

## Acetylenes and Noble-metal Compounds. Part 15.<sup>1</sup> Reactions of Dialkylacetylenes with Bis(acetonitrile)dichloroplatinum(II) and Tin(II) Chloride to give Ionic Cyclobutadieneplatinum-tin Complexes

By Josep Moreto and Peter M. Maitlis,\* Department of Chemistry, The University, Sheffield S3 7HF

Acetylenes ( $C_2R_2$ ,  $R = Me$  or  $Et$ ) react with  $[Pt(NCMe)_2Cl_2]$  and  $SnCl_2$  to give the ionic tetra-alkylcyclobutadiene complexes  $[Pt_2(C_4R_4)_2Cl_3][Pt(C_4R_4)(SnCl_3)_3]$  (2) which can be converted into the tin-fer complexes  $[Pt_2(C_4R_4)_2Cl_4]$  (3) by reaction with  $HCl$  and acetone, or into the salts  $[N(PPh_3)_2][Pt(C_4R_4)(SnCl_3)_3]$  (4) plus (3) by reaction with  $[N(PPh_3)_2]Cl$ . Structures are assigned on the basis of spectroscopic data, in particular the intensities of the  $^{195}Pt$ ,  $^{117}Sn$ , and  $^{119}Sn$  satellites of the methyl resonances in the  $^1H$  n.m.r. spectra of (2 and 4;  $R = Me$ ). Two new complexes of di-*t*-butylacetylene (2,2,4,4-tetramethylhex-3-yne),  $[Pt(C_2Bu^t)_2(NCMe)(SnCl_3)Cl]$  and  $[Pt_2(C_2Bu^t)_2(SnCl_3)_2Cl_2]$ , are also described. The mechanism of the acetylene dimerisation reaction leading to (2) is discussed by comparison with the acetylene oligomerisation reactions induced by  $Pd^{II}$ .

RELATIVELY few reactions have been described in which platinum(II) complexes induce acetylene oligomerisation. Canziani and co-workers<sup>2,3</sup> have reported the isolation of cyclobutadiene, cyclopentadienone, and *p*-quinone complexes from reaction of  $[Pt(CO)_2Cl_2]$  with disubstituted acetylenes. Chisholm and Clark<sup>4</sup> examined the reactions of a number of acetylenes with complexes of the type  $[PtL_2R(solvent)]^+$ . In the case of the reaction of but-2-yne with  $[Pt(PMe_2Ph)_2(CF_3)(Me_2CO)]^+$  they isolated the tetramethylcyclobutadiene complex  $[Pt(PMe_2Ph)_2(CF_3)(\eta^4-C_4Me_4)]^+$ ,<sup>5</sup> while in the others only one acetylene was generally incorporated into the product. However they sometimes noted the formation of tars, the nature of which is not clear and which may arise from a cationic polymerisation of the acetylene.<sup>4</sup>

From the reactions so far described, it appears that  $Pt^{II}$  needs activation (either by a good *trans*-labilising ligand such as  $CO$  or through the creation of a 'vacant site') before it will react with acetylenes. It also appears that reaction is generally limited to the formation of products containing acetylene monomers and dimers; only in the reaction of  $[Pt(CO)_2Cl_2]$  with diphenylacetylene was the formation of any trimer (hexaphenylbenzene) noted.<sup>2</sup>

These observations are in sharp contrast to those we have made concerning the reactions of acetylenes with  $[Pd(NCR)_2Cl_2]$ .<sup>6,7</sup> Here reaction generally occurs extremely readily without activation to give products containing mono-, di-, tri-, and tetra-merised acetylenes and their complexes. One very commonly observed product is the benzenoid trimer, and in many cases this is produced catalytically. The mode of formation of these products has been interpreted in terms of a stepwise oligomerisation process, the extent of which is approximately inversely related to the size of the acetylenic substituent.

We here report reactions of some acetylenes with platinum(II) complexes activated by  $SnCl_2$ ,<sup>8</sup> which give very simple routes to some tetra-alkylcyclobutadieneplatinum complexes.

### RESULTS AND DISCUSSION

When  $[Pt(NCMe)_2Cl_2]$  was treated with either but-2-yne or hex-3-yne no reaction could be observed. How-

ever, when one equivalent of  $SnCl_2$  was added to the solution of (1) and the acetylene,  $RC_2R$ , in dichloromethane at 20 °C the  $SnCl_2$  slowly dissolved to give a yellow solution from which were obtained yellow crystals in 66–68% yield which analysed for  $[(PtSnC_4R_4Cl_4)_n]$ ; [ $R = Me$ (2a) or  $Et$ (2b)].

These complexes were degraded with loss of  $SnCl_2$  in boiling acetone, preferably in the presence of some hydrochloric acid, to give new complexes (3) which analysed for  $[(PtC_4R_4Cl_2)_2]$  and which were identical to the tetramethyl- and tetraethyl-cyclobutadiene platinum complexes already reported by Canziani and Malatesta.<sup>3</sup>

A further pair of complexes, (4a) and (4b), together with (3a) and (3b), were obtained by reaction of (3a) or (2b) with  $[N(PPh_3)_2]Cl$ ; they could also be obtained from reactions of complexes (3a) or (3b) with  $SnCl_2$  and  $[N(PPh_3)_2]Cl$ , and in a similar manner directly from the acetylene.

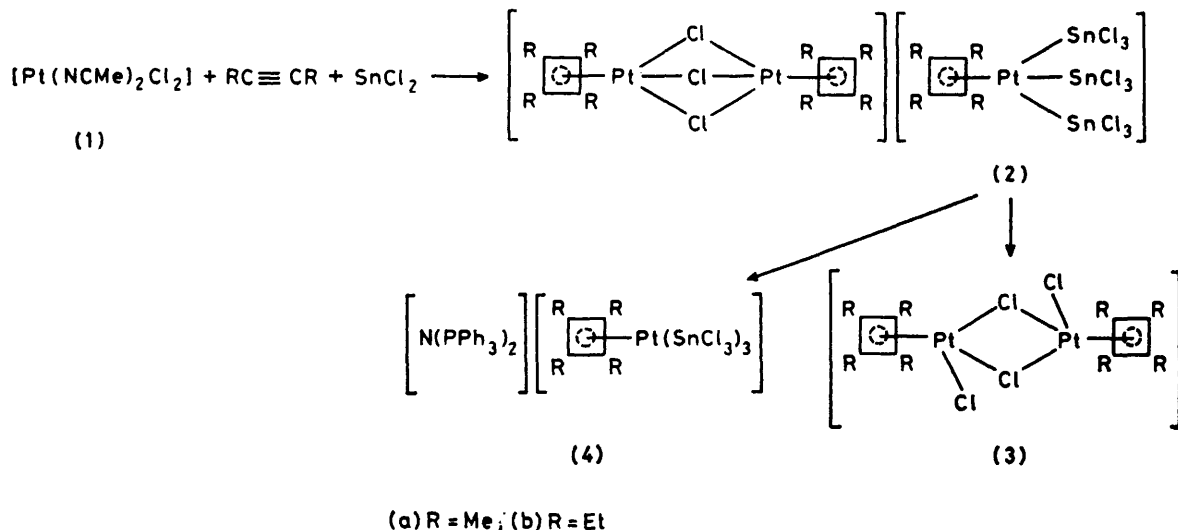
The complexes (4a) and (4b) analysed for  $[N(PPh_3)_2][Pt(C_4R_4)(SnCl_3)_3]$  and are formulated as shown. This is most convincingly illustrated by an analysis of the peak intensities of the satellites to the  $CH_3$  resonance (at  $\delta$  2.42) in the  $^1H$  n.m.r. spectrum of (4a) (Figure). These satellites arise from coupling of the equivalent methyl hydrogens to (a)  $^{195}Pt$  ( $I = \frac{1}{2}$ , 33.7% natural abundance) and (b) to  $^{117}Sn$  and  $^{119}Sn$  (both  $I = \frac{1}{2}$ , 7.7 and 8.7% natural abundance respectively) but only those arising from species containing  $PtSn_3$ ,<sup>†</sup>  $^{195}PtSn_3$ ,  $Pt^{117}Sn$ ,  $Pt^{119}Sn$ ,  $^{195}Pt^{117}Sn$ , and  $^{195}Pt^{119}Sn$  could be observed (Figure), since the abundance of species containing two (or three) active  $Sn$  isotopes was too low. The calculated relative intensities for the resonances are 3.9 : 3.4 : 15.4 : 13.6 : 3.4 : 3.9 : 25.5 : 100 : 25.5 : 3.9 : 3.4 : 13.6 : 15.4 : 3.4 : 3.9, for the peaks corresponding to  $^{195}Pt^{119}Sn$ ,  $^{195}Pt^{117}Sn$ ,  $Pt^{119}Sn$ ,  $Pt^{117}Sn$ ,  $^{195}Pt^{117}Sn$ ,  $^{195}Pt^{119}Sn$ ,  $^{195}PtSn_3$ ,  $PtSn_3$ ,  $^{195}PtSn_3$ ,  $^{195}Pt^{119}Sn$ ,  $^{195}Pt^{117}Sn$ ,  $Pt^{117}Sn$ ,  $Pt^{119}Sn$ ,  $^{195}Pt^{117}Sn$ , and  $^{195}Pt^{119}Sn$ , respectively. The observed intensities, 3 : 3 : 14 : 14 : 3 : 3 : 28 : 100 : 23 : 3 : 3 : 13 : 13 : 2 : 2, correspond well to the calculated values.

It may be noted that the relative intensities prove the presence of the  $Pt(SnCl_3)_3$  unit; by contrast the relative

<sup>†</sup> Isotopes of platinum or tin that have  $I = 0$  are classed together as  $Pt$  or  $Sn$  (no superscript).

intensities for a  $\text{Pt}(\text{SnCl}_3)_3$  unit are calculated to be 1.2 ( $^{195}\text{Pt}^{119}\text{Sn}$ ) : 1.1 ( $^{195}\text{Pt}^{117}\text{Sn}$ ) : 5.3 ( $\text{Pt}^{119}\text{Sn}$ ) : 4.7 ( $\text{Pt}^{117}\text{Sn}$ ) : 1.1 ( $^{195}\text{Pt}^{117}\text{Sn}$ ) : 1.2 ( $^{195}\text{Pt}^{119}\text{Sn}$ ) : 25.4 ( $^{195}\text{PtSn}_3$ ) : 100 ( $\text{PtSn}_3$ ), etc.

two parts, a multiplet of precisely the same form as that observed for (4a) in a similar position ( $\delta$  2.5) and with similar coupling constants, and a singlet (at  $\delta$  1.71) with satellites arising from coupling to only  $^{195}\text{Pt}$ . The



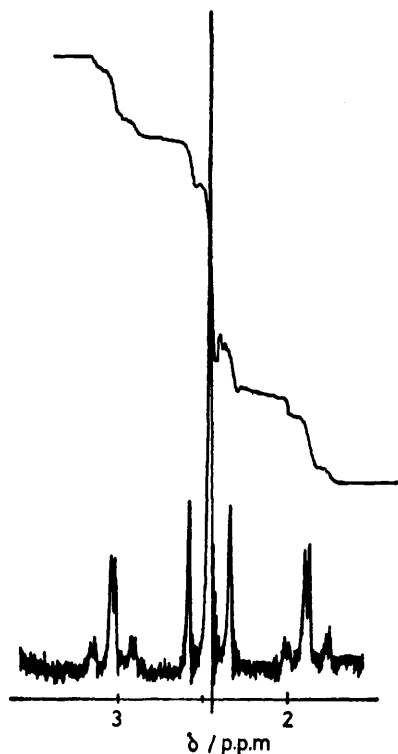
In all the calculations it is assumed that coupling to  $^{119}\text{Sn}$  is larger than to  $^{117}\text{Sn}$ ; as expected, the magnitude

intensity ratio of the two sets of resonances was 1 : 2. Since the  $\text{C}_4\text{Me}_4$  ligand in (4a) and hence also in (2a) is clearly attached to one Pt bearing three  $\text{SnCl}_3$  groups and is part of an anion, we can presume that the cationic part of (2a) must have two  $\text{C}_4\text{Me}_4$  ligands attached to two platinum. The structure shown is therefore proposed for this complex and it will be recognised that the cation is similar to that which has been shown by X-ray crystallography to be present in  $[\text{Pd}_2(\text{C}_4\text{Me}_4\text{Bu}^t)_2\text{Cl}_3]_2[\text{Pd}_2\text{Cl}_6]$ <sup>10,11</sup> and is identical to that present in  $[\text{Pt}_2(\text{C}_4\text{Me}_4)_2\text{Cl}_3][\text{Pt}(\text{CO})\text{Cl}_3]$ .<sup>3,11,12</sup>

The tetraethylcyclobutadiene complexes (2b) and (4b) are very similar to the tetramethylcyclobutadiene complexes (2a) and (4a). Although the  $^1\text{H}$  n.m.r. spectra are too complicated to allow the type of detailed analysis that was possible for the tetramethyl complexes the observed pattern of satellites of the  $\text{CH}_2$  resonance is quite consistent with the proposed structures.

The  $^{13}\text{C}$  n.m.r. spectra of (4a) and (4b) are also in good agreement with the proposed structures.

The far-i.r. spectra of the complexes are also informative. Those complexes containing the  $\text{Pt}(\text{SnCl}_3)_3$  grouping show medium to strong bands at ca.  $355\text{ cm}^{-1}$  and a very strong broad band in the region  $320\text{--}330\text{ cm}^{-1}$ . These bands may be assigned to  $\nu(\text{SnCl}_3)$  when the group is attached to the metal, following the assignment of Adams and Chandler<sup>13</sup> for  $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$  and  $[\text{Pt}(\text{PR}_3)_2(\text{SnCl}_3)_2]$ . It may be noted that  $\text{Cs}[\text{SnCl}_3]$ , which an X-ray structure determination has shown to contain discrete pyramidal  $\text{SnCl}_3^-$  ions,<sup>14</sup> shows bands at  $308\text{s}$  and  $265\text{vs cm}^{-1}$ . The bands in the  $355$  and  $320\text{ cm}^{-1}$  region are the only significant ones in the spectra of complexes (4a) and (4b); the complexes (2a) and (2b) show, in addition, weaker bands (at  $265$  and  $186$ , and  $227\text{ cm}^{-1}$  respectively) which we assign to the triply bridging



Partial  $^1\text{H}$  n.m.r. spectrum of complex (4a) showing coupling of the methyl resonances to  $^{195}\text{Pt}$ ,  $^{117}\text{Sn}$ , and  $^{119}\text{Sn}$  (recorded at 60 MHz, on Perkin-Elmer R-12B)

of  $J(^{119}\text{Sn-H})/J(^{117}\text{Sn-H})$  is close to the theoretical value of 1.046.<sup>9</sup>

The  $^1\text{H}$  n.m.r. spectrum of complex (2a) consisted of

$\text{Pt}_2\text{Cl}_3$  unit in the cation by analogy to those found in  $[\text{Pd}_2(\text{C}_4\text{Me}_2\text{Bu}^t)_2\text{Cl}_3]_2[\text{Pd}_2\text{Cl}_6]$ .<sup>11</sup>

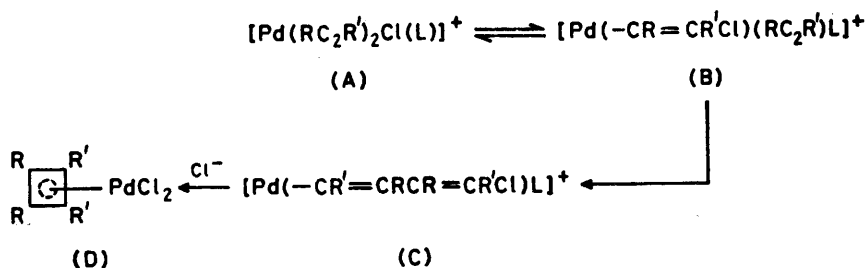
The two cyclobutadiene complexes not containing  $\text{SnCl}_3$ , (3a) and (3b), show very strong bands in the region 297–320  $\text{cm}^{-1}$  together with weak ones at 248–260  $\text{cm}^{-1}$  which we suggest to be characteristic of terminal and bridging  $\nu(\text{Pt}-\text{Cl})$  in the  $\text{Pt}_2\text{Cl}_4$  moiety in such complexes.

*Mechanism of the Acetylene Dimerisation Reaction.*—

It is instructive to compare the reaction of the two small acetylenes but-2-yne and hex-3-yne with  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$ . In the former case reaction, for example with  $[\text{Pd}(\text{NCPH})_2\text{Cl}_2]$ , occurs very readily to give the hexasubstituted benzene together with other trimer compounds (*e.g.* pentamethylvinylcyclopentadiene)<sup>15</sup> and no acetylene dimer products could be detected. Here we find the opposite:  $\text{PtCl}_2$  reacts only stoichiometrically and only when activated (by  $\text{SnCl}_3$ ) \* and the products are cyclo-

reactions, by formation of a  $\sigma$ -alkenylplatinum complex which then undergoes insertion of the second acetylene to give a  $\sigma$ -butadienylplatinum complex. This could then cyclise to the cyclobutadiene. The absence of any detectable amounts of trimers in the  $\text{Pt}^{\text{II}}$ -induced reactions described here implies that cyclisation occurs very much faster than the further insertions which are such a feature of the  $\text{Pd}^{\text{II}}$ -induced reactions of smaller acetylenes.<sup>6,7</sup>

This is not unreasonable since the achievement of the needed coplanar transition state for the conrotatory cyclisation should for steric reasons be easier when the  $\sigma$ -butadienyl ligand bears small substituents (*Me* or *Et*) than when larger substituents (*e.g.* *Bu*<sup>t</sup> and *Me*) are present as in the  $\text{Pd}^{\text{II}}$ -induced reaction where we were able to follow the steps in detail.<sup>11</sup> The observation that some hexaphenylbenzene is formed in the reaction of  $\text{C}_2\text{Ph}_2$  with  $[\text{Pt}(\text{CO})_2\text{Cl}_2]$ <sup>2</sup> again supports this hypothesis



SCHEME 1

butadiene complexes containing acetylenic dimers; no acetylenic trimers or higher oligomers are observed.

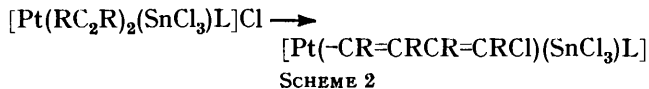
This lends support to the suggestion one of us recently made, in connection with the  $\text{Pd}^{\text{II}}$ -induced dimerisation of methyl-*t*-butylacetylene, that the first step in the reaction was of a quite different type to the subsequent ones and involved the transient formation of a (spectroscopically undetected by n.m.r.) cationic bis( $\pi$ -acetylene) complex (A) (Scheme 1). In that case we proposed an equilibrium leading to a  $\sigma$ -2-chloroalkenyl( $\pi$ -acetylene) complex (B) which then underwent a further fast insertion of the  $\pi$ -complexed acetylene into the Pd-C  $\sigma$  bond to give a  $\sigma, \pi$ -4-chlorobutadienyl palladium complex (C), which could in turn undergo a slow conrotatory cyclisation leading eventually to the cyclobutadiene complex (D).

It is likely that the first step in the reaction of acetylenes with  $\text{Pt}^{\text{II}}$  is the same as that with  $\text{Pd}^{\text{II}}$  but the lower lability of platinum(II) complexes means that stronger activation (by  $\text{SnCl}_3$  or CO) is required in order to produce the necessary vacant site for the second acetylene to co-ordinate to give the analogue to (A).

Further reaction of such a cationic bis(acetylene)-platinum complex might then occur, by a similar route to that which has been proposed for the palladium(II)

since the rather larger phenyl substituents should make achievement of the coplanar butadienylmetal transition state less easy.

However, the absence of any marked degree of catalytic trimerisation of acetylenes, even by activated platinum(II) complexes, suggests that the insertion of an acetylene into a metal-alkenyl bond is much more difficult for Pt than for Pd. This may also imply that the above view of the first step of the dimerisation reaction induced by  $\text{Pt}^{\text{II}}$  is still too simple. One alternative would be that no alkenylplatinum intermediate is formed but that a concerted reaction occurs in which the cationic bis(acetylene) complex is directly transformed into the  $\sigma$ -butadienyl complex (Scheme 2).



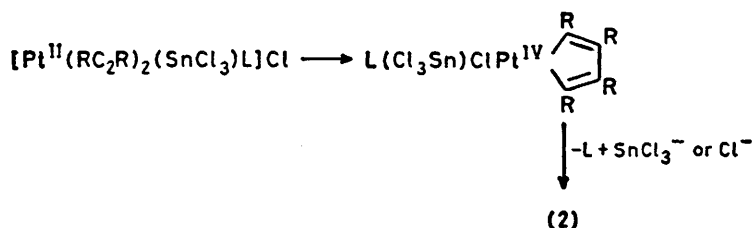
Another possibility, particularly in view of the relative ease with which platinum(IV) complexes can be formed, is that the cationic bis(acetylene) complex is directly converted into a platinacyclopentadiene which then reductively eliminates to give the cyclobutadiene (Scheme 3).

Although no platinum(IV) platinacyclopentadienes appear to have been reported, a number of such platinum(II) complexes, for example  $[\text{Pt}\{\text{C}_4(\text{CO}_2\text{Me})_4\}(\text{PPh}_3)_2]$ ,<sup>16</sup> are known. Further, it has recently been

\* The ability of the  $\text{SnCl}_3$  ligand to activate  $\text{Pt}^{\text{II}}$  (and other metals) towards nucleophilic substitution by virtue of its high *trans* effect has long been recognised.<sup>8</sup>

shown<sup>17</sup> that the thermal decomposition of platinum-cyclopentanes to give C<sub>4</sub> hydrocarbons occurs very much more readily from a platinum(IV) complex {*e.g.* [Pt(CH<sub>2</sub>)<sub>4</sub>(CF<sub>3</sub>)IL<sub>2</sub>]} than from a platinum(II) complex {*e.g.* [Pt(CH<sub>2</sub>)<sub>4</sub>L<sub>2</sub>]} and that the yield of cyclobutane is higher in the former case. The reductive elimination of a metallacyclopentadiene to a η<sup>4</sup>-cyclobutadiene complex is well documented in cobalt chemistry.<sup>18</sup>

or with other acetylenes. On heating, complex (5) underwent loss of acetonitrile to form the di-μ-chloro-complex (7) which again was characterised by analysis and spectroscopy. The lability of these complexes is illustrated by the fact that although the osmometric molecular weight of (7) in chloroform (1 167) is that expected for the dimer (1 188), in acetone it is only 613. This suggests that the complex is dissociating to form a solvated species related to (5) but with acetone in place of



SCHEME 3

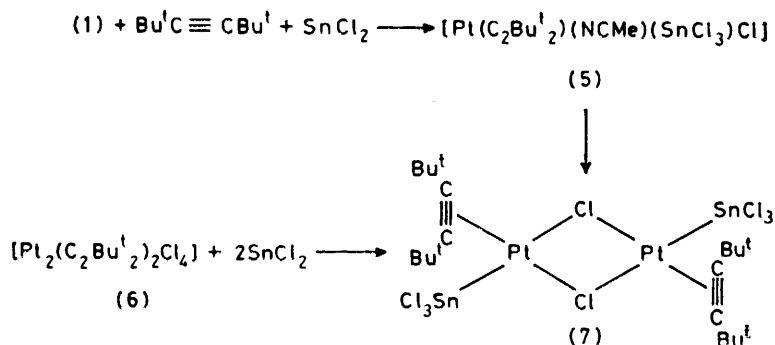
A mechanistic test for the palladium(II) reactions which proved extremely useful was the reaction with methyl-*t*-butylacetylene (4,4-dimethylpent-2-yne).<sup>11</sup> Attempts to induce this acetylene to react with [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] in the presence of SnCl<sub>2</sub> led only to the production of a non-crystalline material; the elemental analysis was close to that expected for [Pt(MeC<sub>2</sub>Bu<sup>t</sup>)(NCMe)(SnCl<sub>3</sub>)Cl] but the <sup>1</sup>H n.m.r. spectrum indicated several components to be present. There was, however, no evidence for any acetylenic dimer complexes. We conclude that, even when activated, the oligomerisation

acetonitrile. The complex (7) could also conveniently be prepared from the known dimeric π-acetylene complex (6)<sup>19</sup> by reaction with SnCl<sub>2</sub>.

Although the reaction of di-*t*-butylacetylene with the Pt<sup>II</sup>-SnCl<sub>2</sub> system did not lead to any acetylene dimer products either, the isolated complexes (5) and (7) give useful pointers to the probable initial intermediates in the reactions with but-2- and hex-3-yne.

## EXPERIMENTAL

Proton n.m.r. spectra were measured at 60, 220, or 100 MHz (Perkin-Elmer R-12B or R-34 or JEOL PFT-100) and <sup>13</sup>C



SCHEME 4

reactions of acetylenes with Pt<sup>II</sup> are hindered by even quite small substituents.

A closely related complex to the above material was obtained from a similar reaction of di-*t*-butylacetylene (2,2,5,5-tetramethylhex-3-yne) with [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] and SnCl<sub>2</sub> (Scheme 4). This complex was characterised as (5) by analysis and spectroscopy, although the stereochemistry is unknown.

There was again no sign of the formation of acetylenic dimers, either on reaction with more di-*t*-butylacetylene

n.m.r. spectra on a JEOL PFT-100 spectrometer. Infra-red spectra were recorded on a Perkin-Elmer 227G and far-i.r. spectra on a PE-180 spectrometer. Microanalyses were carried out by the Department of Chemistry Micro-analytical Service.

[Pt<sub>2</sub>(C<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>Cl<sub>3</sub>][Pt(C<sub>4</sub>Me<sub>4</sub>)(SnCl<sub>3</sub>)<sub>3</sub>] (2a).—Finely powdered anhydrous tin(II) chloride (95 mg, 0.52 mmol) was added to a well stirred solution of [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] (174 mg, 0.5 mmol) and but-2-yne (1 cm<sup>3</sup>, 12.8 mmol) in dichloromethane (100 cm<sup>3</sup>). After stirring for 4 h at 20 °C hexane (150 cm<sup>3</sup>) was carefully added to the clear yellow solution so that

two separate layers were formed. The flask and its contents were set aside for 48 h at 0 °C, then the yellow crystals of complex (2a) (185 mg, 66%) were filtered off, washed with cold dichloromethane (5 cm<sup>3</sup>), and dried in air (Found: C, 16.3; H, 2.2; Cl, 25.4. C<sub>24</sub>H<sub>36</sub>Cl<sub>12</sub>Pt<sub>3</sub>Sn<sub>3</sub> requires C, 17.0; H, 2.1; Cl, 25.2%). Proton n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 2.5 [s with satellites, *J*(Pt-H) = 14.6, *J*(<sup>119</sup>Sn-H) = 69.9, *J*(<sup>117</sup>Sn-H) = 67.2 Hz] and 1.71 [s, with satellites, *J*(Pt-H) = 23.4 Hz], intensity ratio 1 : 2. Far-i.r. spectrum: 355 m—s, 330vs, br, 265(sh) br, and 186m cm<sup>-1</sup>.

The complex (2a) was also prepared (61% yield) by reaction of complex (3a) with one equivalent of SnCl<sub>2</sub> in dichloromethane.

[Pt<sub>2</sub>(C<sub>4</sub>Et<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>][Pt(C<sub>4</sub>Et<sub>4</sub>)(SnCl<sub>3</sub>)<sub>3</sub>] (2b).—This complex (68% yield) was prepared from (1), hex-3-yne, and SnCl<sub>2</sub> in dichloromethane in an analogous way to that described for (2a). In this case, however, it was found more convenient to remove the dichloromethane solvent after the reaction and to crystallise the residue from acetone (Found: C, 23.3; H, 3.0; Cl, 21.9. C<sub>36</sub>H<sub>60</sub>Cl<sub>12</sub>Pt<sub>3</sub>Sn<sub>3</sub> requires C, 23.3; H, 3.3; Cl, 22.9%). Proton n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 1.28, 1.30 [overlapping triplets, intensity ratio 1 : 2 each having *J*(H-H) = 7.5 Hz], and 2.1 [q, with satellites, *J*(Pt-H) = 13 Hz], 2.75 [q, with satellites, *J*(Pt-H) = 13, *J*(Sn-H) = 50 Hz], intensity ratio 2 : 1. Carbon-13 n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 11.1 (CH<sub>3</sub>CH<sub>2</sub>), 18.8 (CH<sub>3</sub>CH<sub>2</sub> in anion), 19.2 (CH<sub>3</sub>CH<sub>2</sub> in cation), and 107.4 (unresolved m, ring carbons). Far-i.r.: 355s, 334 and 323vs, br, and 277m cm<sup>-1</sup>.

[Pt<sub>2</sub>(C<sub>4</sub>Et<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>] (3b).—Hydrochloric acid (90 cm<sup>3</sup>, 2 mol dm<sup>-3</sup>) was added to a solution of complex (2b) (696 mg) in acetone (75 cm<sup>3</sup>). The solution changed colour from orange to yellow and it was set aside to crystallise at 20 °C for 1 week. The yellow needles of (3b) (374 mg, 78%) were filtered off, washed with water, and dried [Found: C, 33.7; H, 4.7; Cl, 16.0%; *M* (mass spectrometric), *m/e* 430 corresponding to C<sub>12</sub>H<sub>20</sub>Cl<sub>2</sub>Pt. C<sub>24</sub>H<sub>40</sub>Cl<sub>4</sub>Pt<sub>2</sub> requires C, 33.5; H, 4.7; Cl, 16.5%; *M* 860]. Proton n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 1.33 [t, *J*(H-H) = 6.7 Hz], 2.1 [q, *J*(H-H) = 6.7 Hz]; couplings to <sup>195</sup>Pt not resolved. Carbon-13 n.m.r. in CD<sub>2</sub>Cl<sub>2</sub>: δ 11.2 [CH<sub>3</sub>, *J*(Pt-C) = 13.9 Hz], 18.5 [CH<sub>2</sub>, *J*(Pt-C) = 12.2 Hz], and 107.8 [ring C, *J*(Pt-C) = 148.0 Hz]. Far-i.r.: 314vs, 297vs, and 248w cm<sup>-1</sup>.

[Pt<sub>2</sub>(C<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>] (3a).—A dichloromethane solution of complex (2a) was prepared as described above from [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] (1.0 g), but-2-yne (2 cm<sup>3</sup>), and SnCl<sub>2</sub> (0.54 g) in dichloromethane (100 cm<sup>3</sup>). The solvent was removed *in vacuo* and the residue was dissolved in aqueous hydrochloric acid (5 mol dm<sup>-3</sup>, 250 cm<sup>3</sup>). This solution was then extracted with portions of dichloromethane until the extracts were no longer yellow. The dichloromethane extracts were combined, dried, and the solvent removed. Yellow crystals of (3a) (0.64 g, 60%) were obtained by crystallisation of the residue from acetone [Found: C, 25.8; H, 2.7; Cl, 19.2%; *M* (mass spectrometric), *m/e* 374 corresponding to C<sub>8</sub>H<sub>12</sub>Cl<sub>2</sub>Pt. C<sub>16</sub>H<sub>24</sub>Cl<sub>4</sub>Pt<sub>2</sub> requires C, 25.7; H, 3.2; Cl, 18.9%; *M* 748]. Proton n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 1.67 [s, *J*(Pt-H) = 19.2 Hz]. Far-i.r. 319vs, 298vs, and 260w (sh) cm<sup>-1</sup>.

[N(PPh<sub>3</sub>)<sub>2</sub>][Pt(C<sub>4</sub>Me<sub>4</sub>)(SnCl<sub>3</sub>)<sub>3</sub>] (4a).—*Method A.* A dichloromethane solution of complex (2a) was prepared as described above, the dichloromethane was removed *in vacuo*, and the residue dissolved in acetone. A solution of [N(PPh<sub>3</sub>)<sub>2</sub>]Cl (0.34 g, 0.6 mmol) in acetone was added to give an immediate precipitate of [Pt(C<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>] which was filtered off. The filtrate was set aside at 0 °C and gave crystals of (4a) contaminated with a little (3a). After

recrystallisation from acetone pure crystals of complex (4a) (42%) were obtained.

*Method B.* Finely ground anhydrous SnCl<sub>2</sub> (0.57 g, 3 mmol) was added to a solution of complex (3a) (0.37 g, 0.5 mmol) in dichloromethane (60 cm<sup>3</sup>). The mixture was stirred (10 h, 20 °C) to give a yellow precipitate (0.75 g). This was dissolved in acetone (12 cm<sup>3</sup>) and [N(PPh<sub>3</sub>)<sub>2</sub>]Cl (0.56 g) was added and the solution was set aside at 0 °C to crystallise. Yellow prisms of complex (4a) (0.92 g, 76%) were obtained.

*Method C.* Finely powdered anhydrous tin(II) chloride (189 mg, 1.0 mmol) was added to a solution of [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] (348 mg, 1.0 mmol) and but-2-yne (1 cm<sup>3</sup>, 12.8 mmol) in dichloromethane (100 cm<sup>3</sup>). The tin chloride slowly dissolved on stirring (20 °C, 18 h); more tin chloride (378 mg, 2 mmol) was added and the stirring continued for another 4 h. The salt [N(PPh<sub>3</sub>)<sub>2</sub>]Cl (600 mg, 1.06 mmol) and hexane (100 cm<sup>3</sup>) were then added and the solution was allowed to crystallise at 0 °C, to give crystals of complex (4a) (885 mg, 58%). This method represents the most convenient synthesis of complex (4a) (Found: C, 35.3; H, 3.0; Cl, 21.1; N, 1.0. C<sub>44</sub>H<sub>42</sub>Cl<sub>9</sub>NP<sub>2</sub>PtSn<sub>3</sub> requires C, 34.8; H, 2.8; Cl, 21.0; N, 0.9%). Proton n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 2.42 [s with satellites, *J*(Pt-H) = 14.6, *J*(<sup>119</sup>Sn-H) = 70.6, *J*(<sup>117</sup>Sn-H) = 67.4 Hz] and 7.5 (m, phenyls). Carbon-13 n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 9.2 [CH<sub>3</sub>, *J*(Pt-H) = *J*(Sn-H) = 18.3 Hz] and 103.8 [ring C, *J*(Sn-C) = 26.0, *J*(Pt-C) = 59.5 Hz]. Far-i.r.: 320vs cm<sup>-1</sup>.

[N(PPh<sub>3</sub>)<sub>2</sub>][Pt(C<sub>4</sub>Et<sub>4</sub>)(SnCl<sub>3</sub>)<sub>3</sub>] (4b).—This complex was prepared (57%) from complex (3b) by reaction with [N(PPh<sub>3</sub>)<sub>2</sub>]Cl in acetone. Complex (4b) was also prepared, more conveniently (59%), by method C for (4a) (Found: C, 37.5; H, 3.3; Cl, 20.2; N, 0.9. C<sub>48</sub>H<sub>50</sub>Cl<sub>9</sub>NP<sub>2</sub>PtSn<sub>3</sub> requires C, 36.7; H, 3.2; Cl, 20.3; N, 0.9%). Proton n.m.r. in (CD<sub>3</sub>)<sub>2</sub>CO: δ 1.32 (t, CH<sub>3</sub>), 2.82 [q with satellites, *J*(Pt-H) = 8, *J*(Sn-H) = 51 Hz], and 7.6 (m, phenyls). Carbon-13 n.m.r. in CD<sub>2</sub>Cl<sub>2</sub>: δ 14.5 [CH<sub>3</sub>, *J*(Sn-C) = 10.7, *J*(Pt-C) = 47.3 Hz], 18.7 [CH<sub>2</sub>, *J*(Sn-C) = *J*(Pt-C) = 18.4 Hz], 106.2 [ring C, *J*(Sn-C) = 25.9, *J*(Pt-C) = 62.6 Hz], 125.2, 129.5, 129.8, 130.1, 132.2, 132.4, 132.6, and 134.0 (phenyl C). Far-i.r.: 318 cm<sup>-1</sup>.

*Reaction of [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] with Bu<sup>t</sup>C<sub>2</sub>Me.*—When excess of 4,4-dimethylpent-2-yne was treated with [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] in the presence of one equivalent of SnCl<sub>2</sub>, in the manner described for the synthesis of (2a), a solid could be obtained by precipitation with hexane, the elemental analysis of which corresponded approximately to [Pt(Bu<sup>t</sup>C<sub>2</sub>Me)(NCMe)(SnCl<sub>3</sub>)Cl] (Found: C, 18.2; H, 2.5; Cl, 24.6; N, 0.8. C<sub>9</sub>H<sub>15</sub>Cl<sub>4</sub>NPtSn requires C, 18.2; H, 2.6; Cl, 23.9; N, 2.4%).

[Pt(Bu<sup>t</sup>C<sub>2</sub>Bu<sup>t</sup>)(NCMe)(SnCl<sub>3</sub>)Cl] (5).—Finely powdered anhydrous SnCl<sub>2</sub> (380 mg, 2 mmol) was added to a solution of [Pt(NCMe)<sub>2</sub>Cl<sub>2</sub>] (696 mg, 2 mmol) and C<sub>2</sub>Bu<sup>t</sup><sub>2</sub> (1.5 cm<sup>3</sup>) in dichloromethane (150 cm<sup>3</sup>) and the resulting suspension was stirred (18 h, 30 °C) to give an orange solution. The solution was concentrated *in vacuo* and when set aside at 0 °C to crystallise it afforded orange crystals of (5) (1.05 g, 83%) [Found: C, 22.5; H, 3.1; Cl, 22.1; N, 1.8%; *M* (osmometric in acetone) 530, 550. C<sub>12</sub>H<sub>21</sub>Cl<sub>4</sub>NPtSn requires C, 22.7; H, 3.3; Cl, 22.3; N, 2.2%; *M* 635]. Proton n.m.r. in CDCl<sub>3</sub>: δ 2.10 (s, MeCN) and 1.51 (s, Bu<sup>t</sup>). Carbon-13 n.m.r. in CD<sub>2</sub>Cl<sub>2</sub>: δ 30.1 [Bu<sup>t</sup>, *J*(Pt-C) = 21.3 Hz] and 31.4 (MeCN). I.r.: ν(CN) at 2190 and 2315 cm<sup>-1</sup>. Far-i.r.: ν(SnCl<sub>3</sub>) at 358vs and 345vs; ν(Pt-Cl<sup>t</sup>) at 247m—w cm<sup>-1</sup>.

[Pt<sub>2</sub>(Bu<sup>t</sup>C<sub>2</sub>Bu<sup>t</sup>)<sub>2</sub>(SnCl<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (7).—A solution of complex

(5) (200 mg) in chlorobenzene (3 cm<sup>3</sup>) was heated (100 °C, 3 h). On cooling this gave orange crystals of complex (7) (97 mg, 52%) [Found: C, 20.8; H, 3.1; Cl, 22.7%; *M* (osmometric in chloroform) 1167. C<sub>20</sub>H<sub>36</sub>Cl<sub>8</sub>Pt<sub>2</sub>Sn<sub>2</sub> requires C, 20.2; H, 3.1; Cl, 23.9%; *M* 1188]. Proton n.m.r. (in CDCl<sub>3</sub>): δ 1.52 (s, Bu<sup>t</sup>). I.r.: ν(C≡C) at 2100 cm<sup>-1</sup>. Far-i.r.: ν(SnCl<sub>3</sub>) at 350vs and 320w; ν(Pt-Cl<sub>b</sub>) at 242w, 222w, and 192m cm<sup>-1</sup>.

This complex was also obtained by reaction of complex (6) with SnCl<sub>2</sub> in dichloromethane.

We thank Mr. G. A. Wright for synthesising some of the acetylenes and the S.R.C. for support of this work.

[9/1464 Received, 14th September, 1979]

#### REFERENCES

- <sup>1</sup> Part 14, E. A. Kelley, G. A. Wright, and P. M. Maitlis, *J.C.S. Dalton*, 1979, 178.
- <sup>2</sup> F. Canziani, P. Chini, A. Quarta, and A. Di Martino, *J. Organometallic Chem.*, 1971, **26**, 285.
- <sup>3</sup> F. Canziani and M. C. Malatesta, *J. Organometallic Chem.*, 1975, **90**, 235.
- <sup>4</sup> M. H. Chisholm and H. C. Clark, *Accounts Chem. Res.*, 1973, **6**, 202 and refs. therein.
- <sup>5</sup> M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, 1972, **94**, 1532.
- <sup>6</sup> P. M. Maitlis, *Accounts Chem. Res.*, 1976, **9**, 93.
- <sup>7</sup> P. M. Bailey, B. E. Mann, I. D. Brown, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1976, 238.
- <sup>8</sup> R. Cramer, *Inorg. Chem.*, 1965, **4**, 445.
- <sup>9</sup> 'NMR and the Periodic Table,' eds. R. K. Harris and B. E. Mann, Academic Press, London, 1978, p. 9.
- <sup>10</sup> E. A. Kelley, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1977, 289.
- <sup>11</sup> E. A. Kelley and P. M. Maitlis, *J.C.S. Dalton*, 1979, 167.
- <sup>12</sup> F. Canziani, personal communication.
- <sup>13</sup> D. M. Adams and P. J. Chandler, *Chem. and Ind.*, 1965, 269.
- <sup>14</sup> F. R. Poulsen and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 150.
- <sup>15</sup> H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 2276; H. Reinheimer, J. Moffat, and P. M. Maitlis, *ibid.*, p. 2285.
- <sup>16</sup> K. Moseley and P. M. Maitlis, *J.C.S. Dalton*, 1974, 169.
- <sup>17</sup> G. B. Young and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1978, **100**, 5808.
- <sup>18</sup> H. Yamazaki and N. Hagihara, *J. Organometallic Chem.*, 1967, **7**, P22; 1970, **21**, 431.
- <sup>19</sup> J. Chatt, R. G. Guy, and L. A. Duncanson, *J. Chem. Soc.*, 1961, 827.