176. *Complexes of Acetylenes with Platinum*(II). *Part I. Alkynes.*

By J. CHATT, R. G. GUY, and (in part) L. A. DUNCANSON.

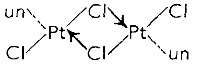
Alkyne–platinum(II) complexes of the chloro-bridged type $[Pt_2Cl_4ac_2]$ and the mononuclear type $M[PtCl_3ac]$ (M = Na or K, ac = alkyne) are described. The simplest alkynes which have formed stable complexes are of the type Bu^{t}C⁝CR (R = Bu^t, Pr^i, Et, Me, or CMe$_2$Ph). Amines (am) react with the complexes to give mononuclear complexes of the type *trans*-$[PtCl_2$ac am$]$.

The infrared spectra of the complexes show that in the complex the frequency of the stretching vibration of the C⁝C bond is lowered by some 200 cm.$^{-1}$. This is consistent with a structure similar to that of the corresponding olefin complexes. The dipole moments of complexes of the type *trans*-$[PtCl_2$un am$]$ (un = Bu^{t}C⁝CBu^t or C_2H_4) show that the Bu^{t}C⁝CBu^t $\longrightarrow$ Pt group moment is about 1·0 D greater than the $C_2H_4 \longrightarrow$ Pt group moment.

STABLE platinum(II) complexes containing olefins as ligands have been known since 1827 when Zeise [1] reported the ethylene complex $K[PtCl_3(C_2H_4)],H_2O$. Since then many olefin complexes of platinum(II) have been described,[2,3] but attempts to prepare the corresponding platinum(II) complexes of acetylene and monosubstituted alkynes led to indefinite, reddish-brown amorphous products, owing probably to replacement of the ethynyl hydrogen atoms. The first stable acetylene complex was reported by Gel'man *et al.*,[4] who showed that the acetylenic glycol HO·CMe$_2$·C⁝C·CMe$_2$·OH (ac) forms a complex, *trans*-$[PtCl_2$ac py$]$, analogous to *trans*-$[PtCl_2(C_2H_4)$ py$]$ (py = pyridine). Later work [5,6,7] showed that this glycol further resembles olefins in forming complexes of the types $K[PtCl_3ac]$ and *cis*-$[PtCl_2$ac $NH_3]$ by the common methods used to prepare the corresponding olefin complexes. Chatt and Duncanson [8] were nevertheless unable to prepare the corresponding complexes of dimethylacetylene and diphenylacetylene by any of these methods, although colour changes were observed which suggested that some unstable complex was formed.

RC⁝CR′

(I)



(II)

In an attempt to find the reason for this difference between the stabilities of complexes derived from the acetylenic glycol and the acetylenic hydrocarbons MeC⁝CMe and PhC⁝CPh we have examined the reactions of a series of acetylenic hydrocarbons and alcohols with (*a*) aqueous potassium tetrachloroplatinate(II), (*b*) ethanolic sodium tetrachloroplatinate(II), (*c*) $K[PtCl_3(C_2H_4)]$ in acetone, and (*d*) $[Pt_2Cl_4(C_2H_4)_2]$ in acetone. We have also examined the infrared spectra of all the complexes which we have obtained from these reactions, with particular reference to the effect of complex formation on the O–H stretching frequencies and bands which we assign, but with rather less certainty, to the C⁝C stretching frequencies.

In this paper we describe the preparation of complexes derived from alkynes of the type (I) and show (i) that the stability depends greatly on the groups R, and (ii) that the complexes are exactly analogous to the olefin complexes.[9] The complexes of acetylenic

---

[1] Zeise, *Pogg. Annalen*, 1827, **9**, 632.

[2] See Keller, *Chem. Rev.*, 1941, **28**, 229.

[3] See Douglas, " The Chemistry of the Co-ordination Compounds," ed. Bailar, Reinhold Publ. Inc., New York, 1956, p. 487.

[4] Gel'man, Bukhovets, and Meilakh, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **46**, 105.

[5] Bukhovets, *Izvest. Sekt. Platiny drug. blagorod. Metal., Inst. obschchei neorg. Khim.*, 1955, **29**, 55.

[6] Bukhovets and Molodova, *Zhur. neorg. Khim.*, 1957, **2**, 776; 1958, **3**, 1540.

[7] Molodova, *Zhur. neorg. Khim.*, 1958, **3**, 2472.

[8] Chatt and Duncanson, *J.*, 1953, 2939.

[9] For a preliminary account of this work, see Chatt, Duncanson, and Guy, *Chem. and Ind.*, 1959, 430.

alcohols and platinum(II) show special features which are discussed elsewhere,[10] and will be described in detail in Part II.

To see whether the hydroxyl groups in the glycol $HO{\cdot}CMe_2{\cdot}C{:}C{\cdot}CMe_2{\cdot}OH$ are essential for the formation of stable complexes, the related alkyne 2,2,5,5-tetramethylhex-3-yne (I; $R = R' = Bu^t$) was first investigated. When an ethanolic solution of sodium chloroplatinate(II) tetrahydrate is treated at room temperature for several days with an excess of 2,2,5,5-tetramethylhex-3-yne ($C_{10}H_{18}$), a red, crystalline solid of composition $C_{10}H_{18}Cl_2Pt$ is formed in 81% yield (method 1). This compound can also be obtained more readily in 74% yield by reaction of the alkyne with ethyleneplatinous chloride (II; un = C_2H_4) in acetone (method 2).

$$2Na_2PtCl_4 + 2C_{10}H_{18} \longrightarrow [Pt_2Cl_4(C_{10}H_{18})_2] + 4NaCl \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$[Pt_2Cl_4(C_2H_4)_2] + 2C_{10}H_{18} \longrightarrow [Pt_2Cl_4(C_{10}H_{18})_2] + 2C_2H_4 \quad . \; . \; . \; . \; . \; . \quad (2)$$

The complex, $C_{10}H_{18}Cl_2Pt$, is dimeric, diamagnetic, and a non-electrolyte in nitrobenzene. It is moderately soluble in light petroleum, very soluble in other common organic solvents, and insoluble in water. It is stable, even on exposure to the atmosphere, in contrast to ethyleneplatinous chloride. It melts at 184—187° with decomposition, and sublimes poorly, with extensive decomposition, at 150°/0·01 mm.

It has the bridged structure (II; un = $Bu^tC{:}CBu^t$) analogous to that of ethyleneplatinous chloride (II; un = C_2H_4). The existence of the halogen bridge was confirmed by bridge-splitting reactions with amines (am) to give mononuclear complexes, and with potassium chloride to give the analogue of Zeise's salt, $K[PtCl_3(C_{10}H_{18})]$, *i.e.*:

$$[Pt_2Cl_4(C_{10}H_{18})_2] + 2am \longrightarrow 2\textit{trans}\text{-}[PtCl_2(C_{10}H_{18})\,am]$$

$$[Pt_2Cl_4(C_{10}H_{18})_2] + 2KCl \longrightarrow 2K[PtCl_3(C_{10}H_{18})]$$

The amine derivatives prepared (am = pyridine, 4-chloropyridine, 4-methylpyridine, piperidine, and *p*-toluidine) are stable, yellow, crystalline solids, readily soluble in all the common organic solvents except light petroleum. The ionic complex, $K[PtCl_3(C_{10}H_{18})]$, is stable in the dry state, but on addition of water it instantly reverts to the bridged complex.

This ionic complex can also be prepared by direct replacement of the ethylene in $K[PtCl_3(C_2H_4)],H_2O$ by the alkyne (method 3). At room temperature displacement of the ethylene is incomplete after 8 days, but in boiling acetone the reaction goes to completion in 3 hours.

$$K[PtCl_3(C_2H_4)],H_2O + C_{10}H_{18} \longrightarrow K[PtCl_3(C_{10}H_{18})] + C_2H_4 + H_2O \quad . \; . \; . \; . \quad (3)$$

The bromo-bridged complex corresponding to (II; un = $Bu^tC{:}CBu^t$) is formed in 26% yield by treatment of potassium bromoplatinate(II) with 2,2,5,5-tetramethylhex-3-yne in aqueous acetone. This deep-red complex is analogous in every way to the chloro-complex, and is equally stable.

The alkynes $Bu^tC{:}CR$ ($R = Pr^i$, Et, CMe_2Ph) readily yield the bridged complexes (II; un = $Bu^tC{:}CPr^i$, $Bu^tC{:}CEt$, and $Bu^tC{:}C{\cdot}CMe_2Ph$ respectively) by both methods 1 and 2. These complexes are stable, and undergo the normal bridge-splitting reactions with amines to give stable complexes of the type *trans*-$[PtCl_2(Bu^tC{:}CR)(\text{amine})]$. 2,2-Dimethylpent-3-yne ($Bu^tC{:}CMe$), however, gives the ionic complex $Na[PtCl_3(Bu^tC{:}CMe)]$ on treatment with ethanolic $Na_2PtCl_4,4H_2O$ (method 1). Aqueous solutions of this complex, in contrast to $K[PtCl_3(Bu^tC{:}CBu^t)]$, are stable, and react with amines in the manner of Zeise's salt to give complexes of the type *trans*-$[PtCl_2(Bu^tC{:}CMe)(\text{amine})]$. Reaction of $Bu^tC{:}CMe$ with ethyleneplatinous chloride (method 2) did not yield the binuclear complex (II; un = $Bu^tC{:}CMe$), which was not obtained even by the reaction of an alcoholic solution of hydrogen chloride on the salt $K[PtCl_3(Bu^tC{:}CMe)]$.

The alkynes $Bu^tC{:}CH$, $Pr^iC{:}CH$, $Pr^iC{:}CEt$, $Pr^iC{:}CMe$, $Bu^nC{:}CBu^n$, $Pr^nC{:}CPr^n$, $EtC{:}CEt$,

---

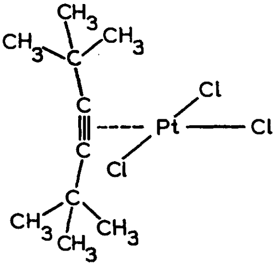
[10] Chatt, Duncanson, and Guy, *Nature*, 1959, **184**, 526.

MeC⋮CMe, PhC⋮CPh, $Bu^t\cdot[C⋮C]_2\cdot Bu^t$, and $Ph\cdot[C⋮C]_2\cdot Ph$ showed colour changes indicative of complex formation when treated by methods 1, 2, and 3. In some cases extensive decomposition products were rapidly formed, and in all cases the products were too unstable to be isolated by rapid evaporation of their solutions at water-pump pressure and below 10°. Attempts to form complexes of the type *trans*-$[PtCl_2ac\ am]$ (ac = alkyne, am = amine) by addition of the appropriate amount of amine to the reaction solution were equally unsuccessful. In general, these alkynes gave intractable brown or black gums when treated by methods 1 and 2, and yellow-brown solids, insoluble in water and of variable composition, when treated by method 3.

Hydration of the triple bond of the alkyne, presumably catalysed by colloidal platinum formed by reduction of the platinum(II) salt, occurred in the reaction of several alkynes with ethanolic $Na_2PtCl_4,4H_2O$; *e.g.*, $Bu^nC⋮CBu^n$ gave decan-5-one, and PhC⋮CPh gave benzyl phenyl ketone.

Infrared Spectra (In collaboration with L. A. Duncanson).—The C⋮C stretching frequency in disubstituted alkynes [11] occurs between 2190 and 2260 cm.$^{-1}$, the intensity of absorption in the infrared region depending on the asymmetry of the alkyne. If the alkynes are bound to the platinum atom in the same manner as olefins, we should find weak absorption bands in the infrared spectra of the complexes corresponding to the C⋮C stretching frequencies, especially when the alkyne is not symmetrical about the triple bond. We have therefore examined the infrared spectra of the powdered crystalline complexes.

The symmetrical complex (II; un = $Bu^tC⋮CBu^t$) has two weak absorption bands at 2023 and 2005 cm.$^{-1}$, and all the other complexes show a single weak absorption band between 2001 and 2028 cm.$^{-1}$ (see Table 1). This absorption band does not correspond to any known C–C absorption, and as it occurs in the spectrum of all types of complexes of alkynes and hydroxyacetylenes with platinum(II),[10] it is attributed to the C⋮C stretching frequency, lowered by some 200 cm.$^{-1}$ by co-ordination to the platinum atom. This lowering of frequency may be compared with (*a*) the lowering of 140 cm.$^{-1}$ in the C:C stretching frequency of olefins on complex formation with platinum(II),[8] (*b*) the lowering of 400 cm.$^{-1}$ in the C⋮C stretching frequency of acetylenes on complex formation with platinum(0),[12] and (*c*) the lowering of 65 cm.$^{-1}$ in the C:C stretching frequency of olefins on complex formation with silver(I).[13]



Probable spatial arrangement of atoms in $[PtCl_3(Bu^tC⋮CBu^t)]^-$.

The existence of the weak absorption near 2000 cm.$^{-1}$ in the complex (II; un = $Bu^tC⋮CBu^t$) is evidence of the loss of a centre of symmetry by the alkyne, but, as with ethylene, its weakness indicates that the symmetry of the alkyne has not been altered by co-ordination to the metal. The alkyne thus appears to be symmetrically co-ordinated about the triple bond, in exactly the same manner as the olefins, and bound to the metal by the same type of double bond as ethylene in Zeise's salt.[8] The σ-component of the bond would be formed by overlap of a $5d6s6p^2$-hybrid orbital of the platinum atom with a π-orbital of the alkyne, and the π-type bond by overlap of a filled $5d6p$-orbital with an antibonding π-molecular orbital of the alkyne. This should lead to the spatial arrangement

---

[11] See Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 59.

[12] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.

[13] Taufen, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3500.

of atoms in $[\mathrm{PtCl_3(Bu^tC⋮CBu^t)}]^-$ shown in the Figure. Since the symmetrical distribution of electron density about the C⋮C axis of the alkyne will be disturbed in the complex it seems probable that the alkyne will also be slightly bent as shown.

The effect of the alkyne on the electronic distribution in the Pt–N bond of *trans*-$[\mathrm{PtCl_2ac\ piperidine}]$ was investigated by measuring the N–H stretching frequency ($\nu_{\mathrm{N-H}}$) of the complexes in dilute carbon tetrachloride solution.[14] It can be seen from Table 1 that $\nu_{\mathrm{N-H}}$ in these complexes is remarkably constant, and appears to be independent of the nature of the group R in $\mathrm{Bu^tC⋮CR}$. It is also very close to the value of 3230 cm.$^{-1}$ obtained for $\nu_{\mathrm{N-H}}$ in *trans*-$[\mathrm{PtCl_2(C_2H_4)piperidine}]$,[14] again indicating that the alkyne must be bonded in essentially the same way as ethylene.

Dipole Moments.—The bond between the alkyne and the metal atom is a combination of two electronic effects, *i.e.*, the σ-bond, involving sharing of the π-electrons of the alkyne, and the π-bond, involving sharing of the $5d$-electrons of the metal. To determine the polarity of the alkyne–platinum(II) bond we have measured the dipole moments of the complexes *trans*-$[\mathrm{PtCl_2(Bu^tC⋮CBu^t)am}]$ (where am = pyridine, 4-methylpyridine, and 4-chloropyridine).

The results (Table 3) show conclusively that the amine molecule is at the positive end of the permanent dipole, and thus appears to be a stronger electron-donor than the alkyne. The moment of the Pt–N bond is unknown, but is perhaps of the order 6 D, so that the moment of the alkyne–Pt entity has a value of about 3·25 D. This is 1·0 D greater than the ethylene–Pt entity which we have remeasured more accurately than previously.[8] A greater electron drift from the alkyne to the metal atom is to be expected because the alkyne has a lower ionisation potential than ethylene (Table 2), but at this point it is not possible to say whether the increase of 1·0 D is due entirely to this effect, or whether a substantial part is due to bending of the alkyne molecule in the complex so that the positively charged t-butyl group moves away from the platinum atom as shown in the Figure.

TABLE 1. *Complexes of alkynes with platinum*(II).

	$\nu_{\mathrm{C⋮C}}$ (cm.$^{-1}$)		$\nu_{\mathrm{N-H}}$ (cm.$^{-1}$)
Alkyne (ac)	$\mathrm{Na[PtCl_3ac]}$	$\mathrm{[Pt_2Cl_4ac_2]}$	*trans*-$[\mathrm{PtCl_2ac\ pip}]$ *
$\mathrm{Bu^tC⋮CBu^t}$	—	2023, 2005	3221
$\mathrm{Bu^tC⋮CPr^i}$	—	2011	3221
$\mathrm{Bu^tC⋮CEt}$	—	2023	3222
$\mathrm{Bu^tC⋮CMe}$	2028	—	3221
$\mathrm{Bu^tC⋮C{\cdot}CMe_2Ph}$	—	2001	3222

* pip = piperidine.

Effect of the Structure of the Alkyne on Complex Formation.—The stabilities of the complexes depend greatly upon the structures of the alkynes they contain. Of the alkynes studied, only those containing at least one t-butyl group adjacent to the triple bond *e.g.*, $\mathrm{Bu^tC⋮CR}$ (R = $\mathrm{Bu^t}$, $\mathrm{Pr^i}$, Et, Me, or $\mathrm{CMe_2Ph}$), formed complexes sufficiently stable to be isolated by the methods we used. The simpler alkynes, *e.g.*, $\mathrm{Bu^tC⋮CH}$, $\mathrm{Pr^iC⋮CEt}$, and $\mathrm{RC⋮CR}$ (R = Me, Et, $\mathrm{Pr^n}$, or $\mathrm{Bu^n}$), and alkynes conjugated to phenyl groups or another triple bond, *e.g.*, $\mathrm{PhC⋮CPh}$ and $\mathrm{Bu^t{\cdot}[C⋮C]_2{\cdot}Bu^t}$ do not form sufficiently stable complexes. There appears to be a similar, although not so marked, dependence of the stabilities of olefin complexes upon the structures of the olefins; both methyl- and phenyl-ethylenes form complexes with platinum(II), and the former are more stable than the latter.[15] The

TABLE 2. *Ionisation potentials of alkynes.**

Alkyne	$\mathrm{EtC⋮CEt}$	$\mathrm{Pr^nC⋮CPr^n}$	$\mathrm{Bu^nC⋮CBu^n}$	$\mathrm{Bu^tC⋮CBu^t}$	$\mathrm{Bu^tC⋮CEt}$
Ionisation potential (±0·03 ev)	9·33	9·19	9·14	9·07	9·20

* Ethylene has an ionisation potential of 10·45 ev.[16]

---

[14] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[15] Anderson, *J.*, 1936, 1042; Joy and Orchin, *J. Amer. Chem. Soc.*, 1959, **81**, 310.

dipole moments reported in this paper show that the olefinic and acetylenic hydrocarbons in their complexes with platinum(II) behave essentially as electron donors and acquire a small positive charge in the complex. It seems logical therefore to suppose that the electron-donating methyl groups would assist, and the electronegative phenyl groups diminish, the tendency to complex formation, but such inductive effects are not sufficient to explain the enormous differences between the stabilities of the alkyne complexes.

The first ionisation potential is a measure of the donor capacity of the alkyne and in Table 2 we list a representative selection of potentials,[16] kindly measured for us by W. C. Price, P. V. Harris, and R. Bralsford. It will be seen that there is no direct correlation between the ionisation potential of an alkyne and its tendency to form stable complexes. Thus di-n-butylacetylene (dec-5-yne) appears to have a greater electron-donor capacity than ethyl-t-butylacetylene (oct-3-yne), but only the latter forms stable complexes.

Other factors which could affect the stabilities of the complexes are: (*a*) the polarisabilities of the groups adjacent to the triple bond, (*b*) the ease with which the alkyne is destroyed, *e.g.*, by isomerisation into an allene,† (*c*) the steric effects of the groups adjacent to the triple bond.

The polarisabilities of the Me, Et, Pr^i, and Bu^t groups are 27, 47, 65, and 84 × 10^{-25} $cm.^3$ respectively,[17] and the high polarisability of the t-butyl group might be expected to assist the electron release from the triple bond to the platinum atom. However, if this were so, we would expect this electron release to affect the NH stretching frequency (ν_{N-H}) in the complexes of the type *trans*-[$PtCl_2(Bu^tC{:}CR)$ (piperidine)], but ν_{N-H} is independent of the group R. Also the total polarisability of the groups adjacent to the triple bond in the alkyne $Bu^tC{:}CMe$ is almost exactly equal to the polarisability of those in $Pr^iC{:}CEt$, yet the former forms complexes and the latter does not. It seems therefore that the polarisability of the groups is not an important factor.

We do not know how the unstable alkyne complexes decompose. The decomposition may involve some attack on the alkyne itself, or upon the platinum atom. If the decomposition involves some rearrangement of the alkyne, perhaps to form an allene, then those alkynes with a t-butyl group adjacent to the triple bond would rearrange less readily and should form the more stable complexes, as is found. Some factor of this type may be responsible for the greater stability of the alkyne complexes which contain t-butyl groups adjacent to the triple bond.

The steric effect of the t-butyl group could also be important. It has been shown that in complex compounds of the type *trans*-[$MClPh(PR_3)_2$](M = Ni,Pt) an *ortho*-substituent in the phenyl group has a very marked stabilising effect,[18] and one result is undoubtedly that it screens the metal atom from attack by solvent or reagent. Even one *ortho*-substituent has so great an effect that it seems possible that the t-butyl group of the alkynes could function in an analogous manner and stabilise the complex.

It should be possible to isolate some of the less stable alkyne complexes as anions by the use of large cations. We have not done this but Bukhovets and Pukhova [19] have recently isolated the complex $Et_3NH[PtCl_3(PhC{:}CPh)]$ from the reaction of $[Et_3NH]_2[PtCl_4]$ with diphenylacetylene in chloroform. The large cation with its relatively low polarising power evidently forms a stable salt with the diphenylacetylene complex ion.

EXPERIMENTAL

The microanalyses were carried out in these laboratories. M. p.s were determined on a Kofler hot-stage and are corrected. Except where otherwise stated, light petroleum had b. p. 60—80°.

---

† We are indebted to Dr. B. L. Shaw for this suggestion.

[16] Cf. Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207.

[17] Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3229.

[18] Chatt and Shaw, *J.*, 1959, 4020; 1960, 1718.

[19] Bukhovets and Pukhova, *Zhur. neorg. Khim.*, 1958, **3**, 1714.

Preparation of Alkynes.—The alkynes, prepared as below, were purified by fractional distillation or recrystallisation immediately before use.

But-2-yne was prepared from ethyl methyl ketone by the general method of Bartlett and Rosen,[20] and had b. p. 27°/752 mm., n_D^{17} 1·3912. Similarly prepared were 3-methylbut-1-yne (b. p. 26·5—27·5°/756 mm., n_D^{20} 1·3758) from isopropyl methyl ketone, and 3,3-dimethylbut-1-yne (b. p. 37·5—38°/760 mm., n_D^{20} 1·3730) from methyl t-butyl ketone. Hex-3-yne (b. p. 81·5—82°/763 mm., n_D^{25} 1·4090), oct-4-yne (b. p. 130°/758 mm., n_D^{20} 1·4238), and dec-5-yne (b. p. 114°/100 mm., n_D^{25} 1·4318) were prepared by Bried and Hennion's method.[21] 2-Methylpent-3-yne was prepared by the alkylation of 3-methylbut-1-yne with methyl iodide in liquid ammonia, and had b. p. 72·5°/751 mm., n_D^{25} 1·4034. Similarly prepared were 2-methylhex-3-yne (b. p. 94—94·5ᶜ/749 mm., n_D^{22} 1·4090) from 3-methylbut-1-yne and ethyl bromide, 2,2-dimethylpent-3-yne (b. p. 82—82·5°/745 mm., n_D^{25} 1·4058) from 3,3-dimethylbut-1-yne and methyl iodide, and 2,2-dimethylhex-3-yne (b. p. 102°/760 mm., n_D^{25} 1·4082) from 3,3-dimethylbut-1-yne and ethyl bromide. 2,2,5-Trimethylhex-3-yne[22] had b. p. 109—110°/753 mm., n_D^{25} 1·4086, and 2,2,5,5-tetramethylhex-3-yne[23] had b. p. 110°/757 mm., n_D^{15} 1·4090. 2,2,7,7-Tetramethylocta-3,5-diyne (m. p. 130—130·5°) was prepared by aerial oxidation of a solution of 3,3-dimethylbut-1-yne and cuprous chloride in ethanolic ammonia. 1,4-Diphenylbut-1,3-diyne (m. p. 87—88°) was similarly prepared from phenylacetylene.

2,2,5-*Trimethyl*-5-*phenylhex*-3-*yne*. 2-Chloro-2,5,5-trimethylhex-3-yne[23] (15·8 g., 0·1 mole) in ether (100 ml.) was added dropwise to a stirred, ice-cold solution of phenylmagnesium bromide (0·2 mole) in ether (100 ml.). The mixture was stirred overnight at room temperature, and then heated under reflux for 2 hr. Hydrolysis at *ca.* −10° with dilute hydrochloric acid and isolation of the product from the ethereal layer gave 2,2,5-*trimethyl*-5-*phenylhex*-3-*yne* (6·75 g., 34%), b. p. 103—104°/12 mm., n_D^{25} 1·4890 [Found: C, 90·2; H, 9·95; microhydrogenation (Pd–AcOH), 1·95H_2. $C_{15}H_{20}$ requires C, 89·95; H, 10·05%; 2H_2].

Preparation of Complexes.—(1) *Complexes of the type* $[Pt_2Cl_4ac_2]$. Method 1. Sodium chloroplatinate(II) tetrahydrate (0·01 mole) in ethanol (40 ml.) was treated with the alkyne (0·02 mole) at room temperature. In 3—5 days the solution became orange-yellow and deposition of sodium chloride ceased. Ethanol was removed from the filtered solution at 15 mm. (water-bath temperature 30°). The solid residue was treated with ether, and unchanged sodium chloroplatinate(II) was filtered off. Evaporation of the solvent at 15 mm. and recrystallisation of the resulting solid from light petroleum gave the complexes described below.

Method 2. Di-μ-chlorodichlorodi(ethylene)diplatinum(II), $[Pt_2Cl_4(C_2H_4)_2]$ (0·001 mole), in acetone (20 ml.) at −70° was treated with a solution of the alkyne (0·003 mole) in acetone (10 ml.). On spontaneous warming, the solution gradually became orange-red. After 2 hr. at room temperature, the solvent was removed at 15 mm., leaving the solid complex which was recrystallised from light petroleum.

The following compounds have been prepared by each of the above methods. The yields quoted are those obtained by methods 1 and 2 respectively. *Di-μ-chlorodichlorodi*-(2,2,5,5-*tetramethylhex*-3-*yne*)*diplatinum*(II), $[Pt_2Cl_4(Bu^tC\vdots CBu^t)_2]$, red prisms, m. p. 184—187° (decomp.) yields 81 and 74% (Found: C, 29·85; H, 4·55%; *M*, ebullioscopically in 0·904% benzene solution, 785. $C_{20}H_{56}Cl_4Pt_2$ requires C, 29·7; H, 4·5%; *M*, 808); *di-μ-chlorodichlorodi*-(2,2,5-*trimethylhex*-3-*yne*)*diplatinum*(II), $[Pt_2Cl_4(Bu^tC\vdots CPr^i)_2]$, red prisms, m. p. 110—114° (decomp.), yields 52 and 78% (Found: C, 27·8; H, 4·25%; *M*, cryoscopically in 1·257% benzene solution, 838. $C_{18}H_{32}Cl_4Pt_2$ requires C, 27·7; H, 4·15%; *M*, 780); *di-μ-chlorodichlorodi*-(2,2-*dimethylhex*-3-*yne*)*diplatinum*(II), $[Pt_2Cl_4(Bu^tC\vdots CEt)_2]$, orange-red prisms, m. p. 95—98·5° (decomp.), yields 91 and 76% (Found: C, 25·5; H, 3·85%; *M*, ebullioscopically in 0·434% benzene solution, 736. $C_{16}H_{28}Cl_4Pt_2$ requires C, 25·55; H, 3·75%; *M*, 752); *di-μ-chlorodichlorodi*-(2-*phenyl*-2,5,5-*trimethylhex*-3-*yne*)*diplatinum*(II), $[Pt_2Cl_4(Bu^tC\vdots C{\cdot}CMe_2Ph)_2]$, red prisms, m. p. 158—161° (decomp.), yields 73 and 60% (Found: C, 38·8; H, 4·35%; *M*, ebullioscopically in 0·833% benzene solution, 978. $C_{30}H_{40}Cl_4Pt_2$ requires C, 38·65; H, 4·3%; *M*, 933).

Di-μ-bromodibromodi-(2,2,5,5-tetramethylhex-3-yne)diplatinum(II), $[Pt_2Br_4(Bu^tC\vdots CBu^t)_2]$. Potassium tetrabromoplatinate(II) (0·01 mole) in water (50 ml.) was treated with 2,2,5,5-tetramethylhex-3-yne (0·011 mole) in acetone (20 ml.) at room temperature. After 8 days the

---

[20] Bartlett and Rosen, *J. Amer. Chem. Soc.*, 1942, **64**, 543.

[21] Bried and Hennion, *J. Amer. Chem. Soc.*, 1937, **59**, 1310.

[22] Helmkamp, Carter, and Lucas, *J. Amer. Chem. Soc.*, 1957, **79**, 1306.

[23] Hennion and Banigan, *J. Amer. Chem. Soc.*, 1946, **68**, 1202.

red-brown solid which had formed was collected and recrystallised from light petroleum. This afforded the *complex* as dark red prisms, m. p. 189—193° (decomp.), in 26% yield (Found: C, 24·2; H, 3·65%; *M*, ebullioscopically in 0·645% benzene solution, 1034. $\mathrm{C_{20}H_{36}Br_4Pt_2}$ requires C, 24·35; H, 3·7%; *M*, 986). No complex of the type $\mathrm{K[PtBr_3ac]}$ was detected in the aqueous mother-liquors.

(2) *Complexes of the type* $\mathrm{M[PtCl_3ac]}$. (*a*) Potassium trichloro-(2,2,5,5-tetramethylhex-3-yne)platinate(II), $\mathrm{K[PtCl_3(Bu^tC{\vdots}CBu^t)]}$. Preparation 1. A solution of Zeise's salt (1 mol.) and 2,2,5,5-tetramethylhex-3-yne (2 mol.) in acetone (25 ml.) was heated under reflux for 3 hr. The cooled solution was filtered from a small amount of colloidal platinum and taken to dryness at 15 mm., yielding the *complex* as yellow prisms, decomp. 210—220°, in 89% yield (Found: C, 24·7; H, 3·8. $\mathrm{C_{10}H_{18}Cl_3KPt}$ requires C, 25·1; H, 3·8%).

Preparation 2. Di-μ-chlorodichlorodi-(2,2,5,5-tetramethylhex-3-yne)diplatinum(II) (0·0005 mole) in acetone (5 ml.) was treated with a solution of potassium chloride (0·001 mole) in water (5 ml.). Reaction was immediate and was accompanied by a colour change from orange-red to yellow. The solution was taken to dryness at 15 mm., the solid residue treated with acetone, and solvent removed at 15 mm. from the filtered solution. The residue, after being washed with ether, yielded the complex as a pale yellow solid, decomp. 210—220°, in quantitative yield (Found: C, 24·7; H, 3·8%).

(*b*) Sodium trichloro-(2,2-dimethylpent-3-yne)platinate(II), $\mathrm{Na[PtCl_3(Bu^tC{\vdots}CMe)]}$. Sodium chloroplatinate(II) was treated with 2,2-dimethylpent-3-yne as described for method 1. The yellow solid obtained on evaporation of the ethanol was treated with acetone, and the filtered solution taken to dryness at 15 mm. The residue was washed with ether, yielding the *complex* as yellow prisms, decomp. 200—210°, in 43% yield (Found: C, 19·55; H, 2·9. $\mathrm{C_7H_{12}Cl_3NaPt}$ requires C, 20·0; H, 2·9%).

(3) *Complexes of the type* trans-$\mathrm{[PtCl_2ac\ am]}$. *General method.* The dinuclear complex $\mathrm{[Pt_2Cl_4ac_2]}$ (0·001 mole) in acetone (5 ml.) was treated with a solution of the amine (0·002 mole) in acetone (5 ml.) at room temperature. The reaction was immediate, and was accompanied by a change in colour from orange-red to yellow. The solution was then taken to dryness at 15 mm. in the cold, and the residue recrystallised.

Prepared in this way were: trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(p-*toluidine*)-*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CBu^t)(}p\mathrm{\text{-}Me{\cdot}C_6H_4{\cdot}NH_2)]}$, yellow prisms from benzene–light petroleum, m. p. 189—193° (decomp.), 70% yield (Found: C, 39·75; H, 5·35; N, 3·0. $\mathrm{C_{17}H_{27}Cl_2NPt}$ requires C, 39·9; H, 5·3; N, 2·75%); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(*piperidine*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CBu^t)(C_5H_{11}N)]}$, yellow needles (from light petroleum), m. p. 154—157° (decomp.) 55% yield (Found: C, 37·05; H, 6·2; N, 3·05. $\mathrm{C_{15}H_{29}Cl_2NPt}$ requires C, 36·8; H, 6·0; N, 2·85%); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)-(*pyridine*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CBu^t)(C_5H_5N)]}$, dark yellow prisms (from light petroleum), m. p. 152—156° (decomp.), 66% yield (Found: C, 37·2; H, 4·85; N, 3·0%; *M*, ebullioscopically in 0·849% benzene solution, 461; in 1·062% benzene solution, 450. $\mathrm{C_{15}H_{23}Cl_2NPt}$ requires C, 37·25; H, 4·8; N, 2·9%; *M*, 483); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(γ-*picoline*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CBu^t)(4\text{-}Me{\cdot}C_5H_4N)]}$, yellow prisms (from benzene–light petroleum), m. p. 154—159° (decomp.), 54% yield (Found: C, 38·75; H, 5·3; N, 3·0. $\mathrm{C_{16}H_{25}Cl_2NPt}$ requires C, 38·65; H, 5·05; N, 2·8%); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(4-*chloropyridine*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CBu^t)(4\text{-}Cl{\cdot}C_5H_4N)]}$, yellow prisms (from benzene–light petroleum), m. p. 160—165° (decomp.), 57% yield (Found: C, 34·85; H, 4·4; N, 3·0. $\mathrm{C_{15}H_{22}Cl_3NPt}$ requires C, 34·8; H, 4·3; N, 2·7%); trans-*dichloro*-(2,2,5-*trimethylhex*-3-*yne*)(*piperidine*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CPr^i)(C_5H_{11}N)]}$, bright yellow prisms [from light petroleum (b. p. 40—60°)], m. p. 60—65° (decomp.), 51% yield (Found: C, 34·95; H, 5·7; N, 3·0. $\mathrm{C_{14}H_{27}Cl_2NPt}$ requires C, 35·5; H, 5·7; N, 2·95%); trans-*dichloro*-(2,2-*dimethylhex*-3-*yne*)-(*piperidine*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CEt)(C_5H_{11}N)]}$, yellow prisms (from light petroleum), m. p. 55—58·5° (decomp.), 38% yield (Found: C, 33·8; H, 5·55; N, 3·15. $\mathrm{C_{13}H_{25}Cl_2NPt}$ requires C, 33·85; H, 5·45; N, 3·05%); trans-*dichloro*-2,2,5-*trimethyl*-5-*phenylhex*-3-*yne*)-(*piperidine*)*platinum*(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}C{\cdot}CMe_2Ph)(C_5H_{11}N)]}$, yellow prisms (from light petroleum), m. p. 96·5—100° (decomp.), 64% yield (Found: C, 43·4; H, 6·0; N, 2·55. $\mathrm{C_{20}H_{31}Cl_2NPt}$ requires C, 43·55; H, 5·65; N, 2·55%).

trans-Dichloro-(2,2-dimethylpent-3-yne)(piperidine)platinum(II), *trans*-$\mathrm{[PtCl_2(Bu^tC{\vdots}CMe)(C_5H_{11}N)]}$. Sodium trichloro-(2,2-dimethylpent-3-yne)platinate(II), $\mathrm{Na[PtCl_3(Bu^tC{\vdots}CMe)]}$ (0·002 mole), in water (7 ml.) was treated at 0° with piperidine (0·002 mole), yielding a yellow oil which rapidly solidified. The *complex* crystallised from light petroleum in yellow prisms, m. p. 100—103° (decomp.), in 67% yield (Found: C, 32·35; H, 5·5; N, 3·25. $C_{12}H_{23}Cl_2NPt$ requires C, 32·2; H, 5·2; N, 3·15%).

Similarly prepared from Zeise's salt, $K[PtCl_3(C_2H_4)],H_2O$, were: *trans*-dichloro(ethylene)-(pyridine)platinum(II), *trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$, yellow needles (from ethanol), m. p. 110—114° (decomp.), 83% yield (Found: C, 22·9; H, 2·55; N, 3·9. Calc. for $C_7H_9Cl_2NPt$: C, 22·55; H, 2·45; N, 3·75%); and trans-*dichloro*(*ethylene*)(*γ-picoline*)*platinum*(II), *trans*-$[PtCl_2(C_2H_4)(4\text{-}Me{\cdot}C_5H_4N)]$, yellow needles from ethanol, m. p. 121—125° (decomp.), 87% yield (Found: C, 25·0; H, 2·95; N, 3·85. $C_8H_{11}Cl_2NPt$ requires C, 24·8; H, 2·85; N, 3·6%).

Determination of Dipole Moments.—These were determined as described previously.[24] The measurements and estimated values are recorded in Table 3. The margin of error is less than ±0·1 D for dipole moments >4 D, and less than ±0·2 D for dipole moments between 4 and 2·5 D. For dipole moments <2·5 D the margin of error will be greater than this, but is difficult to estimate. The errors in determining dipole moments of <2·5 D are largely due to the uncertainty in the magnitude of the atom polarisation which has been assumed to be 15% of the electron polarisation given in Table 3. ω = weight fraction of solute; $\Delta\varepsilon$ = difference between the dielectric constant of the solution and that of pure benzene; Δn = difference in refractive indices; Δv = difference in specific volumes; ${}_{T}P$ = total, ${}_{E}P$ = electron, and ${}_{O}P$ = orientation polarisations; μ = dipole moment.

TABLE 3. *Dipole moments of acetylene and olefin complexes of platinum*(II) *in benzene at* 25°.

No.	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$
1	*trans*-$[PtCl_2(Bu^tC\vdots CBu^t)(C_5H_5N)]$			
	4·41	1·958	—	—
	4·882	1·963	—	—
	25·60	—	4·30	—
	35·44	—	4·19	—
	5·590	—	—	0·590
	6·980	—	—	0·573
2	[*trans*-$[PtCl_2(Bu^tC\vdots CBu^t)(4\text{-}Me{\cdot}C_5H_4N)]$			
	6·397	2·588	—	—
	7·508	2·567	—	—
	22·73	—	3·33	—
	35·93	—	3·74	—
	2·891	—	—	0·588
	3·824	—	—	0·601
3	*trans*-$[PtCl_2(Bu^tC\vdots CBu^t)(4\text{-}Cl{\cdot}C_5H_4N)]$			
	4·369	0·652	—	—
	5·430	0·695	—	—
	9·927	0·783	—	—
	25·70	—	3·96	—
	40·60	—	4·08	(0·58)
4	*trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$			
	4·603	4·438	—	—
	4·617	4·381	—	—
	36·29	—	7·80	—
	36·31	—	7·36	—
	5·915	—	—	0·626
5	*trans*-$[PtCl_2(C_2H_4)(4\text{-}Me{\cdot}C_5H_4N)]$			
	3·863	5·654	—	—
	4·060	5·669	—	—
	26·88	—	7·09	—
	31·80	—	6·86	—
	6·977	—	—	0·645
	7·223	—	—	0·568

No.	${}_{T}P$	${}_{E}P$	${}_{O}P$	μ (D)
1	260	91	155	2·75
2	323	90	220	3·3
3	157 *	97 *	45 *	1·5 *
4	368	73	284	3·75
5	475	76	388	4·35

* Calc. by using estimated values of densities and refractivities. Estimated values are given in parentheses. Those of $-\Delta v/\omega$ are needed only approximately and were estimated from experience of measurements on similar compounds.

Infrared Spectra.—The infrared spectra were measured with a Grubb–Parsons GS2A prism-grating spectrometer. For determination of $\nu_{C{:}C}$ (stretching) the finely powdered solids were suspended in "Nujol," and for ν_{N-H} (stretching) a dilute solution of the complex in carbon tetrachloride was used.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

[*Received, August 25th,* 1960.]

---

[24] Chatt and Shaw, *J.*, 1959, 705.