X-Ray and Nuclear Magnetic Resonance Spectroscopic Determination of the Structure of Chloro-[4-(chloro-t-butyl)methylene-2,5-di-t-butyl-1–3-η-cyclopent-2-enyl]triphenylphosphinepalladium and a Novel Example of Stereochemically Non-rigid Behaviour in Allylic Complexes

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Summary The structure of the t-butylacetylene trimer complex $[Pd\{Cl(Me_3CC_2H)_3\}Cl]_2$ (I) has been elucidated from its ^{1}H and ^{13}C n.m.r. spectra as well as by an *X*-ray structure determination of its triphenylphosphine adduct, $[Pd\{Cl(Me_3CC_2H)_3\}Cl(PPh_3)]$; complex (I) exists in two η^3-allylic forms, an exocyclic and an endocyclic one, which interconvert.

The cyclotrimerisation of disubstituted acetylenes with $PdCl_2$ and other Pd^{II} species has been shown in many cases to proceed through substituted 5-methylcyclopentadiene complexes.[1] Monosubstituted acetylenes also react very readily with $PdCl_2$ but the structures of the metal complex products have so far not been elucidated. We report here the characterisation of the complex formed from t-butylacetylene.

The complex (I), $[Pd\{Cl(Me_3CC_2H)_3\}Cl]_2$, was originally prepared by Avram *et al.*, who proposed a tri-t-butylbicyclo[2,2,0]hexadiene structure for the organic ligand.[2] This was shown to be inconsistent with the data[3] and a subsequent publication by Avram[4] on the organic degradation products of (I) indicated the likelihood that the ligand contained a five-membered ring.

Crystals of (I) were not suitable for *X*-ray analysis and the structure determination was carried out on the monomeric triphenylphosphine derivative, $[Pd\{Cl(Me_3CC_2H)_3\}Cl(PPh_3)]$,$MeCO_2H$, crystallised from acetic acid. *Crystal data:*

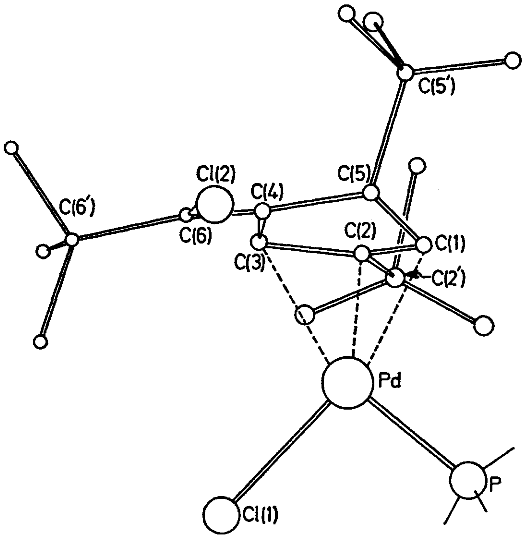
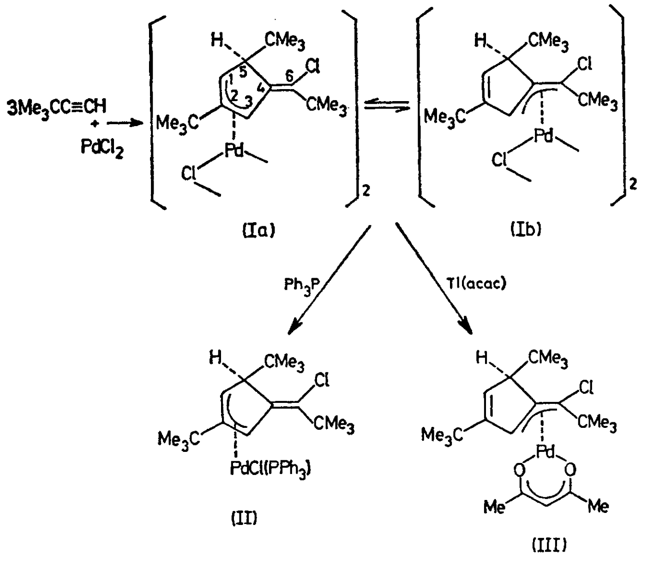


Figure. The structure of chloro-[4-(chloro-t-butyl)methylene-2,5-di-t-butyl-1—3-η-cyclopent-2-enyl]triphenylphosphinepalladium (AcOH of crystallisation, Ph groups and H-atoms omitted for clarity). Bond lengths: Pd–C(1) 2·13; Pd–C(2) 2·16; Pd–C(3) 2·28; Pd–Cl(1) 2·412; Pd–P 2·300; C(4)–C(5) 1·54; C(4)–C(6) 1·34; C(5)–C(1) 1·51; C(1)–C(2) 1·42; C(2)–C(3) 1·43; C(3)–C(4) 1·49; C(5)–C(5′) 1·62; C(2)–C(2′) 1·55; C(6)–C(6′) 1·54 Å. E.s.d.'s average 0·01 (Pd–C); 0·003 (Pd–Cl and Pd–P), and 0·02 Å (C–C).

$C_{36}H_{45}Cl_2PPd,C_2H_4O_2$, $M = 712{\cdot}09$, monoclinic, $a = 10{\cdot}738(5)$, $b = 9{\cdot}725(5)$, $c = 36{\cdot}46(2)$ Å, $\beta = 90{\cdot}2(1)°$, $Z = 4$, space group $P2_1/c$.

Three-dimensional X-ray data were collected with the crystal mounted along the a axis, using Mo-K_α radiation (graphite monochromator) and a Stoe STADI 2 diffractometer. 3056 independent reflections were collected with $I_{obs} > 3\sigma(I_{obs})$, and the structure was solved using standard Patterson and Fourier methods. Block diagonal least-squares refinement has reduced R to 0·067, allowing anisotropic temperature factors for the Pd, P, and Cl atoms.



The essential features of the molecule are shown in the Figure. The acetic acid of crystallisation is situated such that the hydroxy-oxygen atom is 3·03 Å from the chlorine that is bonded to the palladium atom, and thus indicates hydrogen bonding. The organic ligand consists of a (chloro-t-butylmethylene)cyclopent-2-enyl unit, which is approximately planar and the three endocyclic carbon atoms, C(1), C(2), and C(3), are somewhat asymmetrically bonded to the metal. Bond lengths and bond angles are normal except that ∠C(4)C(6)C(6′) (133·5°) is greater, and ∠C(6′)C(6)Cl(2) (110°) is smaller, than expected.

The chlorine-bridged dimer (I) is shown by its ^{1}H and ^{13}C n.m.r. spectra (Table) to be composed of two interconverting isomers which are frozen at < − 30 °C. From the ^{13}C data we deduce that in (Ia, 30%) the metal is bonded to the ligand in the same way as in (II) and that (Ib, 70%) has the structure shown, with the metal bonded to carbon atoms C(3), C(4), and C(6). The monomeric acetylacetonate (III), in contrast, exists only in the form corresponding to (Ib).

The interconversion (Ia) ⇋ (Ib) appears to be the first example of a novel type of stereochemically non-rigid behaviour in which the metal is bonded either to three cyclic carbon atoms or to two cyclic and one exocyclic carbon. The process is intramolecular and the rate in $CDCl_3$ is unaffected by the addition of dimethyl sulphoxide; $E_a = 41{\cdot}5$ kJ mol^{-1}.

The structures now proposed[4] for the organic degradation products are in good agreement with that for (I).

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Table

^{13}C n.m.r.[a]

Complex	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(5′), C(2′), C(6′)	Me
(II)[b]	77·6 (3)[d]	132·4[c] (6)[d]	96·8 (24·5)[d]	138·9[c] (4·5)[d]	62·1	140·2[c] (6)[d]	42·8, 37·2, 32·8 (4·5)[d]	30·8, 30·3, 28·9
(Ia)[e]	78·8[c]	132·6[c]	80·9[c]	136·0[c]	61·2	131·4[c]	41·9, 36·2 f	f f f
(Ib)[e]	132·6	157·0	80·9	126·4	63·0	102·4	44·0, 37·3, 32·2	30·7, 30·7, 29·4
(III)[g]	129·1	155·9	74·7	125·7	62·4	96·3	43·0, 36·7, 32·1	30·0, 30·0, 29·0

^{1}H n.m.r. (δ)[a]

	H(1)	H(3)	H(5)	Bu^t
(II)[b]	3·50(dt)	6·86(dd)	2·88(dd)	0·61, 1·20, 1·49
(Ia)[e]	4·80	5·85	3·08	0·90 f f
(Ib)[e]	4·92	5·97	3·56	0·99, 1·25, 1·34
(III)[g]	6·19(t)	5·05(d)	3·73(d)	1·10, 1·25, 1·32

[a] Measured in $CDCl_3$ with respect to internal $SiMe_4$ with increasing frequency taken as being positive. [b] Phenyl resonances at 128·5 130·2, 132·6 and 134·0 [^{13}C] and δ 7·35, 7·6 [^{1}H]. [c] Tentative assignments. [d] Coupling to ^{31}P. [e] At −50 °C (^{13}C) and −30 °C (^{1}H). [f] Obscured by resonances due to (Ib). [g] Acac resonances at 27·4, 27·8 (Me), 98·2 (CH), 185·0, 185·7 (CO) [^{13}C] and δ 1·82, 1·89 (Me), 5·19 (CH) [^{1}H].

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