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Mechanism of the Formation of Cyclobutadiene–Palladium Chloride Complexes: the *X*-Ray Structures of [Pd(bipy){CBu^t=CMeCMe=CBu^tCl}Cl] and $[Pd_2Cl_3(\eta^4\text{-}C_4Bu^t{}_2Me_2)_2]_2[Pd_2Cl_6]$ †

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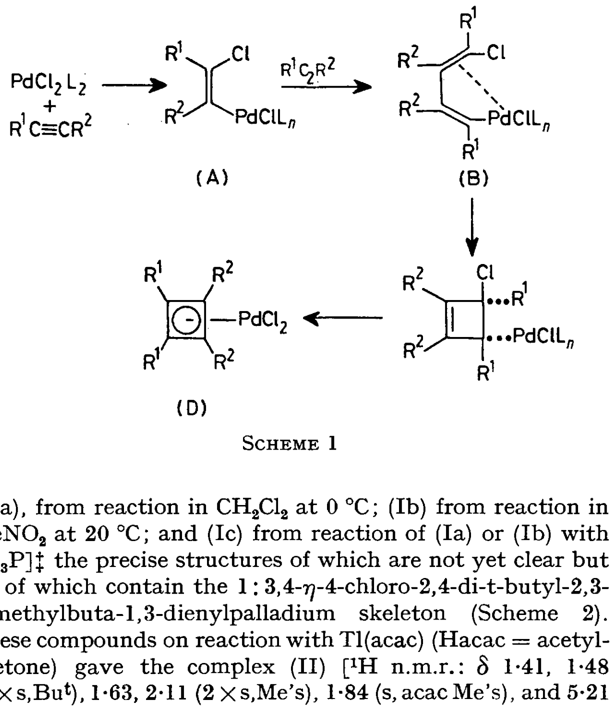
Summary At low temperatures $Bu^tC{\equiv}CMe$ reacts with $PdCl_2(PhCN)_2$ to give complexes [PdCl(Q)X] [where Q is the σ-butadienyl ligand $-C(Bu^t)$=CMeCMe=CBu^tCl and X = ½($PdCl_2$), $PdCl_2$(PhCN), or PdClQ], characterised as [Pd(Q)(acac)] (Hacac = acetylacetone) and by an *X*-ray structure of [Pd(Q)(bipy)Cl] (bipy = 2,2′–bipyridyl); the complexes [PdCl(Q)X] rearrange to the cyclobutadiene complexes $[\{PdCl_2(C_4Bu^t{}_2Me_2)\}_2]$ or $[Pd_2Cl_3(C_4Bu^t{}_2Me_2)_2]_2$-$[Pd_2Cl_6]$, the latter being identified by an *X*-ray determination.

IN the mechanism which one of us has put forward to account for the products of the reactions of acetylenes with Pd^{II}, it was proposed that cyclobutadiene complexes arose, as did other acetylene oligomers and their complexes, from a σ-(4-chlorobuta-1,3-dienyl)palladium intermediate (B) (Scheme 1).[1] This intermediate is formed by a *cis*-insertion of the acetylene into a Pd–Cl bond followed by a fast *cis*-insertion of a further acetylene into the resultant 2-chloroalkenylpalladium complex (A). Steric constraints determine the extent of the oligomerisation reaction and, when sufficiently bulky acetylenic substituents are present, intermediates (B) cyclise, presumably in a conrotatory electrocyclic manner, to the cyclobutenyl complex (C) which then *trans*-eliminates Cl^- to give the cyclobutadiene (D). We now present evidence in support of this proposal.

4,4-Dimethylpent-2-yne [t-butyl(methyl)acetylene (bma)] was treated with $PdCl_2(PhCN)_2$ to give a series of complexes [(Ia), from reaction in CH_2Cl_2 at 0 °C; (Ib) from reaction in $MeNO_2$ at 20 °C; and (Ic) from reaction of (Ia) or (Ib) with Ph_3P]‡ the precise structures of which are not yet clear but all of which contain the 1:3,4-η-4-chloro-2,4-di-t-butyl-2,3-dimethylbuta-1,3-dienylpalladium skeleton (Scheme 2). These compounds on reaction with Tl(acac) (Hacac = acetylacetone) gave the complex (II) [^1H n.m.r.: δ 1·41, 1·48 (2×s,Bu^t), 1·63, 2·11 (2×s,Me's), 1·84 (s, acac Me's), and 5·21 (s, acac H); ^{13}C n.m.r.: δ 19·1, 25·2 (⩾C–*C*–Me), 27·0, 29·0



SCHEME 1

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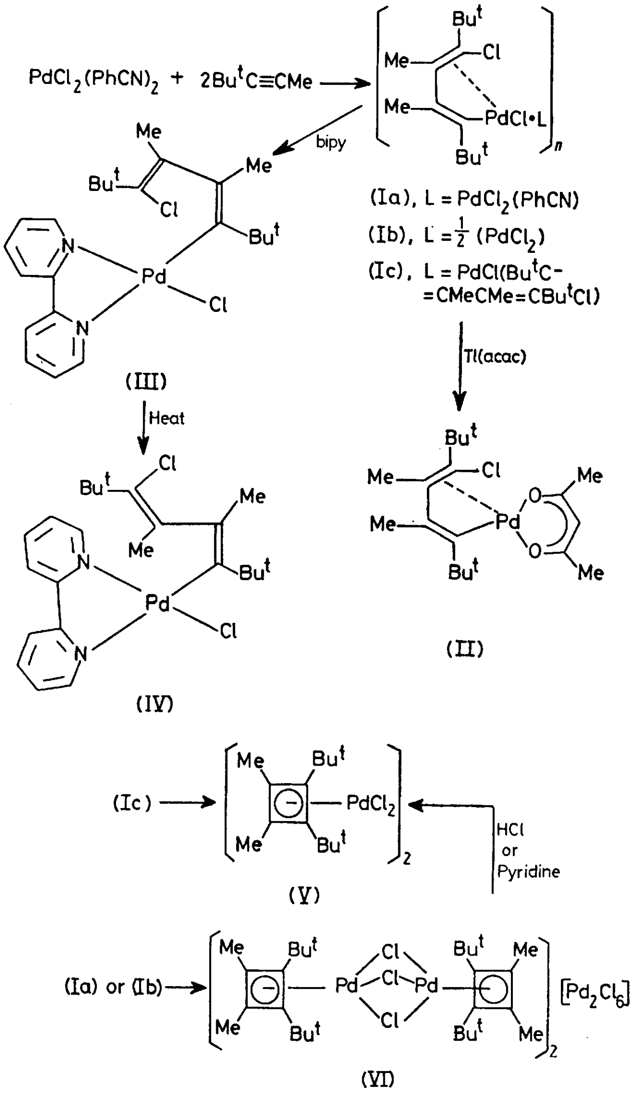
† No reprints available.

‡ All new complexes gave satisfactory elemental analyses and molecular weights, when the solubility and stability were sufficient.

(acac Me), 30·3, 33·1 (–CMe_3), 37·7, 44·4 (–CMe$_3$), 99·3 (acac CH), 84·0, 124·9, 127·3, 141·3 ($\geqslant C$–), and 184·2 and 189·7 (acac C=O)].



SCHEME 2

Further characterisation of the compounds (Ia—c) was afforded by their reaction with 2,2′-bipyridyl (bipy) which gave initially the isomer (III); on standing or on brief heating in solution, (III) isomerised to (IV). Complexes (III) and (IV) were identified spectroscopically and by an X-ray crystal structure determination of (IV) (Figure 1).§

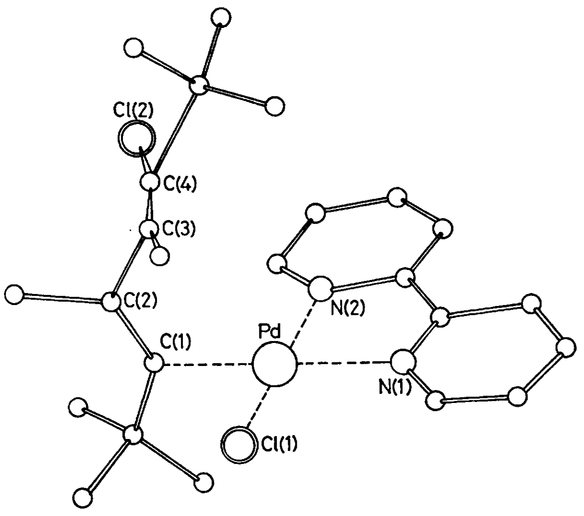


FIGURE 1. The structure of complex (IV) (hydrogen atoms omitted). Bond lengths: Pd–Cl(1), 2·319(3); Pd–N(1), 2·148(8); Pd–N(2), 2·050(7); Pd–C(1), 2·027(10); C(1)–C(2), 1·344(14); C(2)–C(3), 1·501(14); C(3)–C(4), 1·331(14); and C(4)–Cl(2), 1·77(1) Å.

Crystal data: (IV), $C_{24}H_{32}Cl_2N_2Pd$, M 525·8, monoclinic, a = 11·817(3), b = 13·328(4), c = 16·355(4) Å, β = 104·7(1)°, Z = 4, space group $P2_1/n$ (non-standard setting of No. 14, C^5_{2h}). Three-dimensional X-ray data were collected, with the crystal mounted along a diagonal of the A face, using Mo-K_α radiation (graphite monochromator) and a Stoe STADI-2 diffractometer. 2913 independent reflections were collected with $I_{obs} \geqslant 3\sigma(I_{obs})$; the structure was solved using Patterson and Fourier methods. Block diagonal least-squares refinement has reduced R to 0·060. At this stage, temperature factors are anisotropic on the palladium and chlorine atoms and isotropic on the other non-hydrogen atoms.¶

The structure of this complex shows that the molecule contains the σ-4-chloro-1,4-di-t-butyl-2,3-dimethylbutadienyl ligand with the expected geometry about the C=C bonds but, in contrast to (I) and (II), the C(3)–C(4) double bond is of course not co-ordinated. The existence of the two isomers (III) and (IV) arises from the non-bonded repulsions between the substituents on the butadienyl ligand and the co-ordinated bipy which prevent free rotation about the C(2)–C(3) bond. Inspection of models shows that (III) is the kinetically preferred product.

When (Ic) was warmed in solution it slowly rearranged to (V) [^{1}H n.m.r.: δ 1·55 (s, Bu^t), 2·02 (s, Me)]. However, under the same conditions (Ia) or (Ib) rearranged to give a highly insoluble cyclobutadiene complex of empirical formula [$\{Pd_3Cl_6(C_4Bu^tMe_2)_2\}_n$] (VI). This material was also formed from the room-temperature reaction of bma and $PdCl_2(PhCN)_2$ in CH_2Cl_2 and other solvents and it could be converted into the 'normal' cyclobutadiene complex (V) by reaction with either HCl or pyridine. The structure of (VI) was elucidated by an X-ray determination which showed it

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ The two tertiary butyl substituents on (IV) have been treated as groups of fixed geometry; at a relatively advanced stage of the refinement a difference Fourier synthesis showed some rotational disorder in one of these tertiary butyl groups. The refinement was continued with two sets of methyl carbon atoms for this particular group, with their temperature factors correlated, and the populations of the two sets were allowed to refine; these populations are currently in the ratio 0·67 : 0·33.

to be ionic; the cation consists of two cyclobutadiene–palladium units linked by three chlorine bridges (Figure 2) and the anion is $Pd_2Cl_6^{2-}$.§

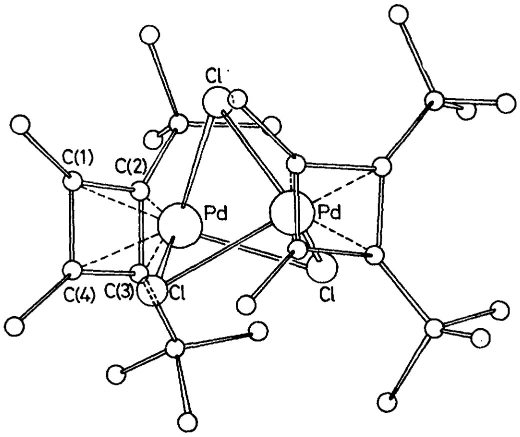


Figure 2. The structure of the cation of complex (VI) (hydrogen atoms omitted). Bond lengths: Pd–Cl (average), 2·498(6); Pd–C(1), 2·165(15); Pd–C(2), 2·132(16); Pd–C(3), 2·105(15); Pd–C(4), 2·115(16); C(1)–C(2), 1·448(22); C(2)–C(3), 1·493(22); C(3)–C(4), 1·459(22); and C(4)–C(1), 1·430(22) Å; internal bond angles in the C_4 ring are 91, 89, 89, and 91°. The $Pd_2Cl_6^{2-}$ ion is centrosymmetric and has Pd–Cl (terminal), 2·26; and Pd–Cl (bridging), 2·32 Å.

Crystal data: (VI), $2[C_{28}H_{48}Cl_3Pd_2]^+[Cl_6Pd_2]^{2-}$, M 1833·2, triclinic, $a = 16{\cdot}44(3)$, $b = 14{\cdot}91(3)$, $c = 15{\cdot}13(3)$ Å, $\alpha = 123{\cdot}11(3)$, $\beta = 113{\cdot}00(3)$, $\gamma = 113{\cdot}02(3)°$, $Z = 1$, space group $P\bar{1}$. Three-dimensional X-ray data were collected with the crystal mounted along an A face diagonal, using Mo-K_α radiation (graphite monochromator) and a Stoe STADI-2 diffractometer. 4712 independent reflections were collected with $I_{obs} \geqslant 3\sigma(I_{obs})$; three independent palladium atoms were found using Patterson superposition methods, and the remaining non-hydrogen atoms were found from difference Fourier syntheses. Block diagonal least-squares refinement has reduced R to 0·049, allowing anisotropic thermal motion for the palladium and chlorine atoms and isotropic thermal parameters for the carbon atoms.

Cyclobutadiene complexes of the formula $[Pd_3Cl_6(C_4R^1_2R^2_2)_2]$ ($R^1 = R^2 =$ aryl; $R^1 =$ Ph, $R^2 = Bu^t$)[2] are formed from a variety of acetylenes $R^1C_2R^2$ and $PdCl_2$; they had previously been formulated as $[(C_4R^1_2R^2_2)(PdCl_2)_3(C_4R^1_2R^2_2)]$ with Cl- and $PdCl_2$-bridges. Their far-i.r. spectra have now been found to be inconsistent with this formulation but they are, however, in agreement with the structure (VI). For example, (VI) shows very strong bands at 331 and 342 cm^{-1}, which we assign to $Pd_2Cl_6^{2-}$ [3] and at 195, 202, and 225(sh) cm^{-1} which we assign to the Pd_2Cl_3 bridge.

The 'normal' cyclobutadiene complexes $[\{PdCl_2(C_4R^1_2R^2_2)\}_2]$ are dimeric in solution and show a very strong band at 290—300 cm^{-1} in the far-i.r. region; there was no strong band at *ca.* 205 cm^{-1} due to a Pd_2Cl_3 unit. However, on reaction of (V) with, for example, NH_4PF_6 the ionic complex $[Pd_2Cl_3(C_4Bu^t_2Me_2)_2][PF_6]$ was obtained, which only showed a strong broad band at 205 cm^{-1} indicating that the cation in (VI) was very easily formed.

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