99(1)	P(1)–C(11)	1.79(2)
C(1)–C(2)	1.48(3)	P(1)–C(21)	1.89(2)
C(2)–C(3)	1.42(3)	P(1)–C(31)	1.85(2)
C(3)–C(4)	1.34(4)	P(2)–C(41)	1.78(1)
C(3)–C(5A)	1.45(7)	P(2)–C(51)	1.87(2)
C(3)–C(5B)	1.64(7)	P(2)–C(61)	1.81(1)
C(6)–C(7)	1.20(2)		

The average C–C distances in each phenyl group are: 1.406(10), 1.385(9), 1.406(10), 1.405(10), 1.356(9), and 1.401(11) Å

P(1)–Pt–C(2)	90.3(4)	C(2)–C(3)–C(4)	122(2)
P(1)–Pt–C(6)	88.3(4)	C(2)–C(3)–C(5A)	124(3)
P(2)–Pt–C(2)	91.7(4)	C(2)–C(3)–C(5B)	110(3)
P(2)–Pt–C(6)	89.3(4)	C(4)–C(3)–C(5A)	113(3)
P(1)–Pt–P(2)	173.6(2)	C(4)–C(3)–C(5B)	124(3)
C(2)–Pt–C(6)	175.0(6)	C(6)–C(7)–C(8)	178(2)
Pt–C(2)–C(1)	119(1)	C(7)–C(8)–C(9)	121(2)
Pt–C(2)–C(3)	117(2)	C(7)–C(8)–C(10)	117(2)
Pt–C(6)–C(7)	179(1)	C(9)–C(8)–C(10)	122(2)
Pt–P(1)–C(11)	112.4(6)	C(11)–P(1)–C(21)	100.9(7)
Pt–P(1)–C(21)	117.5(5)	C(11)–P(1)–C(31)	106.2(7)
Pt–P(1)–C(31)	115.2(5)	C(21)–P(1)–C(31)	103.2(7)
Pt–P(2)–C(41)	116.4(5)	C(41)–P(2)–C(51)	105.4(7)
Pt–P(2)–C(51)	106.6(5)	C(41)–P(2)–C(61)	98.4(6)
Pt–P(2)–C(61)	120.8(5)	C(51)–P(2)–C(61)	108.2(7)
C(1)–C(2)–C(3)	124(2)		

the presence of a molecule of benzene solvent disordered over two positions related by a C_2 axis. Further refinement * in both space groups was made using full-matrix least squares [23] and (to minimize computing expenses) using the rigid-body constraint for all the benzene rings and anisotropic thermal parameters for Pt, P, and Cl. Convergence was now reached for both models (centric, R 0.058; acentric, R 0.056) which gave similar molecular parameters as can be seen from the data in Table 3. In order to choose between the disordered centrosymmetric and the undisordered non-centrosymmetric models, Hamilton's significance test [24] was applied, using the generalized R factors whose value was $R^* = R_c/R_a = 0.074\,5/0.069\,2 = 1.077$. This value, compared with the tabular ratio R^* (57,3 749,0.005) = 1.012, indicated that the hypothesis that the two structures were not significantly different had to be rejected at the 0.005 significance level, *i.e.* the non-centrosymmetric model must be assumed. The final parameters in Table 1 are those corresponding to this assumption.

TABLE 5

Equations of least-squares planes and, in square brackets, distances (Å) from these planes

(*a*) Benzene solvate of complex (1) *

Plane (1): co-ordination plane, Cl, P(1), P(2), C(2), Pt

$$-0.006\,5X - 0.048\,0Y - 0.998\,8Z = -3.661\,3$$

[Cl −0.020, P(1) 0.055, C(2) −0.291, P(2) 0.136, Pt 0.120]

Plane (2): 1-isopropenylvinyl ligand, C(1), C(2), C(3), C(4), C(5)

$$-0.999\,2X + 0.015\,0Y - 0.038\,2Z = 2.277\,4$$

[C(1) −0.025, C(2) 0.011, C(3) 0.024, C(4) −0.022, C(5) 0.012, Pt 0.036]

(*b*) Complex (2)

Plane (1): co-ordination plane, P(1), P(2), C(2), C(6), Pt

$$-0.591\,9x + 0.690\,2y - 0.416\,3z = 0.969\,9$$

[P(1) −0.038, P(2) −0.037, C(2) 0.001, C(6) −0.009, Pt 0.083]

Plane (2): 1-isopropenylvinyl ligand, C(1), C(2), C(3), C(4)

$$0.907\,3x + 0.218\,8y - 0.359\,2z = 1.531\,2$$

[C(1) 0.004, C(2) −0.004, C(3) −0.005, C(4) 0.005, C(5A) −0.260, C(5B) 0.481, Pt −0.092]

Plane (3): isopropenylethynyl ligand, C(6), C(7), C(8), C(9), C(10)

$$-0.372\,4x + 0.782\,2y - 0.499\,5z = 1.466\,9$$

[C(6) 0.001, C(7) −0.005, C(8) 0.027, C(9) −0.009, C(10) −0.014, Pt 0.044]

* The transformation matrix from monoclinic x, y, z to orthogonal X, Y, Z is:

$$\begin{matrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{matrix}$$

It is interesting to consider the differences in bond distances and angles calculated from the different refinements (Table 3). From these data it appears that there are no significant differences in the structural parameters involving the co-ordination polyhedron. The same could be said for the other parameters excepting the distance C(3)–C(5) and the angles C(2)–C(3)–C(5), C(4)–C(3)–C(5), and C(11)–P(1)–C(31) for which the Δ/σ values are just

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* We are indebted to a referee for the suggestion that the previous choice of the space group required further refinement.

[23] G. Sheldrick, 'SHELX-76' system of computer programs, University of Cambridge, 1976.

[24] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

significant. So whatever the model is, the relevant results from the chemical point of view are practically the same at the level of the accuracy achieved with this analysis.

For complex (2) disorder was found involving the C(5) methyl carbon.* The structure was refined by block-diagonal least squares with occupancy factors of 0.5 for C(5A) and C(5B), first isotropically down to R 0.054 and then anisotropically down to R 0.050. The function minimized in both analyses was $\Sigma w|\Delta F|^2$. The weighting scheme was $w = 1/[\sigma^2(F) + 0.000\,1F^2]$ for complex (1); unit weights were used for complex (2).

Attempts to locate the hydrogen atoms were unsuccessful. Atomic scattering factors used throughout the calculations were taken from ref. 25. All the calculations were made on a CYBER 7600 computer at the Centro di Calcolo Elettronico dell'Italia Nord-Orientale (Bologna). The final positions and thermal parameters for the atoms are in Tables 1 and 2. Observed and calculated structure factors together with the thermal parameters are listed in Supplementary Publication No. SUP 22095 (46 pp., 1 microfiche).† The most relevant bond distances and angles and the equations of molecular planes are given in Tables 3—5. All the average values were calculated using the formulae $\mu_{\text{av.}} = \sum_i(\mu_i/\sigma_i^2)/\sum_i\sigma_i^{-2}$ and $\sigma_{\text{av.}} = (\sum_i\sigma_i^{-2})^{-\frac{1}{2}}$ where μ_i are the individual observations and σ_i are their standard deviations.

[6/1486 *Received, 29th July, 1976*]

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* Of course a model with a very high thermal motion for C(5) could be considered, but the distinction between the two possibilities (if possible) was not considered worthwhile for the purposes of the present study.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[25] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.