Acetylenes and Noble-metal Compounds. Part 13.[1] Formation of Cyclobutadienepalladium Complexes from σ,π-Butadienyl Complexes in the $PdCl_2$-induced Dimerisation of t-Butyl(methyl)acetylene(4,4-Dimethylpent-2-yne)

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4,4-Dimethylpent-2-yne [t-butyl(methyl)acetylene, bma] reacts with $[Pd(NCPh)_2Cl_2]$ (1) at 20 °C in CH_2Cl_2 to give the ionic cyclobutadiene complex $[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3]_2[Pd_2Cl_6]$ (2), which on reaction with pyridine gives the cyclobutadiene complex $[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_4]$ and $[Pd(py)_2Cl_2]$. At −50 °C in CH_2Cl_2 the π-acetylene complex $[Pd_3(bma)_2Cl_6L_n]$ is formed, which rearranges (at 0 °C) to the σ,π-butadienyl complex $[Pd_3(CBu^t{=}CMeCMe{=}CBu^tCl)_2Cl_4]$ (10A). Complex (10A) reacts with bipy to give the kinetically favoured adduct $[Pd(CBu^t{=}CMeCMe{=}CBu^tCl)(bipy)Cl]$ (11) which rearranges to the thermodynamically more stable isomer (12), the *X*-ray structure of which has been determined. ^1H and ^{13}C n.m.r. spectra have been used to deduce the structures of complexes (10A), (11), $[\{Pd(CBu^t{=}CMeCMe{=}CBu^tCl)Cl\}_2]$, and $[Pd(CBu^t{=}CMeCMe{=}CBu^tCl)L]$ (L = pentane-2,4-dionate or S_2CNMe_2). The rearrangement (11) ⟶ (12) ($\Delta G^\ddagger = 95$ kJ mol^{-1}) involves a rotation about the sterically hindered =CMe–CMe= bond of the ligand. The rearrangement of the σ,π-butadienyl complexes (10A) and (10B) to the cyclobutadiene complexes (2) and (3) respectively is shown to have $\Delta G^\ddagger$ = 95—97 kJ mol^{-1} and to involve an essentially non-polar transition state. The mechanism of the formation of the σ,π-butadienyl complex (10A) is discussed and reasons are proposed for the acceleration in rate caused by positive charge on the complex and the absence of a detectable σ-alkenylpalladium intermediate.

REACTIONS of $PdCl_2$ with acetylenes in which acetylene trimers or tetramers (either complexed or as the free ligands) are obtained are now moderately well understood.[2] The first stages of the stepwise insertion mechanism which has been invoked to explain the formation of such compounds can also serve to explain the formation of cyclobutadiene metal complexes which are obtained from acetylenes (RC≡CR′) bearing moderately bulky ligands (R = aryl, R′ = aryl [2,3-7] or Bu^t; [8] see also ref. 9).

In order to probe this reaction further we have examined the reactions of 4,4-dimethylpent-2-yne [t-butyl(methyl)acetylene, bma]. This acetylene has one very bulky substituent (t-butyl) and one smaller one (methyl) and we anticipated that it would react cleanly to give dimers without any higher acetylene oligomers being formed. A further and very significant advantage of this acetylene is that its substituents (Me, Bu^t) appear as singlets in the ^1H n.m.r. spectrum and therefore allow reactions to be conveniently studied by n.m.r. spectroscopy. Part of this work has appeared as a communication.[10]

RESULTS AND DISCUSSION

Reactions to give Cyclobutadiene Complexes.—At 20 °C in dichloromethane the acetylene (bma) reacted with bis(benzonitrile)dichloropalladium (1) to give a precipitate which analysed for $[Pd_3(C_4Bu^t{}_2Me_2)_2Cl_6]$ (2); owing to its insolubility only limited solution spectroscopic investigations were possible. However, when bma and (1) were allowed to react slowly in dilute dichloromethane–tetrachloroethane solution at 20 °C over 3 weeks small red crystals of complex (2) were obtained which were suitable for *X*-ray analysis.[10] This revealed that complex (2) was ionic and possessed the structure shown.

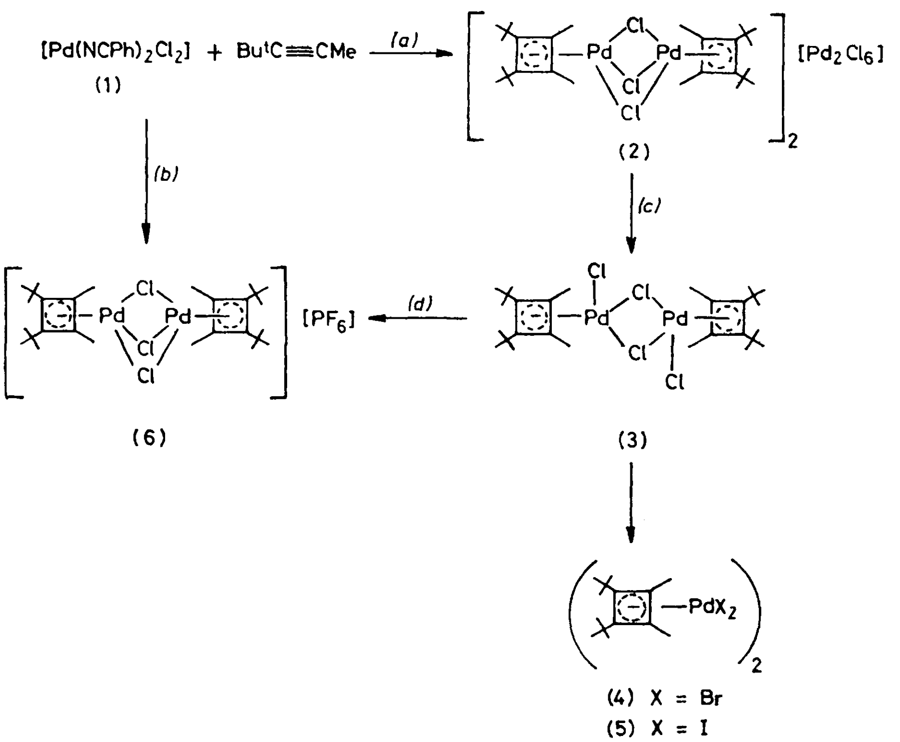
Complex (2) could be degraded to the ' normal ' cyclobutadiene complex $[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_4]$ (3) with pyridine (py). By this reaction the ' extra ' $PdCl_2$ in (2) was converted into the insoluble $[Pd(py)_2Cl_2]$ which was removed by filtration. The chloro-complex (3) could in turn be transformed into the bromo- (4) or the iodo-complex (5) by metathetical reactions with hydrobromic acid or sodium iodide respectively (Scheme 1). All attempts to form the chloro-complex (3) directly from bma and (1) were unsuccessful and the same product (2) was obtained even with very high ratios of acetylene to palladium. This observation suggested, in view of the structure found, that the acetylene did not react with the $[Pd_2Cl_6]^{2-}$ ion (see below).

The observation that the cyclobutadienepalladium entity was well stabilised as a cationic complex suggested that other ionic derivatives should be formed readily and we were able to obtain the hexafluorophosphate salt (6) simply by reaction of the chloro-complex (3) with $[NH_4][PF_6]$ in dichloromethane–acetone solution.

The cyclobutadiene complexes (2)—(6) were all characterised by elemental analyses and molecular-weight determinations [except for (2)]. The ^1H n.m.r. spectra only showed two singlets in the ratio of 1 : 3 (due to the methyl and t-butyl groups) in each case (Table 1). The complexes were mostly too insoluble for ^{13}C spectra but the chloride (3) showed the five signals expected for a cyclobutadiene complex [δ 12.7 (Me), 29.5 (CMe_3), 33.7 (CMe_3), 118.7 (*C*Me), and 121.9 p.p.m. (CBu^t)]. The C_4 ring resonances could not be detected in a $[^2H_3]$nitromethane solution of (2) but the other peaks were seen in virtually the same positions [δ 12.7 (Me), 29.6 (CMe_3), and 34.6 p.p.m. (CMe_3)].

Infrared spectra of complexes (2)—(6) were essentially identical in the region 625—4 000 cm^{-1} indicating that the same organic ligand was present in each. The far-i.r. spectra of the chloro-complexes were of substantial help in assigning structures. The $[Pd_2Cl_6]^{2-}$ ion (as the $[NBu^n{}_4]^+$

salt) showed very strong bands at 334 and 348 cm^{-1} in good agreement with those reported by Goggin,[11] and we identify the very strong bands at 331 and 342 cm^{-1} in the spectrum of (2) to be due to the $[Pd_2Cl_6]^{2-}$ ion; the remaining strong bands of (2) (a broad envelope with peaks at 195 and 202 and a shoulder at 225 cm^{-1}) we therefore ascribe to the Pd_2Cl_3 bridge in the cationic part of (2). This is confirmed by the absence of bands in the far-i.r. spectrum of the $[PF_6]^-$ complex (6) except for a very strong band at 205 cm^{-1}, again arising from the Pd_2Cl_3 bridge deformations. The cyclobutadiene chloro-complex (3) showed bands at 200w, 227m—w, and 292vs cm^{-1}, the last of which we propose to be particularly characteristic for the Pd_2Cl_4 grouping found in (3) and in other analogous cyclobutadiene complexes.* For example, $[Pd_2(C_4Ph_4)_2Cl_4]$ shows bands at 213m, 300sh, and 306vs cm^{-1} and again this easily forms the ionic $[Pd_2(C_4Ph_4)_2Cl_3][PF_6]$ which just shows lower-frequency bands, in this case at 214s and 237s cm^{-1}.



SCHEME 1 (a) CH_2Cl_2, 20 °C; (b) $Ag[PF_6]$, MeCN; (c) py; (d) $[NH_4][PF_6]$

TABLE 1

^1H n.m.r. spectra

	Compound	δ/p.p.m.				
		Me[C(4)]	Me[C(5)]	Bu^t[C(3)]	Bu^t[C(6)]	Others
(10A)	$[Pd_3(C_4Bu^t{}_2Me_2Cl)_2Cl]$ [a]	2.26	1.87	1.46	1.20	
(10B)	$[Pd_2(C_4Bu^t{}_2Me_2Cl)_2Cl_2]$ [a]	2.23	1.83	1.42	1.19	
(11)	$[Pd(C_4Bu^t{}_2Me_2Cl)(bipy)Cl]$ [a]	2.1	1.65 [b]	1.51	1.4 [b]	7.45, 8.0, 9.2 (bipy)
(12)	$[Pd(C_4Bu^t{}_2Me_2Cl)(bipy)Cl]$ [c]	2.02	2.38	1.53	0.84	7.45, 8.0, 9.2 (bipy)
(17)	$[Pd(C_4Bu^t{}_2Me_2Cl)(MeSCH_2CH_2SMe)Cl]$ [a]	2.02	1.43	1.49	1.37	2.48 (S–CH_3), 2.98 (CH_2)
(13)	$[Pd(C_4Bu^t{}_2Me_2Cl)(acac)]$ [c]	2.17	1.80	1.47	1.30	5.21 (C–H) ,1.87 (CH_3)
(14)	$[Pd(C_4Bu^t{}_2Me_2Cl)(S_2CNMe_2)]$ [c]	2.18	1.86	1.44	1.13	3.30, 3.37 (CH_3)
(15)	$Bu^tCH{=}CMeCMe{=}CClBu^t$ [c]	1.79 (d)	1.90	1.29	1.09	5.05 (q) (=CH–)
(16)	$CH_2{=}CMeCH_2CBu^t{=}CMeCMe{=}CClBu^t$ [c]	1.70 [b]	1.88 [b]	1.27	1.19	1.87 (CH_3), 4.7 (=CH_2), 2.56, 2.82 [dd, J(H–H) 17 Hz, CH_2]
		Me	Bu^t			
(2)	$[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3]_2[Pd_2Cl_6]$ [d]	2.02	1.46			
(3)	$[\{Pd(C_4Bu^t{}_2Me_2)Cl_2\}_2]$ [c]	2.02	1.46			
(4)	$[\{Pd(C_4Bu^t{}_2Me_2)Br_2\}_2]$ [c]	2.15	1.49			
(5)	$[\{Pd(C_4Bu^t{}_2Me_2)I_2\}_2]$ [e]	2.10	1.48			
(6)	$[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3][PF_6]$ [e]	1.98	1.49			

[a] In $[^2H_2]$dichloromethane. [b] Broad resonance. [c] In $[^2H]$chloroform. [d] In $[^2H_3]$nitromethane. [e] In $[^2H_6]$acetone.

The facility with which such ionic species, in particular (2), are formed prompts us to propose that the initial

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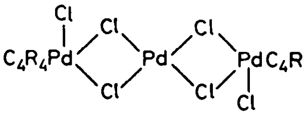
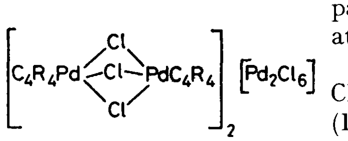
* This band must arise from both the bridging and the terminal ν(M–Cl) which are sometimes coincident; in other cases they are separated and the band due to the bridging mode is seen as a shoulder on the low-frequency side of the main peak.

products obtained from a variety of diarylacetylenes and (1) are also of this type. These complexes were previously formulated as (A)[5] and should now also be formulated as (B).[12]



(A) R = Ph or C_6H_4X-*p*



(B)

Canziani and Malatesta[13] recently reported an analogous reaction of acetylenes with $[Pt(CO)_2Cl_2]$:

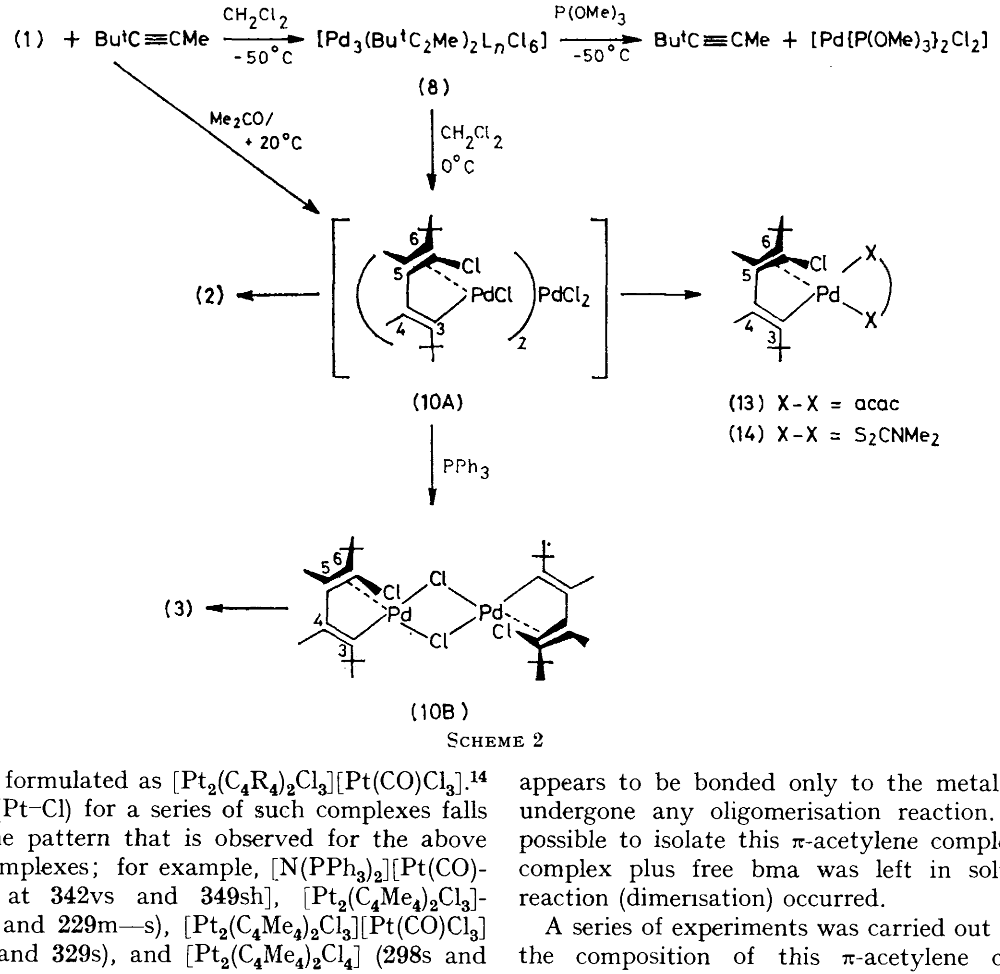
$$RC_2R + [Pt(CO)_2Cl_2] \longrightarrow \underset{(7)}{[Pt_3(CO)(C_4R_4)_2Cl_6]}$$

Complexes (7) have now also been shown to be ionic with Pt_2Cl_3 bridges analogous to those found in (2) and (6): here the counter anion is $[Pt(CO)Cl_3]^-$ and the complexes are correctly formulated as $[Pt_2(C_4R_4)_2Cl_3][Pt(CO)Cl_3]$.[14] Again, the ν(Pt–Cl) for a series of such complexes falls into the same pattern that is observed for the above palladium complexes; for example, $[N(PPh_3)_2][Pt(CO)Cl_3]$[ν(Pt–Cl) at 342vs and 349sh], $[Pt_2(C_4Me_4)_2Cl_3][PF_6]$ (168w and 229m—s), $[Pt_2(C_4Me_4)_2Cl_3][Pt(CO)Cl_3]$ (230s, 327s, and 329s), and $[Pt_2(C_4Me_4)_2Cl_4]$ (298s and 316vs cm^{-1}).

A simple direct synthesis of the hexafluorophosphate salt (6) was devised: silver hexafluorophosphate and $[Pd(NCMe)_2Cl_2]$ (molar ratio 0.5 : 1) were allowed to react in acetonitrile; the precipitated silver chloride was removed and the resulting solution gave an immediate reaction leading to an essentially quantitative yield of (6) when treated with bma.

In order to establish further details concerning the mode of formation of the cyclobutadiene complex, in particular (2), from bma, reactions were carried out at lower temperatures and under different conditions.

Intermediates in the Formation of $[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3]_2[Pd_2Cl_6]$ (2).—(*i*) *At* −50 °C. When a solution of (1) was allowed to react with one of bma (both in dichloromethane at −50 °C) the ^1H n.m.r. spectrum at −50 °C showed two new resonances, at δ 1.50 and 2.12 p.p.m. in a 3 : 1 intensity ratio, in addition to those of free bma (δ 1.10, and 1.70 p.p.m.). Addition of trimethyl phosphite at −50 °C caused the disappearance of the bands at 1.50 and 2.12 p.p.m. and those of the free acetylene correspondingly increased in intensity (Scheme 2). We assign the two lower-field resonances to a π-acetylene complex; because the free bma resonances are regenerated on reaction with $P(OMe)_3$ the acetylene appears to be bonded only to the metal and has not undergone any oligomerisation reaction. It was not possible to isolate this π-acetylene complex and if the complex plus free bma was left in solution further reaction (dimerisation) occurred.



Scheme 2

A series of experiments was carried out to investigate the composition of this π-acetylene complex. Dichloromethane solutions were made up of (1) and differing amounts of bma at −50 °C, and the relative amounts of Pd* and free and complexed bma were determined by

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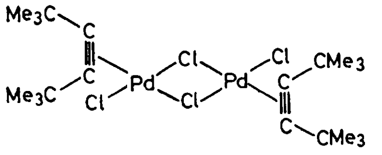
* The relative amounts of $[Pd(NCPh)_2Cl_2]$ were determined by integration of the phenyl resonance against the methyl and t-butyl resonances.

integration of the ^{1}H n.m.r. spectra. The ratio of co-ordinated bma : Pd stayed sensibly constant at 0.67 ± 0.02 : 1 over a concentration range bma(total) : Pd of 1.5—6.5 : 1 and we therefore propose that the complex (8) formed has a stoicheiometry $[Pd_2(bma)_2L_nCl_6]$ where L = benzonitrile and n is unknown.

Complex (8) may be compared with the stable and readily prepared 1 : 1 complex of 2,2,5,5-tetramethylhex-3-yne (di-t-butylacetylene), which presumably has structure (9),[15] and also with the 1 : 2 complex of but-2-yne, $[Pd_2(C_2Me_2)L_nCl_4]$ (10), which was also shown to exist at low temperature.[16] The structures of (8) and (10) are not known, and the reason for the differences in stoicheiometry between the three complexes is not clear but it may be due to the differing sizes of the acetylenic substituents.



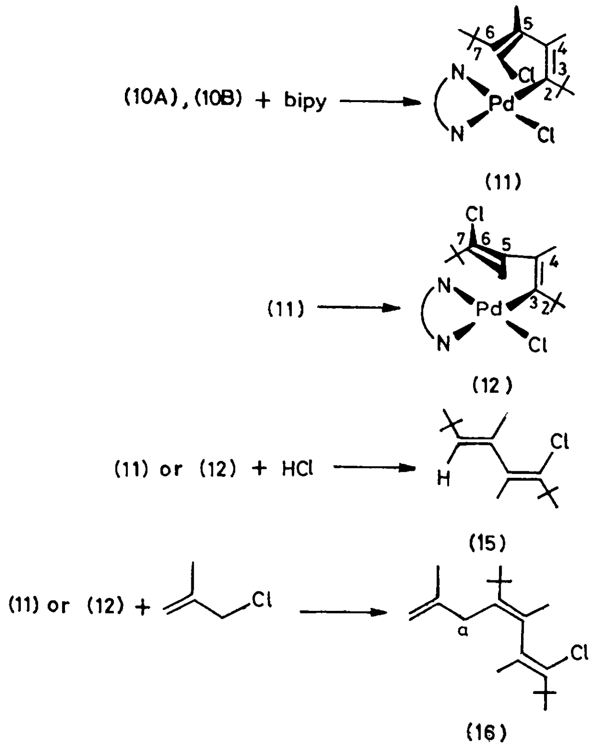
(9)

(*ii*) *At* 0 °C. The reaction of bma with $[Pd(NCPh)_2Cl_2]$ (molar ratio 2 : 1) in dichloromethane at 0 °C was monitored by ^{1}H n.m.r. spectroscopy. In the initial spectrum obtained immediately after mixing, eight peaks were observed, two of which were identified as arising from free bma [δ 1.10 (Bu^t) and 1.70 p.p.m. (Me)] and two were due to the π-co-ordinated bma [1.50 (Bu^t) and 2.12 p.p.m. (Me)]. The four remaining signals (δ 1.19, 1.40, 1.83, and 2.21 p.p.m.) were observed in a 3 : 3 : 1 : 1 ratio [complex (10A)]. After 1 h at 0 °C the n.m.r. spectrum showed a decrease in the amount of free bma, no π-co-ordinated bma, and two new peaks in a 3 : 1 ratio in addition to the four unassigned signals observed in the initial spectrum. A precipitate of complex (2) was obtained after 3 h and the major peaks observed in the spectrum were those of the cyclobutadiene complex (2) and unchanged bma.

The reaction was repeated and, after 10 min at 0 °C, it was quenched with 2,2′-bipyridyl (bipy). The n.m.r. spectrum now indicated the formation of a new complex (11). A precipitate of $[Pd(bipy)Cl_2]$ was also obtained from the reaction. Complex (11) was isolated from solution as a yellow solid which was, however, thermally rather unstable and which rearranged, rapidly in solution but slowly also even in the solid, to an isomeric complex (12). Complexes (11) and (12) were shown to possess the same 6-chloro-2,2,4,5,7,7-hexamethylocta-3,5-dien-3-ylpalladium (' σ-butadienylpalladium ') unit, as discussed below.

Attempts were made to isolate the species responsible for the four unassigned resonances in the low-temperature reaction by precipitation with light petroleum. These were only partially successful since the material coprecipitated with $[Pd(NCPh)_2Cl_2]$ (1) from which it was difficult to separate because of its lability. However, this material (10A) was easily prepared directly from bma and (1) at 20 °C in more polar solvents (*e.g.* acetone or nitromethane) from which it precipitated pure and in high yield after a few minutes.

The n.m.r. spectrum of (10A) was identical to that of the unassigned species in the solution experiments carried out at 0 °C, and on reaction with bipyridyl the complex (11) was again obtained. Furthermore, on leaving a solution of (10A) to stand at 20 °C for a few minutes the peaks of the cyclobutadiene complex (2) were observed in the n.m.r. spectrum and this complex then slowly precipitated. On warming, complex (10A) was totally transformed into (2) within a short time. Elemental analysis of (10A) indicated it to have the same empirical formula as (2), $[Pd_3(C_4Bu^t{}_2Me_2)_2Cl_6]$. However, the n.m.r. spectrum clearly showed that a cyclobutadiene ligand was not present since both the methyls and the t-butyls were inequivalent.



SCHEME 3

Reaction of (10A) with triphenylphosphine did not give an adduct, but instead caused a degradation to another complex (10B) and $[Pd(PPh_3)_2Cl_2]$. Elemental analysis and molecular-weight determination on complex (10B) showed it to be $[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_4]$ and isomeric with the cyclobutadiene complex (3), and indeed in solution (10B) was slowly transformed into (3). However, the n.m.r. spectrum of (10B) again indicated the presence of a similar σ-butadienyl ligand to that present in (10A) and reaction with bipyridyl also gave complex (11) (Schemes 2 and 3).

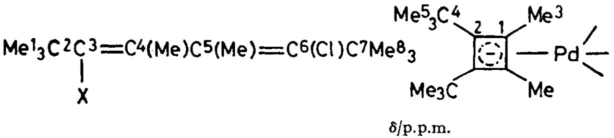
Rearrangement of the σ,π-*Butadienyl to the Cyclobutadiene Complexes*.—The rearrangement reactions of the 1-σ : 3—4-η-butadienyl complexes (10A) and (10B) were monitored by ^{1}H n.m.r. spectroscopy, observing the disappearance of the four butadienyl and the appearance of the two cyclobutadiene resonances. It was possible to monitor the rearrangement of complex (10B) in acetone, dichloromethane, or benzene, but the rearrangement of (10A) could only be followed in dichloromethane, due to its low solubility in other solvents (Scheme 2). Spectra were recorded every 2 min over at least 50 min at 34 °C and the rate constants were obtained from successive integrations of the t-butyl resonances. The reactions all exhibited first-order behaviour and gave the following rate constants and $\Delta G^{\ddagger}$ values (at 307 K):

	(10A) ⟶ (2)		(10B) ⟶ (3)	
Solvent	$10^4k/\mathrm{s}^{-1}$	$\Delta G^{\ddagger}$/ kJ mol^{-1}	$10^4k/\mathrm{s}^{-1}$	$\Delta G^{\ddagger}$/ kJ mol^{-1}
CH_2Cl_2	2.8 ± 0.1	96.2	4.0 ± 0.1	95.2
[$^2H_6$]Acetone			3.5 ± 0.5	95.6
C_6H_6			2.1 ± 0.2	96.9

Although the differences in rate between the various reactions are only small, complex (10B) rearranged *ca.* 40% faster than (10A) and the rearrangement of (10B) to (3) is rather slower in the less-polar solvent benzene. These data suggest a similar ring-closure mechanism for each reaction and one that goes through a transition state of not markedly polar character. This in turn implies that the rate-determining step in the overall rearrangement is *not* an ionisation. Since the product (2) from (10A) is ionic, this suggests that the ion is formed from a more covalent species in a fast step subsequent to the rearrangement. This would certainly be consistent with the rate-determining, slow, step being the ground-state-allowed conrotatory ring closure of the σ-butadienyl to a σ-cyclobutenyl complex, followed by a fast *trans*-elimination of Cl (see further below).

TABLE 2

^{13}C n.m.r. spectra



$$\underset{\displaystyle X}{\mathrm{Me^1{}_3C^2C^3}}\!=\!\mathrm{C^4(Me)C^5(Me)}\!=\!\mathrm{C^6(Cl)C^7Me^8{}_3}$$

		δ/p.p.m.						
	Compound	C(1)	C(2)	C(3)	C(4)	C(5)		
(3)	[{Pd($C_4Bu^t{}_2Me_2$)Cl_2}$_2$] [a]	118.7	121.9	12.7	29.5	33.7		
(2)	[Pd_2($C_4Bu^t{}_2Me_2$)$_2Cl_3$]$_2$[Pd_2Cl_6] [b]	n.o.	n.o.	12.7	29.6	34.6		
		C(3)	C(4,5)	C(6)	C(2,7)	Me(1,8)	Me(4,5)	Others
(10A)	[Pd_3($C_4Bu^t{}_2Me_2Cl$)$_2Cl_4$] [a]		127.5	84.6	39.0 45.4	30.8 33.5	19.1 25.4	
(10B)	[Pd_2($C_4Bu^t{}_2Me_2Cl$)$_2Cl_2$] [a]	144.4	126.1 132.7	83.5	38.6 44.8	30.8 33.3	19.05 25.2	
(11)	[Pd($C_4Bu^t{}_2Me_2Cl$)(bipy)Cl] [a]	149.1	130.2 134.6	141.7	40.3 41.3	30.1 32.3	23.6 25.6	bipy: 156.0, 152.5 (2,2′); 121.7, 122.6, 126.6, 126.2 (3,3′) and (5,5′); 138.9 (4,4′); 149.2, 152.4 (6,6′)
(12)	[Pd($C_4Bu^t{}_2Me_2Cl$)(bipy)Cl] [c]	149.6	133.5 135.0	137.3	38.5 39.1	30.3 32.4	17.9 22.9	bipy: 154.8, 153.6 (2,2′); 121.3, 121.7, 126.2 (3,3′) and (5,5′); 138.1, 138.8 (4,4′); 149.1, 150.0 (6,6′)
(17)	[Pd($C_4Bu^t{}_2Me_2Cl$)(MeSCH$_2$CH$_2$SMe)Cl] [a]	147.5	135.2 136.0	139.1	39.0 40.5	31.3 32.1	22.6 23.9	18.2, 19.6 (S–CH_3) 41.8 (CH_2)
(13)	[Pd($C_4Bu^t{}_2Me_2Cl$)(acac)] [c,d]	141.3	124.8 127.3	84.0	37.7 44.4	30.3 33.1	19.05 25.2	99.3 (C–H) 26.9, 28.9 (CH_3) 184.2, 189.7 (C=O)
(14)	[Pd($C_4Bu^t{}_2Me_2Cl$)(S_2CNMe_2)] [c]	153.2	126.4 136.5	90.7	40.8 44.4	31.3 33.2	20.4 25.9	39.7 (NCH_3) 208.2 (N=C)
(15)	Bu^{t}CH=CMeCMe=CClBu^t [c]	135.1	136.2 137.1	139.1	32.0 32.3	30.7 31.0	15.8 20.8	
(16)	CH_2=CMeCH$_2$CBu^t=CMeCMe=CClBu^t [c]	146.1	135.4 136.8	138.1	31.9 35.0	30.4 30.8	19.8 23.8	101.1 (=CH_2) 146.1 (=CMe–) 18.7 (CH_3)

[a] In [$^2H_6$]dichloromethane. [b] In [$^2H_3$]nitromethane: n.o. = not observed. [c] In [^{2}H]chloroform. [d] At 0 °C.

Chemistry and Structures of the σ-Butadienyl Complexes.—Both the complexes (10A) and (10B) gave the bipy complex (11) on reaction with bipyridyl. In solution this complex slowly isomerised to another more stable isomer (12), a crystal of which was suitable for an *X*-ray diffraction study.[10] This showed that the Pd was co-ordinated to bipy and to C(3) of a ' σ-butadienyl ' ligand. The remaining co-ordination site on the metal was occupied by a terminal chlorine (Scheme 3).

Elemental analyses and molecular-weight determinations showed complexes (11) and (12) to be isomers and each exhibited a terminal ν(Pd–Cl) at 325 cm^{-1}. The complexes were distinguished by their ^{1}H n.m.r. spectra (Table 1). Both showed bipy resonances at low field and the presence of two inequivalent methyl and t-butyl substituents. One methyl and one t-butyl resonance were in similar positions in the two spectra [Me: δ 2.1 (11), 2.02 (12). Bu^t: 1.51 (11), 1.53 p.p.m. (12)] and suggested that these groups have similar environments in each isomer. The other methyl and t-butyl groups were at different positions and their resonances in complex (11) (Me: 1.65. Bu^t: 1.4 p.p.m.) were significantly broadened; these resonances were sharpened when a solution was cooled to 0 °C and we ascribe the broadening to a restricted rotation of these groups. No such effect is observed in the ^{13}C spectrum of (11) and we therefore discount the presence of other types of isomers.

The n.m.r. spectrum of (12) was entirely consistent with the *X*-ray crystal structure and in particular it showed one t-butyl to be at unusually high field (δ 0.84 p.p.m.); the structure of (12) shows that the t-butyl on C(3) is situated above one of the bipy rings and it would be expected to be rather shielded by comparison with the t-butyl on C(5) (δ 1.53 p.p.m.).

The similarity of both the ^{1}H and the ^{13}C n.m.r.

spectra (Table 2) of (11) and (12) and the differences between them were consistent with each isomer having a different conformer of the same σ-butadienyl ligand. The presence of the same ligand in each isomer was confirmed by their reactions with hydrogen chloride gas which gave the same chlorobutadiene, (15), identified by n.m.r. and mass spectrometry.

Space-filling C.P.K. models indicate that the σ-butadienyl ligand in [Pd(bipy)(CBu^t=CMeCMe=CBu^{t}Cl)-Cl] can exist in two skew conformers which arise as a consequence of restricted rotation about the C(4)-C(5) bond. The *X*-ray structure indicates that isomer (12) has the butadienyl chlorine in a position opposite the Pd-Cl and a model shows the other conformer, (11), to have the butadienyl chain arranged such that the two chlorines are on the same side of the molecule and close to each other. It is this interaction which is probably responsible for the lability of conformer (11).

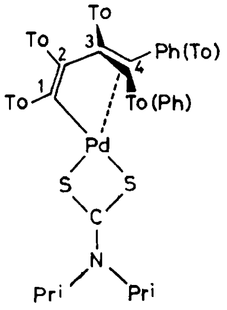
The model of complex (11) also shows that the methyl on C(5) and the t-butyl on C(6) are not free to rotate owing to interaction with the bipyridyl ligand. This can explain the broadness of the two lines in the ambient-temperature ^{1}H n.m.r. spectrum, which is due to an exchanging system. Since observations at higher temperatures were not possible owing to the rearrangement (11) $\longrightarrow$ (12) and the complex was rather insoluble at lower temperatures, only a spectrum at 0 °C could be obtained. This showed a sharpening of the resonances consistent with a freezing out of one of the rotamers.

In order to show the existence of a large barrier to rotation about the C(4)-C(5) bond in the butadienyl ligand a derivative was examined. Both (11) and (12) reacted with 3-chloro-2-methylpropene to give the same compound (16). If (16) had the freedom to rotate about the C(4)-C(5) bond then the two hydrogens on the saturated CH$_2$ [C(a)] should be equivalent and should give rise to a singlet. The ^{1}H n.m.r. spectrum, however, showed these hydrogens as an AB system. On heating a solution of (16) to 60 °C line broadening of less than 2 Hz was observed. Using the empirical relation $k = \pi\Delta\nu$ (where $\Delta\nu$ is the line broadening observed) a maximum value for k (*ca.* 6 s^{-1}) was obtained which is consistent with a $\Delta G^\ddagger$ at 333 K of *at least* 77 kJ mol^{-1} for the barrier to rotation about C(4)-C(5).

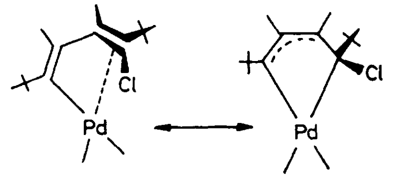
The rearrangement of (11) to (12) was a first-order process in [^{2}H]chloroform at 60 °C with $t_{\frac{1}{2}} = 190$ s and $k_1 = 3.6 \times 10^{-3}$ s^{-1}. This gives a value of $\Delta G^\ddagger$ of 97 kJ mol^{-1} for the isomerisation which is entirely consistent with the barrier to rotation in (16).

The elucidation of the structures of complexes (11) and (12) strongly suggests that (10A) and (10B) contain the same organic σ-butadienyl ligand, and this is supported by their ^{1}H n.m.r. spectra (Table 1). In order to obtain a more extensive series of complexes which could be compared to (10A) and (10B), complex (10A) was treated with Tl(acac) (acac = pentane-2,4-dionate) to give (13) and [Pd(acac)$_2$], and with sodium dimethyldithiocarbamate to give (14) and [Pd(S$_2$CNMe$_2$)$_2$]. These complexes were both of the form [PdL(CBu^t=CMeCMe=CBu^{t}Cl)] as shown by elemental analyses and the molecular weights which indicated them to be monomeric. Since the ligand L (acac or S$_2$CNMe$_2$) is bidentate, in order to satisfy the square-planar co-ordination requirement of Pd^{II}, the butadienyl ligand must likewise be bidentate, and we propose that it is 3-σ : 5—6-η- (σ,π-) bonded to the metal.

This suggestion is confirmed by the ^{13}C spectra (Table 2) of these complexes which show that, while the butadienyl sp^2 carbons C(3), C(4), and C(5)* are roughly in the same positions in complexes (11)—(14) as well in the organic compounds (15) and (16), there is a significant shift for the resonance ascribed to C(6). This occurs in the region δ 137—142 p.p.m. for (11), (12), and (15)—(17) but at δ 84.0 and 90.7 p.p.m. for (13) and (14) respectively. We ascribe this change in chemical shift to arise from complexing the C(5)-C(6) bond of the butadienyl ligand to the metal. A similar structure has recently been shown to exist in the dithiocarbamate (18) [17] and a number of other σ,π-butadienyl structures have now been confirmed.[18,19] Furthermore, the terminal =C$<$[C(4)] resonances of complex (18) (two isomers present) are also at significantly higher field, in this case at δ 107.5 and 108.5 p.p.m. The observation that the analogous carbon, C(6) in (13) and (14), lies at even higher field suggests that this carbon has even more sp^3 character than in (18) and that a metallocyclobutenyl form of type (D) is also a significant contributor to the overall structure as well as the σ,π-form (C).



(18)



(C) (D)

To = p-MeC$_6$H$_4$

The similarity of the ^{13}C spectra, in particular of the chemical shifts of the C(6) carbons, of (10A) and (10B) to those of (13) and (14) strongly suggests that these molecules also contain σ,π-butadienyl ligands and we formulate (10B) as the chloride-bridged dimer shown.

The structure of the parent complex, (10A), was more difficult to elucidate because the structures of related complexes were not known and because of the high lability of the complex. The far-i.r. spectrum of (10A) showed ν(Pd-Cl) bands at 224w, 278w—m, and 349vs

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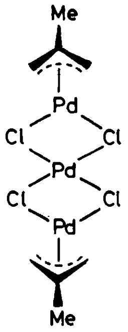
* The sp^2 resonances C(2)—C(5) of the butadienyl ligand in (11) and (12) occur in the same region as the aromatic bipy resonances; in order to differentiate between them the 2,5-dithiahexane complex (17), which possesses no aromatic carbons, was prepared and the resonances of (11) and (12) assigned by comparison. The complex (17) is largely but not entirely one isomer, but the configuration of the dithiahexane ligand is not known.

cm^{-1} and this was not too dissimilar to that of the formally related complex $[Pd_3(2\text{-methylallyl})_2Cl_4]$ (19) [ν(Pd–Cl) at 200w, 246w, 268m, and 326vs cm^{-1}]. A crystal-structure determination of complex (19)[20] has shown the two η^3-allylic units to be joined by a Pd_3Cl_4 bridge and, by analogy, we suggest the structure shown for (10A). The main difference is that while the organic ligand in (19) is symmetrically η^3-bonded, the organic ligand in (10B) is much more asymmetric.

Molecular models of (10A) and (10B) show that the ligand adopts a conformation such that the fifth co-ordination site of the metal is totally blocked by the butadienyl chlorine which is close to the bridging chlorines on Pd. Nucleophilic attack can therefore only occur at the remaining (sixth) site of the metal and this must lead to the adduct isomer with both Pd–Cl (terminal) and the C–Cl on the same side, as shown in the bipy complex (11).



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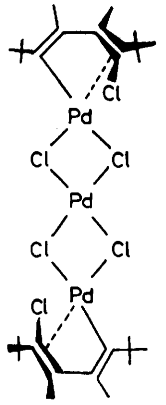
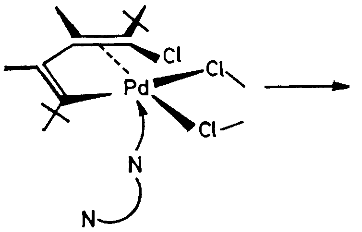


(10A)

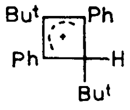


It may also be noted that while the σ-butadienyl ligand in (11) or (12) must adopt skew conformations on steric grounds, the butadienyl ligand in (10) [and in (13) and (14)] must have skew conformations in order that the C(5)–C(6) bond may be aligned in such a manner to give best overlap with the orbitals of the metal to which it is π-bonded.

Mechanism of the Acetylene Dimerisation Reaction.— The results obtained in this work support the general scheme which has been put forward to account for the formation of cyclobutadiene complexes from a $PdCl_2$-induced dimerisation of two acetylenes.[2] We have evidence for two key intermediates: a π-acetylene complex (8) (at low temperatures) and the σ-butadienyl intermediate (10) which cyclises to the cyclobutadiene. Our results also allow us to fill in further details in two parts of the reaction scheme.

One of these is concerned with the first stages of the reaction. We have observed that while $[Pd(NCPh)_2Cl_2]$ reacts quite readily with bma to give (10A) and (2), the reaction [to give (3)] is very much accelerated in the presence of 0.5 equivalent of $Ag[PF_6]$. Furthermore, in separate experiments we have shown that the $[Pd_2Cl_6]^{2-}$ dianion (in $[NBu^n_4][Pd_2Cl_6]$) is quite inactive towards bma. This last result also explains why the reaction of a large excess of bma with (1) stops at complex (2) and why the $[Pd_2Cl_6]^{2-}$ counter ion in (2) does not also react with bma.

We have, in other studies,[21] observed that the creation of a cationic metal centre (from $[MCl_2L_2] + Ag[PF_6]$) considerably facilitates reaction of organic ligands and a recent theoretical study[22] has made a similar point. However, the effect of the positive charge in the systems studied here *cannot* be to cause a cationic dimerisation of the acetylenes; this can be shown by a comparison of the stereochemistry of the cyclic C_4 products obtained from the $PdCl_2$-induced acetylene dimerisations with that from the acid-induced reaction. Thus, $PhC{\equiv}CBu^t$ reacts with fluorosulphuric acid at −78 °C to give only the cyclobutenyl cation (20).[23] None of the cation (21) or any other isomer is formed because the cation (20) is so substantially stabilised by the 1,3-arrangement of the phenyls.



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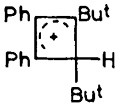

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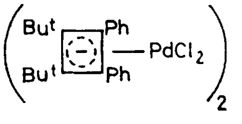

(22)

In contrast, the reaction of $PdCl_2$ with $PhC{\equiv}CBu^t$ gives (22).[8,9] Although this reaction has not been examined in as much detail as the one described here with bma the two reactions are clearly mechanistically identical. This is particularly demonstrated by the stereochemistry of the cyclobutadiene ligand in (22) which has the two t-butyls vicinal as is the case in complexes (2), (3), (6), *etc.* This indicates that (22) must arise from $PhC{\equiv}CBu^t$ *via* a very similar set of intermediates to those which have been demonstrated for the bma reactions. Hence, we can rule out for both these $PdCl_2$-induced dimerisations any C_4 intermediates in which a substantial positive charge is localised on the organic ligand.

Three further questions require comment. (*i*) Since we have shown that the formation of a π-acetylene complex occurs readily even at −50 °C, what is the nature of the rate-determining step in the dimerisation? (*ii*) If the oligomerisation takes place in a series of stepwise reactions, the first insertion * step (bma into Pd–Cl) occurs in a Markownikow and the second insertion (bma

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* The term ' insertion ' is used here in a descriptive sense; it is probable that these reactions in fact occur by a migration of the Cl (or the alkenyl) on to the co-ordinated acetylene.

into Pd–alkenyl) in an anti-Markownikow sense. It should also be noted that the $PdCl_2$-induced tri- and tetra-merisation reactions of smaller acetylenes may also be interpreted in terms of identical first (Markownikow) and second (anti-Markownikow) steps; furthermore, *all* successive insertion steps are then also anti-Markownikow.[2] Why then, does the first insertion (in which the Pd becomes attached to the carbon bearing the *least* bulky substituent) occur in the opposite sense to all the following ones? (*iii*) Why has it not been possible to detect the σ-alkenyl intermediate?

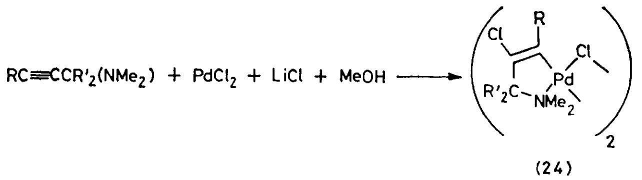
A plausible answer to the first question is that although the π-acetylene complex is easily formed further reaction does not occur until and unless a positive charge is created on the complex. This can occur (slowly) by the replacement of Cl^- by a second acetylene or (faster) by the removal of a Cl^- by silver ion; moreover, it is probable that in the presence of Ag^+ a second acetylene enters the co-ordination sphere of the Pd. Thus we now suggest that the seond step of the reaction is the formation of a bis(acetylene) cationic complex (23):

$$\text{bma} + (1) \rightleftharpoons [\text{Pd(bma)LCl}_2]$$

$$[\text{Pd(bma)LCl}_2] + \text{bma} \rightleftharpoons \underset{(23)}{[\text{Pd(bma)}_2\text{LCl]Y}}$$

$$[\text{L} = \text{PhCN or Pd}_2(\text{NCPh})\text{Cl}_4;\ \text{Y} = \text{Cl},\ \tfrac{1}{2}\text{Pd}_2\text{Cl}_6,\ \text{or PF}_6]$$

Only one reaction has been reported in which Pd • • • Cl has added to an alkyne to give a σ-(2-chloroalkenyl)-palladium complex;[24] however, in this case the product, complex (24), must be formed by a *trans*-attack of Cl^- on the acetylene. This is not unexpected since the reaction is carried out in a highly ionising medium.



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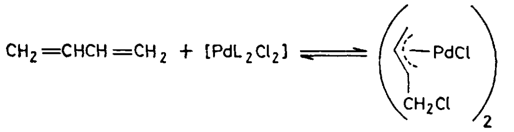
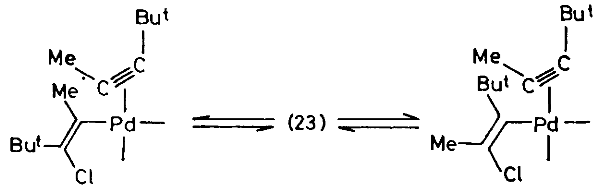


(25)

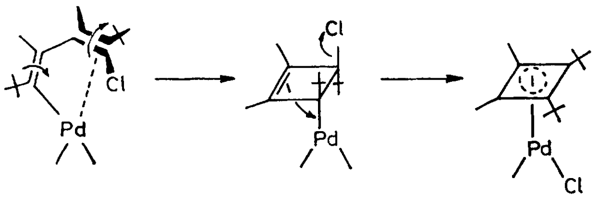
The reactions of 1,3-dienes provide a better model; for example, butadiene readily reacts with $[Pd(NCPh)_2Cl_2]$ in apolar media to give a π-allylic complex in which a C–Cl bond has been formed, (25), presumably by a *cis*-addition of Pd–Cl. It was also shown that the carbon-bonded chlorine in (25) was very labile and easily displaced; for example, reaction of (25) with a strong ligand (dimethyl sulphoxide, phosphine, *etc.*) regenerated butadiene.[25]

We therefore postulate that a related labile equilibrium occurs in the bis(acetylene) complex (23) and that the Pd–Cl can add to the triple bond in either of the two ways (i) or (ii). Since steric hindrance at the Pd will be less for isomer (i) than for (ii), isomer (i) may be expected to be the more favoured and to be the form which undergoes the second fast insertion step, which is essentially irreversible since a C–C bond is formed. This hypothesis accounts for the difference in orientation of the acetylene in the first and in the subsequent insertion steps, and it also explains why it has not been possible to detect the σ-alkenyl intermediate.



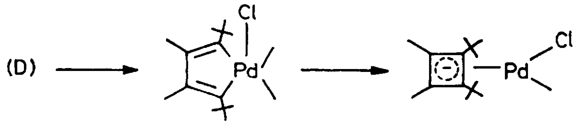
(i) (ii)

The second point on which we may comment is the cyclisation of the σ-butadienyl complex (10A) [or (10B)] to the cyclobutadiene (2) [or (3)]. The rate studies showed this to be an intramolecular process with only a small solvent dependence and this is certainly consistent with the proposed mechanism of an allowed conrotatory cyclisation to a σ-cyclobutenyl complex followed by a *trans*-elimination of Cl^-. $\Delta G^‡$ for this reaction at 307 K ranges from 95 to 97 kJ mol^{-1} (depending on the solvent) and is the same for (10a) ⟶ (2) as for (10B) ⟶ (3). If a requirement for the conrotatory cyclisation of the butadienyl ligand in (10) is that the diene first becomes planar *s-cis*, then a part at least of this activation will be needed in order to twist the diene from the ground-state conformation, where the π-bonding of C(5)–C(6) to the metal requires a skew geometry, to the planar *s-cis* transition state. It is not clear whether this process is related to the isomerisation (11) ⟶ (12) for which a very similar $\Delta G^‡$ is found.



We also find that when bma and (1) react in the presence of 0.5 equivalent of $Ag[PF_6]$ the cationic cyclobutadiene complex (6) is formed in a very fast reaction in which no σ-butadienyl intermediate could be detected. A possible rationalisation for this observation is that a positive charge on a metal complex often implies either a vacant site or the presence of a very labile ligand. In either case the remaining ligands would have more room in which to undergo conformational changes of the type discussed above. In other studies we have also found that cyclobutenyl ring-*opening* reactions are inhibited in cationic complexes[26] and there is some evidence to suggest that this effect of charge may be rather general in cyclisation and ring-opening reactions.[27]

We cannot completely rule out the possibility that cyclisation of the ligand in (10) occurs by a totally different path, *via* a metallacyclopentenyl (D) and a metallacyclopentadiene intermediate (E) which then reductively eliminates:



(E)

The reductive elimination of a metallacyclopentadiene to a cyclobutadiene complex has been demonstrated to occur in cobalt-induced acetylene dimerisations [28] and probably occurs in a number of other related reactions.[29] However, in this case the fact that metallacyclopentenyls such as (D) appear to be rather high-energy intermediates, coupled with the point that in (E) the Pd is in the rather high formal oxidation state of IV, makes this a less likely path.

Further reactions of the butadienylpalladium complexes, in particular their carbonylation reactions, will be published shortly.[30]

EXPERIMENTAL

Microanalytical and molecular-weight data (determined by the Sheffield University Microanalytical Service) are collected in Table 3; ^{1}H n.m.r. (60 MHz, Perkin-Elmer R-12B; 220 MHz, Perkin-Elmer R-34) and ^{13}C n.m.r. (JEOL PFT-100) data are collected in Tables 1 and 2 respectively. Far-i.r. spectra were determined on a Perkin-Elmer 180 spectrometer. All the reactions were carried out under an atmosphere of nitrogen even though the products were rarely air-sensitive. V.p.c. separations were carried out on a Perkin-Elmer F/11 vapour-phase chromatograph using a 6 ft glass column packed with OV-17 [2% methylphenyl silicone on Chromasorb G (80—100 mesh)]. Light petroleum is that fraction of b.p. 80—100 °C unless otherwise stated.

TABLE 3

Analyses and molecular weights (calculated values in parentheses)

	Complex	Analysis (%) C	H	N	Cl	Other	*M*
(2)	$[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3]_2[Pd_2Cl_6]$	36.7 (36.7)	5.3 (5.3)		23.2 (23.2)		
(3)	$[\{Pd(C_4Bu^t{}_2Me_2)Cl_2\}_2]$	45.4 (45.5)	6.5 (6.5)		19.2 (19.2)		723 (739.1)
(4)	$[\{Pd(C_4Bu^t{}_2Me_2)Br_2\}_2]$	37.1 (36.7)	5.0 (5.2)			Br 35.6 (34.9)	887 (916.7)
(5)	$[\{Pd(C_4Bu^t{}_2Me_2)I_2\}_2]$	30.5 (30.4)	4.3 (4.4)			I 41.2 (40.5)	1 062 (1 114.7)
(6)	$[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3][PF_6]$	39.3 (39.6)	5.4 (5.6)		13.2 (12.5)		848 (848.8)
(10A)	$[\{Pd(CBu^t{=}CMeCMe{=}CBu^tCl)Cl\}_2PdCl_2]$	37.3 (36.7)	5.1 (5.3)		22.0 (23.2)		1 006 (916.1)
(10B)	$[\{Pd(CBu^t{=}CMeCMe{=}CBu^tCl)Cl\}_2]$	45.9 (45.5)	6.4 (6.5)		18.3 (19.2)		718 (739.1)
(13)	$[Pd(CBu^t{=}CMeCMe{=}CBu^tCl)(acac)]\cdot 0.1CH_2Cl_2$ *	51.6 (51.6)	7.1 (7.1)		8.9 (9.6)		425 (433.3)
(14)	$[Pd(CBu^t{=}CMeCMe{=}CBu^tCl)(S_2CNMe_2)]$	44.1 (44.9)	6.5 (6.6)	3.0 (3.1)	7.7 (7.8)	S 12.9 (14.1)	405 (454.2)
(17)	$[Pd(CBu^t{=}CMeCMe{=}CBu^tCl)$-$(MeSCH_2CH_2SMe)Cl]$	43.4 (43.9)	6.9 (6.9)		13.9 (14.4)	S 12.8 (13.0)	510 (492)

* The ^{1}H n.m.r. spectrum shows the presence of dichloromethane.

$[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3]_2[Pd_2Cl_6]$ (2).—4,4-Dimethylpent-2-yne (0.48 g, 5.0 mmol) was stirred with bis(benzonitrile)dichloropalladium (0.96 g, 2.5 mmol) for 2 h in dichloromethane (20 cm^3) at 20 °C. A thick precipitate was formed and this was filtered off, washed with light petroleum, and dried in air. The filtrate was evaporated to 5 cm^3 and another precipitate of complex (2) was obtained after standing for 0.25 h. Total yield 0.57 g (80%).

$[\{Pd(C_4Bu^t{}_2Me_2)Cl_2\}_2]$ (3).—Pyridine (0.15 g, 2 mmol) was added dropwise to a stirred suspension of (2) (0.92 g, 1 mmol) in dichloromethane (20 cm^3). A yellow solution was obtained which deposited dichlorobis(pyridine)palladium as a yellow solid after 10 min. This was filtered off and the filtrate evaporated to dryness; the residue was washed with light petroleum to give yellow crystals (yield 0.61 g, 74%).

$[Pd_2(C_4Bu^t{}_2Me_2)_2Cl_3][PF_6]$ (6).—(*a*) A solution of (3) (0.37 g, 0.5 mmol) in dichloromethane (10 cm^3) was filtered into a solution of ammonium hexafluorophosphate (0.81 g, 5 mmol) in acetone (10 cm^3). A pale yellow solution was obtained after filtering off the precipitated ammonium chloride. The solution was evaporated under reduced pressure, and the yellow residue was washed with water and then dissolved in acetone. The acetone solution was allowed to crystallise to give yellow platelets of complex (6) (yield 0.39 g, 91%).

(*b*) Silver hexafluorophosphate (30 mg, 0.1 mmol) was added to a solution of bis(acetonitrile)dichloropalladium (50 mg, 0.2 mmol) in CD$_3$CN (0.5 cm^3); the solution was filtered and transferred to an n.m.r. tube. 4,4-Dimethylpent-2-yne (80 mg, 0.8 mmol) was added and the ^{1}H n.m.r. spectrum immediately recorded. This showed four peaks in a 2 : 2 : 1 : 1 ratio at δ 1.1, 1.4, 1.69, and 1.93 p.p.m., identical to that of a 1 : 1 mixture of (6) and free 4,4-dimethylpent-2-yne. Thus 2 equivalents of acetylene have reacted to give the cationic cyclobutadiene complex (6).

$[\{Pd(C_4Bu^t{}_2Me_2)Br_2\}_2]$ (4).—Hydrobromic acid (0.16 g, 2 mmol) was added to a stirred solution of complex (3) (0.37 g, 0.5 mmol) in dichloromethane (20 cm^3) and an orange solution was formed. Water (20 cm^3) was added and the dichloromethane layer was separated, washed with water, and dried over sodium sulphate. The solution was evaporated to a small volume (5 cm^3) and light petroleum added; orange crystals of complex (4) were obtained (yield 0.32 g, 73%).

[{Pd($C_4Bu^t{}_2Me_2$)I_2}$_2$] (5).—Sodium iodide (0.15 g, 1 mmol) was added to a stirred solution of complex (3) (0.37 g, 1 mmol) in acetone (30 cm^3) to give a purple solution. The sodium chloride formed was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane and crystallised from dichloromethane and light petroleum to give purple crystals of complex (5) (yield 0.34 g, 62%).

[{Pd(CBu^t=CMeCMe=CBu^{t}Cl)}$_2$PdCl$_2$] (10A).—4,4-Dimethylpent-2-yne (0.48 g, 5.0 mmol) was added to a stirred suspension of [Pd(NCPh)$_2$Cl$_2$] (0.96 g, 2.5 mmol) in acetone (10 cm^3) at 20 °C and a red solution was obtained. After some minutes a yellow precipitate formed and the solution became lighter in colour. The precipitate of complex (10A) was filtered off, washed with light petroleum, and dried in air (yield 0.45 g, 61%). A similar reaction occurred in nitromethane but the product was more difficult to purify than when obtained from acetone.

[{Pd(CBu^t=CMeCMe=CBu^{t}Cl)Cl}$_2$] (10B).—4,4-Dimethylpent-2-yne (0.48 g, 5.0 mmol) was added to a stirred solution of [Pd(NCPh)$_2$Cl$_2$] (0.96 g, 2.5 mmol) in dichloromethane (20 cm^3) cooled in an ice-water bath. After 10 min triphenylphosphine (0.65 g, 2.5 mmol) dissolved in dichloromethane (5 cm^3) was added and a yellow precipitate of dichlorobis(triphenylphosphine)palladium was obtained. The suspension was filtered and the filtrate evaporated at 0 °C under reduced pressure to leave a yellow solid. This solid, complex (10B), was washed with light petroleum and dried in air (yield 0.53 g, 72%).

[Pd(CBu^t=CMeCMe=CBu^{t}Cl)(acac)] (13).—A suspension of pentanedionatothallium(I) (1.2 g, 4 mmol) and (10A) (0.92 g, 1 mmol) in dichloromethane (20 cm^3) at 0 °C was stirred for 0.5 h. The cream precipitate of thallium chloride was filtered off and the filtrate was evaporated to dryness under reduced pressure to give a yellow solid. This was extracted with pentane, the solution evaporated to dryness, and the residue was crystallised at 0 °C from dichloromethane and methanol (yield 0.52 g, 79%).

[Pd(CBu^t=CMeCMe=CBu^{t}Cl)(S$_2$CNMe$_2$)].—Sodium dimethyldithiocarbamate dihydrate (0.8 g, 4 mmol) dissolved in acetone (10 cm^3) was added to a suspension of (10A) (0.92 g, 1 mmol) in dichloromethane (10 cm^3) at 0 °C and the mixture was stirred for 0.5 h. The yellow precipitate of [Pd(S$_2$CNMe$_2$)$_2$] was filtered off and the filtrate evaporated to dryness. The residue was extracted with pentane and evaporated to dryness to leave a yellow solid, which was crystallised at 0 °C from dichloromethane and diethyl ether (yield 0.62 g, 60%).

[Pd(CBu^t=CMeCMe=CBu^{t}Cl)(bipy)Cl] (*Isomer* 11).—4,4-Dimethylpent-2-yne (0.48 g, 5.0 mmol) was added to a stirred solution of [Pd(NCPh)$_2$Cl$_2$] (0.96 g, 2.5 mmol) in dichloromethane (15 cm^3) at 0 °C. 2,2′-Bipyridyl (0.95 g, 5 mmol) was added after 10 min and the (2,2′-bipyridyl)-dichloropalladium formed was filtered off. The yellow filtrate was then evaporated to dryness under reduced pressure and the residue washed with diethyl ether and crystallised at 0 °C from dichloromethane and light petroleum, to give yellow needles (yield 0.41 g, 57%).

[Pd(CBu^t=CMeCMe=CBu^{t}Cl)(bipy)Cl] (*Isomer* 12).—A solution of complex (11) (0.52 g, 1 mmol) in chloroform (25 cm^3) was heated under reflux for 0.5 h. The cooled solution was filtered and evaporated to give a yellow oil. This was crystallised from dichloromethane and light petroleum to give yellow crystals (yield 0.48 g, 95%).

[Pd(CBu^t=CMeCMe=CBu^{t}Cl){MeS(CH$_2$)$_2$SMe}Cl] (17).—4,4-Dimethylpent-2-yne (0.48 g, 5.0 mmol) was added to a stirred solution of [Pd(NCPh)$_2$Cl$_2$] (0.96 g, 2.5 mmol) in dichloromethane (15 cm^3) at 0 °C. 2,5-Dithiahexane (0.6 g, 5 mmol) was added after 10 min and the yellow precipitate of dichloro(2,5-dithiahexane)palladium was filtered off. The yellow filtrate was evaporated to dryness under reduced pressure and the residue washed with diethyl ether and crystallised from dichloromethane and light petroleum (b.p. 60—80 °C) to give yellow platelets (yield 0.39 g, 48%).

Reaction of (11) *or* (12) *with* HCl.—Hydrogen chloride gas was passed through a solution of (12) (0.52 g, 1 mmol) in dichloromethane (20 cm^3); immediate precipitation of yellow [Pd(bipy)Cl$_2$] occurred and the solution became lighter in colour. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was extracted with pentane and chromatographed on silica gel in pentane. The first 100 cm^3 of eluate were collected and evaporated to give a colourless oil (yield 0.21 g, 91%). Mass spectrum: parent ion at m/e 228. The products were identical from both complexes (11) and (12). This was shown by ^{1}H and ^{13}C n.m.r. spectroscopy, and vapour-phase chromatography (v.p.c.) (retention time 13 min, OV-17 column, initial temperature 100 °C rising at 2° min^{-1}).

Reaction of (11) *or* (12) *with* 3-*Chloro*-2-*methylprop*-1-*ene*.—3-Chloro-2-methylprop-1-ene (0.1 g, 1.1 mmol) was added to a solution of (12) (0.52 g, 1 mmol) in benzene (20 cm^3) and the mixture heated under reflux for 3 h. After cooling the reaction mixture, the yellow precipitate of [Pd(bipy)Cl$_2$] was filtered off and the filtrate was evaporated under reduced pressure. The residual oil was chromatographed on silica gel in pentane. Evaporation of the eluate under reduced pressure gave the product as a colourless oil (yield 0.24 g, 84%). The same compound was obtained from both isomers (11) and (12). This was shown by ^{1}H n.m.r. and mass spectrometry (parent ion m/e 282).

Reaction of Bu^{t}C$_2$Me *with* [Pd(NCPh)$_2$Cl$_2$] *at* −50 °C.—Bis(benzonitrile)dichloropalladium (38 mg, 0.1 mmol) was dissolved in dichloromethane (0.5 cm^3); the solution was filtered and transferred to an n.m.r. tube, which was then cooled to −78 °C in an acetone–solid CO$_2$ bath. 4,4-Dimethylpent-2-yne (bma, 22 μl, 0.2 mmol) was added and the ^{1}H n.m.r. spectrum was recorded at −50 °C. This showed peaks at δ 1.70 (Me), 1.10 (Bu^t) (free acetylene) and 2.12 (Me) and 1.50 p.p.m. (Bu^t) (co-ordinated acetylene). The spectrum was integrated several times over the methyl, t-butyl, and phenyl regions, and the average value of the integration taken in order to determine an accurate ratio for free bma : co-ordinated bma : [Pd(NCPh)$_2$Cl$_2$]. The experiment was repeated using other ratios of acetylene : palladium and the results are shown below:

total bma :	Pd	free bma :	co-ordinated bma	co-ordinated bma :	Pd
1.5	1	1.25	1	2	3
2.75	1	3	1	2	3
6.5	1	9	1	2	3

Addition of excess of trimethyl phosphite (90 mg, 0.3 mmol) to a solution at −50 °C (made up as described above) regenerated the free acetylene and gave [Pd{P(OMe)$_3$}$_2$Cl$_2$], identified by its ^{1}H n.m.r. spectrum.

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