Reversible Cyclobutane Formation: the Ring Closure of σ,π-2-(Pentamethylcyclopentadienyl)-2-phenylethylpalladium Compounds to (2-4-η-1,2,3,4,5-Pentamethyl-6-*endo*- and -6-*exo*-phenylbicyclo[3.2.0]hept-2-enyl)palladium Compounds

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The cyclisation of the dynamic σ,π-complex $[\{Pd(\alpha\text{-} \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)Cl\}_2]$ (1α,β) is shown to lead to the bicyclo[3.2.0]hept-2-enylpalladium complexes, $[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)Cl]_2$ (1γ, phenyl *endo* to palladium) and $[Pd(\delta\text{-}C_5Me_5CHPhCH_2)Cl]_2$ (1δ; phenyl *exo*). The *exo*-phenyl isomer is the most stable end product and the cyclisation to a cyclobutane (1α,β) $\longrightarrow$ (1γ) is reversible. Solvate complexes of the $\alpha \rightleftharpoons \beta$ form $[Pd(\alpha\text{-} \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)L_2][PF_6]$ (L = MeCN or Me_2CO) were obtained but attempts to prepare the cyclo-octadiene (cod) or cyclo-octatetraene (cot) derivatives led to the γ (phenyl *endo*) cyclised forms, $[Pd(\gamma\text{-}C_5Me_5CHPhCH_2(L_2)][PF_6]$ (L_2 = cod or cot), from which the pure halides $[\{Pd(\gamma\text{-}C_5Me_5CHPhCH_2)X\}_2]$ (X = Cl, Br, or I) and the pentane-2,4-dionate were prepared. Analogous derivatives of the δ-series (phenyl *exo*) were also synthesised. The ^1H and ^{13}C n.m.r. spectra have been measured; a novel form of isomerism about the halide bridge is described for (1γ), and the Karplus relation of coupling constant to dihedral angle has been shown to be obeyed in a near-planar cyclobutane by a comparison of the hydrogen positions determined from the *X*-ray structure of $[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)(acac)]$ and the cyclobutane J(H–H) values in a number of complexes.

The reversible cyclisation of a σ,π-complex to a cyclobutane derivative allows a reinterpretation of the cubane to cuneane isomerisation catalysed by $[PdCl_2(PhCN)_2]$.

In 1973 one of us reported,[1] in the course of an investigation of the chemistry of the 'lightly stabilised' Pd–C σ,π-bonded dynamic chloro-complex, $[\{Pd(\alpha \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)Cl\}]$, (1$\alpha\beta$) (which is in dynamic equilibrium between the forms α and β) that it underwent spontaneous cyclisation to an isomeric chloro-complex, (1δ) in [^{2}H]chloroform solution at +20 °C (Scheme 1). The reaction was complete in 5 days. When the reaction was followed by ^1H n.m.r. spectroscopy resonances were observed which grew to a maximum after *ca.* 20 h, after which they slowly decayed. The elucidation of the nature of this apparent intermediate and our observation that the reaction involved was an example of a novel process in organo-transition metal chemistry, the reversible formation of a C–C bond in a cyclobutane ring, forms the subject of this paper. A preliminary communication of part of this work has appeared.[2]

In order to simplify a somewhat complex series of reactions the following code has been adopted: the arabic numerals refer to the co-ligand [(1), chloride, (2), pentanedionate, *etc.*)] while the Greek letter is used to designate the form of the organic ligand. Thus, $\alpha\beta$ indicates the dynamic σ,π-system $[Pd(\alpha\text{-}C_5Me_5CHPhCH_2)X] \rightleftharpoons [Pd(\beta\text{-}C_5Me_5CHPhCH_2)X]$ (Scheme 1), γ indicates the *endo*-6-phenylbicyclo[3.2.0]heptenyl and δ the *exo*-6-phenyl-bicyclo[3.2.0]heptenyl series. Thus (1δ) refers to the chloro-complex of the *exo*-6-phenyl isomer, and (3$\alpha\beta$) to the bis-acetonitrile cationic complex of the α- and β-forms in dynamic equilibrium.

RESULTS AND DISCUSSION

Reactions of Complex (1$\alpha\beta$) *with L* (MeCN or Me_2CO) *and* L_2 [*Cyclo-octa*-1,5-*diene* (*cod*) *or Cyclo-octatetraene*

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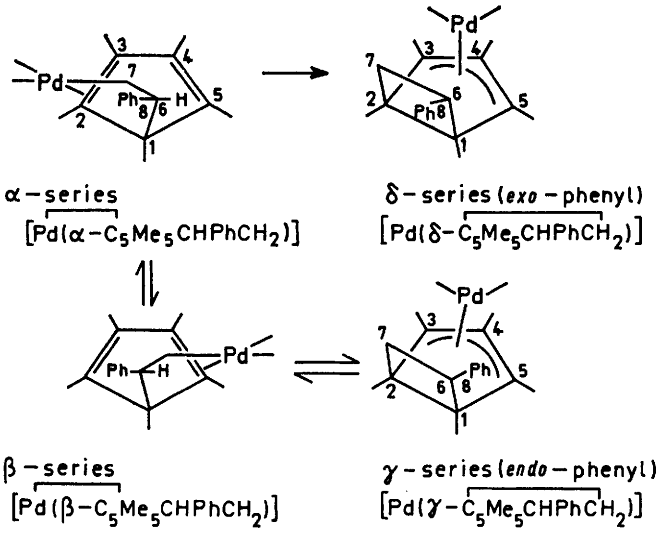
[1] T. Hosakawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1973, **95**, 4914.

[2] D. J. Mabbott, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1975, 521.



$$[\mathrm{Pd}(\alpha\text{-}\rightleftharpoons\beta\text{-}\mathrm{C_5Me_5CHPhCH_2})\mathrm{Cl}]_2 + \mathrm{MeCOCH_2COMe\text{–}base}$$
(1αβ)

$$\longrightarrow [\mathrm{Pd}(\alpha\text{-}\rightleftharpoons\beta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{acac})]$$
(2αβ)

$$(1\alpha\beta) + \mathrm{Ag[PF_6]\text{–}MeCN} \longrightarrow [\mathrm{Pd}(\alpha\text{-}\rightleftharpoons\beta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{MeCN})_2][\mathrm{PF_6}]$$
(3αβ)

$$(1\alpha\beta) + \mathrm{Ag[PF_6]\text{–}Me_2CO} \longrightarrow [\mathrm{Pd}(\alpha\text{-}\rightleftharpoons\beta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{Me_2CO})_2][\mathrm{PF_6}]$$
(4αβ)

$$(4\alpha\beta) + \mathrm{LiCl\text{–}Me_2CO} \longrightarrow (1\alpha\beta)$$

$$(4\alpha\beta) + \mathrm{MeCOCH_2COMe\text{–}base} \longrightarrow (1\alpha\beta)$$

$$(4\alpha\beta) + \mathrm{cod} \longrightarrow [\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{cod})][\mathrm{PF_6}]$$
(5γ)

$$(4\alpha\beta) + \mathrm{cot} \longrightarrow [\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{cot})][\mathrm{PF_6}]$$
(6γ)

$$(5\gamma) \text{ or } (6\gamma) + \mathrm{LiX\text{–}Me_2CO} \longrightarrow [\{\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})\mathrm{X}\}_2]$$
(1γ; X = Cl)
(7γ; X = Br)
(8γ; X = I)

$$(5\gamma) + \mathrm{MeCOCH_2COMe\text{–}base} \longrightarrow [\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{acac})]$$
(2γ)

$$(1\gamma) \overset{20\,^\circ\mathrm{C}}{\rightleftharpoons} (1\alpha\beta) \longrightarrow [\{\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})\mathrm{Cl}\}_2]$$
(1δ)

$$(2\gamma) \xrightarrow{20\,^\circ\mathrm{C}} (2\alpha\beta)$$

$$(1\delta) + \mathrm{Ag[PF_6]\text{–}MeCN} \longrightarrow [\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{MeCN})_2][\mathrm{PF_6}]$$
(3δ)

$$(1\delta) + \mathrm{Ag[PF_6]\text{–}cod} \longrightarrow [\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{cod})][\mathrm{PF_6}]$$
(5δ)

$$(1\delta) + \mathrm{Ag[PF_6]\text{–}cot} \longrightarrow [\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{cot})][\mathrm{PF_6}]$$
(6δ)

$$(5\delta) + \mathrm{LiX\text{–}Me_2CO} \longrightarrow [\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})\mathrm{X}]_2$$
(1δ; X = Cl)
(7δ; X = Br)

$$(5\delta) + \mathrm{MeCOCH_2COMe\text{–}base} \longrightarrow [\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})(\mathrm{acac})]$$
(2δ)

SCHEME 1

(cot)] in the Presence of Ag[PF$_6$].—Reaction of the chloro-complex (1αβ) with Ag[PF$_6$] in acetonitrile solution gave the yellow bis-acetonitrile cationic complex (3αβ) which was stable at −10 °C. The ^{1}H n.m.r. spectrum at +30 °C was broad owing to an exchange process which was frozen out at −30 °C to give a spectrum which showed nine resonances of differing intensities in the methyl region. This suggested that the acetonitrile complex was also composed of two isomers [Pd(α-C$_5$Me$_5$CHPhCH$_2$)(MeCN)$_2$]$^+$ $\rightleftharpoons$ [Pd(β-C$_5$Me$_5$CHPhCH$_2$)(MeCN)$_2$]$^+$ in dynamic equilibrium, as had been found for (1αβ) and its pentanedionato-derivative (2αβ).[1] When set aside in solution at −20 °C for 4 h the acetonitrile complex partially isomerised as shown by the growth of new peaks in the ^{1}H n.m.r. spectrum.

Attempts to isolate the bis-acetone complex (4αβ) analogous to (3αβ) were unsuccessful since this complex was only stable in solution. On removal of solvent, decomposition to palladium metal and the α- and β-pentamethylcyclopentadienylstyrenes occurred.[1] A solution of the acetone complex in [^{2}H$_6$]acetone showed very similar characteristics to the acetonitrile complex; the ^{1}H n.m.r. spectrum at +25 °C was broad but when the solution was cooled to −10 °C five strong sharp methyl resonances appeared [at δ 0.96, 1.62, 1.87, 1.91, and 2.14] which were probably due to the predominant 'frozen out' isomer [*i.e.* (4α) or (4β)], together with other, smaller resonances. Again, this sample partially isomerised at +25 °C during 2 h to give new resonances [at δ 1.07, 1.11, 1.26, and 1.35].

The reversibility of the formation of the acetone-solvated complex and the fact that no reorganisation of the organic ligand (α- $\rightleftharpoons$ β-C$_5$Me$_5$CHPhCH$_2$Pd) had occurred was shown by adding lithium chloride or pentane-2,4-dione–sodium carbonate to a freshly prepared cold solution of complex (4αβ). These reactions gave the chloride (1αβ) and the pentanedionato-complex (2αβ) in 73 and 55% yields respectively.

In contrast to the above reactions, which occurred without any rearrangement of the organic ligand, when the acetone complex (4αβ) was treated with either cod or cot new cationic complexes (5γ) and (6γ) containing cod and cot respectively were isolated in which the organic ligand had undergone isomerisation from the αβ to the γ-form. Attempts to prepare related complexes from (4αβ) with other dienes (norbornadiene, dicyclopentadiene, hexa-1,5-diene, or cyclo-octa-1,3-diene) all led to decomposition and no complexes could be isolated or detected.

In their n.m.r. spectra the new cod and cot complexes (5γ) and (6γ) showed sharp resonances for the organic ligand which were not temperature-dependent. The spectra did, however, show exchange processes involving the cod or cot presumably related to those of the η^3-allylic complexes, [Pd(all)(cod)]$^+$ and [Pd(all)(cot)]$^+$, which have been discussed elsewhere.[3]

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[3] D. J. Mabbott, B. E. Mann, and P. M. Maitlis, *J.C.S. Dalton*, in the press.

The γ-endo-6-*Phenylbicyclo*[3.2.0]*hexenyl Complexes.*—On reaction of the cod or cot complexes (5γ) or (6γ) with lithium halides or pentane-2,4-dione–sodium carbonate a series of new complexes, (1γ), (7γ), (8γ), and (2γ) *respectively*, were obtained which showed static ^{1}H n.m.r. spectra different from those of the complexes (1αβ) or (2αβ) as well as from that of (1δ), the previously observed rearrangement product of (1αβ).

In these preparations of (1γ), (2γ), (7γ), and (8γ) some of the cod complex (5γ) was always recovered, even in the presence of a large excess of reactant. It is clear, therefore, that an equilibrium is involved which it is difficult

$$[\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})\mathrm{cod}][\mathrm{PF_6}] + \mathrm{MX} \rightleftharpoons [\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})\mathrm{X}] + \mathrm{cod} + \mathrm{M}[\mathrm{PF_6}]$$

to move entirely over to the right-hand side.

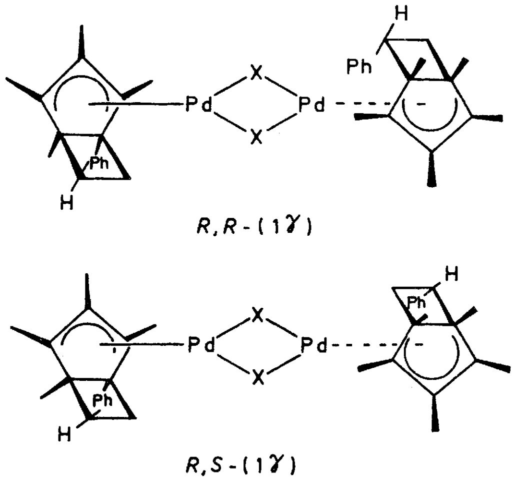
The organic ligand in all these complexes was the same (γ-$\mathrm{C_5Me_5CHPhCH_2}$) form. It was further established that this ligand also had an η^3-bicyclo[3.2.0]heptenyl skeleton but that it differed from the ligand in complex (1δ) and its derivatives in that the phenyl on the cyclobutane ring was *endo* to the metal in the γ-form but *exo* in the δ. This was shown most clearly by the *X*-ray structure of the pentanedionato-derivative (2γ),[2,4] but a comparison of the ^{1}H and ^{13}C n.m.r. spectra (Tables 1 and 2) of the complexes (1γ) and (1δ), (7γ) and (7δ), (5γ) and (5δ), (6γ) and (6δ), and (2γ) and (2δ) also indicated the basic structural similarities. The range of *exo*-phenyl (δ-$\mathrm{C_5Me_5CHPhCH_2PdX}$) derivatives was also extended and the new compounds (3δ), (5δ), (6δ), and (7δ) were synthesised as shown (Scheme 1).

N.m.r. Spectra.—The 100 MHz ^{1}H n.m.r. spectrum of the complex (1γ) showed, in addition to the cyclobutane CH and $\mathrm{CH_2}$ and the phenyl resonances, five signals in the methyl region; four of these were sharp singlets but the lowest field resonance appeared as a doublet. At 220 MHz all five of the methyl resonances were doubled and the change in separation of the lowest-field doublet from *ca.* 6 Hz at 100 MHz to 16 Hz at 220 MHz indicated that the doubling was not due to coupling but arose from the presence of two isomers. The presence of two isomers was confirmed by the observation of a doubling of the ^{13}C resonances of the skeletal carbons, C(1), C(2), C(4), and C(5), of the bicyclo[3.2.0]heptenyl ligand but no doubling could be resolved on the other carbons or the methyls.

The 100 MHz ^{1}H spectrum of the bromo-complex (7γ) also showed a doubling of the lowest-field methyl, while the iodo-complex (8γ) merely showed this resonance as broader ($W_{\frac{1}{2}} = 12$ Hz) than the others ($W_{\frac{1}{2}} = 6$ Hz). None of the monomeric complexes (5γ), (6γ), or (2γ), showed any sign of such a doubling and the existence of two such isomers must, therefore, be due to the halide bridge.

Six such isomers may be distinguished which fall into two types, depending on whether the two allylic groups in the dimer are *cis* (eclipsed) or *trans* to each other. In each case, the metal is on the same side of the ring as the fused cyclobutane and the phenyl is *endo* to the metal.

Each half of the dimer $[\mathrm{Pd}(\gamma\text{-}\mathrm{C_5Me_5CHPhCH_2})]$ can exist as the enantiomeric *R*- and *S*-forms and hence for both the *cis*- and the *trans*-arrangement *R,R*-, *S,S*-, and *R,S*-forms will be possible. The *R,R*- and *S,S*-forms are enantiomeric and hence cannot be resolved by conventional n.m.r. spectroscopy but the *R,S*- (*meso*) form will have a different spectrum. Models show that the *cis* (eclipsed) arrangement of allylic units is very unlikely for (1γ) since the non-bonded interactions between the organic ligands on the two halves of the dimer would be very large, and hence we suggest that the observed two forms are a mixture of the enantiomers, *R,R*- and *S,S*-, and the meso, *R,S*-, form where the allylic groups are staggered (*trans*) with respect to each other (Scheme 2). This type of isomerism has not been observed for the related $[\mathrm{Pd}(\delta\text{-}\mathrm{C_5Me_5CHPhCH_2})]$ series of compounds with phenyl *exo* to the metal.



SCHEME 2

Since the precision of the *X*-ray structure determination of the pentanedionato-derivative (2γ) of the γ-$\mathrm{C_5Me_5CHPhCH_2}$-ligand was great enough to locate the hydrogen atoms it was possible to use the results to test the validity of the Karplus relation for cyclobutanes.[5] The cyclobutane ring in complex (2γ) is very nearly square planar, the dihedral angle between the planes defined by C(1)C(5)C(7) and C(5)C(6)C(7) being 9°. The spectra of both the pentanedionato (2γ) and the cot (6γ) complexes were analysed in detail. The latter was the better resolved and the three protons on the cyclobutane ring were analysed as an AMX spectrum.

Three coupling constants, $J(\mathrm{a,b}) = J(\mathrm{a,c}) = 10$ and $J(\mathrm{b,c}) = 13$ Hz, were obtained for (6γ). The 13 Hz coupling was clearly the geminal one; from the Karplus relation, the dihedral angle between $\mathrm{H_a}$–C(6) and $\mathrm{H_b}$–C(7) should be $<20°$, while the dihedral angle between $\mathrm{H_a}$–C(6) and $\mathrm{H_c}$–C(7) should be between 140 and 160° for

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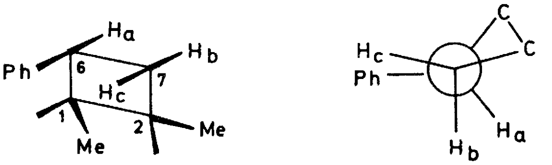
[4] P. M. Bailey and P. M. Maitlis, unpublished results.

[5] S. Sternhell, *Quart. Rev.*, 1969, **23**, 246.

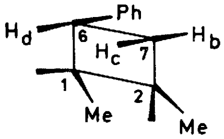
couplings of 10 Hz. From the crystal structure of (2γ) these angles are *ca.* 17 and 143° respectively.

The spectrum of the pentanedionato-complex (2γ) was measured at 220 MHz to obtain the best resolution of the cyclobutane protons which formed an ABX type spectrum. An analysis of the pattern showed that J(AX) must be opposite in sign to J(BX) and since vicinal coupling constants between protons on adjacent sp^3 carbon atoms are normally positive, the negative coupling must be the geminal one, *i.e.* J(b,c) = −13 Hz. This agrees well with literature values.[6] The vicinal coupling constants were found to be +10 and +8 Hz respectively and the values given for other complexes in Table 1 are assigned by analogy.



γ-Form

The coupling constants by themselves cannot, however, define whether H_b or H_c is *endo* to the metal. An assignment was, therefore, made on the chemical-shift argument in that the *X*-ray structure of (2γ) shows that H_c (*endo*) is only 2.7 Å from the palladium and is, therefore, in contact (sum of van der Waals radii = 3.1 Å). We have previously observed that hydrogens close to Pd^{II} and occupying an apical position with respect to the co-ordination plane of the metal suffer a downfield shift,[7] a phenomenon which has been interpreted theoretically.[8] We expect, therefore, the lower-field geminal cyclobutane protons to be H_c and all the assignments have been made on this basis.



δ-Form

By analogy with these assignments, we have revised the assignments of coupling constants and chemical shifts that were reported for the protons of the cyclobutane ring in the *exo*-phenyl chloro-complex (1δ), [{Pd(δ-$C_5Me_5CHPhCH_2$)Cl}$_2$]; data for the new complexes (3δ), (5δ), (6δ), and (7δ) of the same series are also given. The largest coupling, J(b,c) (−12 to −14 Hz) is again assigned to the geminal coupling and H_c, the methylenic proton *endo* to the metal, is again expected to be at lower field than H_b. The small variations observed in J(H–H) clearly reflect small changes in the dihedral angles arising from the adoption of slightly different conformations by the cyclobutane ring due to differing non-bonded intereactions, probably with the other ligands on the metal.

The ^{13}C n.m.r. spectra of the σ,π-complexes (1αβ) and (2αβ) were also measured at −40 °C and showed, as expected from the ^{1}H spectra, the presence of two isomers, α- and β-$C_5Me_5CHPhCH_2PdX$. At higher temperatures the spectra were broad indicating that the dynamic process previously observed in the ^{1}H spectra was occurring.[1]

Reversible Cyclobutane Formation.—The internal cyclisation of the σ,π-chloro-complex (1αβ) to the complex (1δ) had already been established as had the fact that rearrangement in this sense was not observed for the pentanedionato-complex (2αβ) *below* its decomposition point. The new Pd(γ-$C_5Me_5CHPhCH_2$) chloro- and pentanedionato-complexes (1γ) and (2γ) also rearranged in chloroform at 25 °C, in the first case to the complex (1αβ) and then to the δ-complex (1δ), and in the second case only as far as the complex (2αβ).

The extra peaks observed during the rearrangement of pure (1αβ) to (1δ) referred to above corresponded closely, but not exactly, to those of the [{Pd(γ-$C_5Me_5CHPhCH_2$)Cl}$_2$] complex (1γ). This lack of exact correspondence is not surprising since we have shown that the n.m.r. spectrum of (1γ) in particular is very sensitive to the nature of the other half of the dimer, and in a solution containing (1αβ), (1γ), and (1δ) crossed-dimer species are to be expected, *e.g.* [(α- $\rightleftharpoons$ β-$C_5Me_5CHPhCH_2)PdCl_2$Pd(γ- or δ-$C_5Me_5CHPhCH_2$)] or [(γ-$C_5Me_5CHPhCH_2$)PdCl_2Pd(δ-$C_5Me_5CHPhCH_2$)]. This difficulty was circumvented by conversion of the rearrangement product of the chloride (1αβ) into the pentanedionates (2) by reaction with pentanedionatothallium after 20 h/25 °C. This had the double advantage of converting the dimeric into the monomeric species, (2αβ), (2γ), and (2δ), and also of partially quenching the reaction since the rearrangement (2αβ) $\longrightarrow$ (2δ) does not proceed under these conditions. When this solution was examined by ^{1}H n.m.r. spectroscopy, the presence of all three pentanedionato-complexes, (2αβ), (2γ), and (2δ), was clearly observed, in particular their methyl and acac-H resonances [at δ, (2αβ), 0.87, 1.63, 1.67, 5.21; (2γ), 0.46, 0.96, 1.36, 1.38, 2.10, 5.20; (2δ), 1.03, 1.10, 1.22, 1.32, 2.00, 5.11]. The ratio of (2αβ) : (2γ) : (2δ) was 70 : 15 : 15.

This experiment demonstrated conclusively that the chloride (1αβ) underwent a reversible cyclisation to (1γ) and also an irreversible cyclisation to (1δ), and that the rates were very comparable. The relative tendencies for cyclisation of the α $\rightleftharpoons$ β to the γ or the δ-$C_5Me_5CHPhCH_2$ isomer must be quite evenly balanced and appears to depend strongly on the other ligands present. Thus the cationic solvate complexes (3αβ) and (4αβ) already rearrange at −20 °C in solution, and it was not possible to

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[6] R. C. Cookson, J. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, 1966, Suppl. **7**, 355.

[7] D. M. Roe, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1972, 1273.

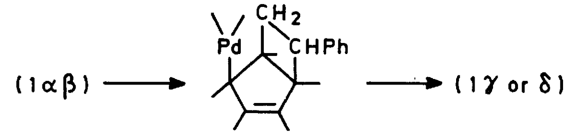
[8] A. D. Buckingham and W. Urland, *Mol. Phys.*, 1973, **26**, 1571; A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 4583.

prepare the cod or cot complexes (5αβ) or (6αβ); instead, on addition of either of these dienes to (4αβ) there was a clean *reaction* leading to the γ-forms (5γ) and (6γ) respectively.

The δ-isomers were the final products probably because they were the thermodynamically most stable forms, presumably because these isomers, with the phenyl *exo* to the metal, are subject to smaller non-bonded interactions than those with the phenyl *endo*.

It is tempting to suggest that the observed cyclisations to the δ- and γ-forms arise from a 1,2-*cis*-addition of Pd–σ–C to the co-ordinated double-bonds of the α- and β-forms respectively in a transition state where the co-ordinated double-bond is coplanar with the Pd–σ–C bond. Models of the α- or β-forms show that it would be quite easy to achieve coplanarity by a conformational change, which might well occur during the ' flipping ' of the metal from one double-bond to the other (α ⇌ β) which is observed in both complexes (1αβ) and (2αβ).[1] This process is closely related to the rotation of co-ordinated double bonds about their bonds to metals, which has been widely studied and shown to be a comparatively low-energy process.[9] However, the alternative possibility that the cyclisation proceeds by a 1,4-addition of Pd–σ–C to the diene cannot be entirely discounted on the present evidence. In that case the α-isomer would cyclise to the γ and the β to the δ-form.

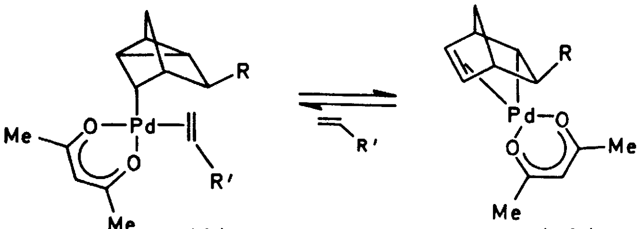
In either case the immediate product would be the η^1-allyl which would then rearrange to the more stable η^3-allylic form:



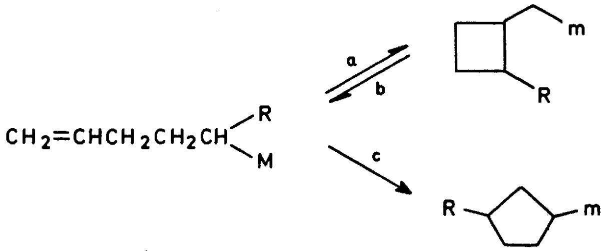
Quite the most remarkable feature of the reaction is the ease with which the C–C bond can be cleaved again in the γ-form. This type of cleavage has been observed for Pd^{II} in the nortricyclenyl (9)–norbornenyl (10) system[10] where a cyclopropane ring is formed or cleaved but it has not, to our knowledge, been observed for 4-membered rings.

However, such processes have been described in main-group organometallic chemistry, where evidence for both ring-opening and -closing reactions of the types (a) and (b) as well as the ring closure (c) have been cited for m = MgCl (Scheme 3) as well as for Li, Na, *etc.*[11,12] The formation of the four-membered rings is helped by a favourable transition state (I), for internal cyclisation where M–C and the double-bond are coplanar, and by the presence of methyl groups α to the metal.

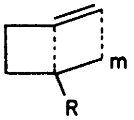
Our observation of the reversible process α/β ⇌ γ-$C_5Me_5CHPhCH_2Pd$ suggests that under suitable conditions this may be a general reaction path. It is tempting, therefore, to suggest that palladium(II)-catalysed skeletal isomerisation reactions that take place under conditions where the formation of carbonium ions is rather unlikely (*i.e.* in solvents of low polarity) can proceed in this way. One such example is the [$PdCl_2$-$(PhCN)_2$]-catalysed isomerisation of cubane to cuneane which proceeds rapidly in chloroform.[13] An alternative pathway to the ionic mechanism that has been suggested is shown in Scheme 4.



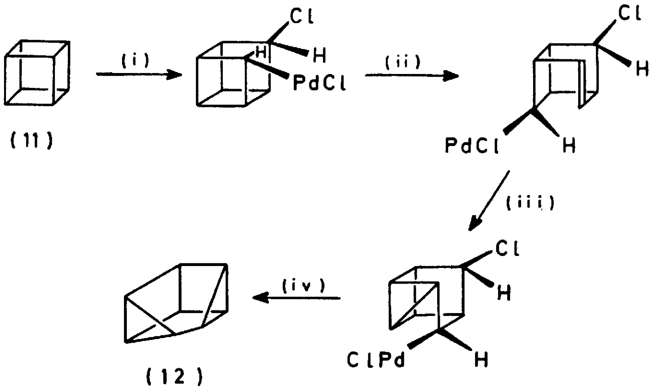
(9) (10)



SCHEME 3



(I)



SCHEME 4

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TABLE 1

^{1}H N.m.r. spectra at 100 MHz (δ), J(H–H) in parentheses (Hz)

Compound	Methyl	H_a	H_b	H_c	H_d	Ph	Other
(5γ) ^{b}	1.22, 1.46, 1.86, 1.86, 2.09	3.79 (10, 9)	*h*	3.41 (−14, 9)		7.39	2.33, 2.68, 5.80
(6γ) ^{b}	1.23, 1.47, 1.62, 1.68, 2.18	3.82 (10, 10)	2.61 (−13, 10)	3.28 (−13, 10)		7.38	5.98 ^{f}
(1γ) ^{a,d}	0.93, 0.99, 1.11, 1.21, 2.00 ^{e} 0.94, 1.02, 1.12, 1.23, 2.05 ^{e}	3.65 ^{c}	2.05 ^{c}	3.34 ^{c}		7.23 7.55	
(7γ) ^{a}	0.99, 1.14, 1.14, 1.36, 1.98 ^{e} 1.94 ^{e}	3.63 ^{c}	2.12 ^{c}	3.21 ^{c}		7.38	
(8γ) ^{a}	1.06, 1.24, 1.50, 1.70, 1.82 ^{g}	3.57 ^{c}	2.11 ^{c}	3.57 ^{c}		7.36	
(2γ) ^{a}	1.02, 1.09, 1.21, 1.31, 1.99	3.40 (10, 8)	2.02 (−13, 10)	3.31 (−13, 8)		7.21	1.54, 1.93, 5.11
(1δ) ^{a}	0.40, 0.91, 1.34, 1.37, 1.97		1.98 ^{c}	3.10 (−12, 10)	4.99 (10, 8)	7.21	
(3δ) ^{b}	0.51, 1.06, 1.47, 1.50, 2.22		2.27 ^{c}	2.94 (−13, 10)	4.63 (10. 8)	7.31	2.27
(5δ) ^{b}	0.61, 1.15, 1.91, 1.94, 2.19		*h*	*h*	4.24 (10, 9)	7.34	2.57, 6.07
(6δ) ^{b}	0.61, 1.15, 1.71, 1.74, 2.29		2.47 (−14, 9)	2.91 (−14, 10)	4.64 (10, 9)	7.34	6.26
(7δ) ^{a}	0.41, 0.91, 1.48, 1.51, 1.89		2.05 ^{c}	3.06 ^{c}	4.98 (11, 8)	7.17	
(2δ) ^{a}	0.46, 0.96, 1.34, 1.37, 2.10		1.91 ^{c}	2.92 (−13, 10)	4.57 (10. 8)	7.22	1.91, 5.20

[a] In [^{2}H]chloroform. [b] In [$^{2}H_6$]acetone. [c] J(H–H) not resolved. [d] At 220 MHz. [e] Two isomers, see text. [f] $W_{\frac{1}{2}}$ = 27 Hz at +30 °C. [g] $W_{\frac{1}{2}}$ = 12 Hz at +30 °C. [h] Not observed; broad or obscured.

TABLE 2

^{13}C-{^{1}H} N.m.r. spectra (in δ, $C_5Me_5CHPhCH_2$—ligand only)

Compounds	C(1), C(5)	C(2), C(4)	C(3)	C(6)	C(7)	Phenyls		Methyls
						C(8) ^{f}	C(*o*-), C(*m*-), C(*p*-)	
(5γ) ^{c}	52.4, 61.7	115.6, 122.1	130.4	44.0	37.4	143.7	129.8, 128.3, 128.0	13.6, 14.2, 16.8, 18.7, 23.6
(6γ) ^{c}	52.7, 62.0	*e*	130.8	44.0	37.7	143.2	130.0, 129.1, 128.2	14.0, 14.0, 16.2, 18.3, 23.4
(1γ) ^{a}	48.7, 58.4 ^{d}	96.6, ^{d} 96.2	113.3	42.7	33.3	140.1	128.1, 128.1, 125.9	13.3, 13.3, 14.3, 17.8, 22.1
	48.4, 58.4 ^{d}	97.4, 96.6 ^{d}	113.8	43.0	34.8	140.6		
(2γ) ^{a}	48.2, 57.9	87.7, 88.2	113.8	43.0	32.6	141.7	127.5, 127.3, 125.1	11.6, 12.7, 13.0, 18.1, 22.3
(1δ) ^{a}	49.9, 57.4	99.6, 103.1	113.4	44.6	31.5	141.1	128.5, 127.8, 125.7	12.7, 13.5, ^{d} 15.0, 19.4
(3δ) ^{a}	50.4, 57.9	103.0, 106.7	119.5	44.7	31.7	139.9	128.3, 128.3, 126.4	12.7, 13.4, ^{d} 15.0, 19.4
(5δ) ^{c}	53.1, 60.9	119.5, 124.3	129.7	46.3	32.5	140.5	129.7, 129.7, 128.0	13.3, 14.5, ^{d} 16.1, 20.5
(6δ) ^{b}	52.3, 60.0	*e*	*e*	45.6	32.0	140.9	129.2, 129.2, 127.4	13.3, 13.6, ^{d} 15.3, 19.8
(2δ) ^{a}	49.3, 56.7	90.0, 92.9	112.6	43.9	31.3	141.7	128.4, 128.0, 125.7	11.7, ^{d} 12.8, 15.1, 19.5

[a] In [^{2}H]chloroform. [b] In [$^{2}H_6$]acetone. [c] In [$^{2}H_3$]nitromethane. [d] Two resonances merged. [e] Not observed; broad or obscured. [f] C(8) is the phenyl carbon attached to C(6).

Here the first step (i) is a *trans*- (*exo*) addition of Pd–Cl across an edge of cubane (11), followed by (ii), a cyclobutylmethyl–alk-1-en-4-yl rearrangement in sense (b) above. If this is now followed by an alkenyl–cyclopentenyl ring closure (iii) [step (c) above] then the resultant tetracyclic species can eliminate $PdCl_2$ (iv) with the formation of a C–C bond to give cuneane (12). All the steps involved have their analogues in well-established organometallic reactions, and models of the intermediates show that no undue steric strains are present.

EXPERIMENTAL

All reactions were run under nitrogen. Yields and microanalytical data are given in Table 3, n.m.r. spectra are summarised in Tables 1 and 2.

[{Pd(α- $\rightleftharpoons$ β-$C_5Me_5CHPhCH_2$)Cl}$_2$], (1αβ).—This compound was obtained (60% yield) by a modification of the literature method 1 in which the temperature was held at 0 °C during the addition of bis(benzonitrile)dichloropalladium to the dichloromethane solution of but-2-yne and diphenylmercury. At −40 °C the ^{13}C n.m.r. spectrum showed the presence of two isomers; the major isomer was identified as the α-form {δ 120.9, 128.8 [C(1), C(2)], 134.6, 148.2 [C(3), C(4)], 65.0 [C(5)], 56.2 [C(6)], 46.4 [C(7)], and 141.5 [C(8)]} and the minor as the β-form {δ 119.9 [C(1), C(2) merged], 135.7, 148.6 [C(3), C(4)], 62.6 [C(5)], 46.7 [C(7)], and 141.1 [C(8)]}.

TABLE 3

Analytical data, decomposition points, and yields

Compound	Decomp. pt. (θ_c/°C)	Analyses: Found (calc.) (%)			Yield %
		C	H	Other	
(3αβ)	99—101	45.8 (46.1)	5.2 (5.1)	4.8 (4.9)N	54
(5γ)	178—180	52.3 (52.2)	5.9 (5.9)		78
(6γ)	113—115	52.5 (52.5)	5.4 (5.2)		78
(1γ)	117—120	56.6 (56.7)	6.1 (6.0)	9.2 (9.3)Cl	47
(7γ)	106—108	50.6 (50.8)	5.7 (5.4)	18.6 (18.8)Br	77
(8γ)	108—110	46.6 (45.7)	5.2 (4.9)	27.0 (26.9)I	76
(2γ)	101—102	62.3 (62.1)	7.0 (6.8)		60
(3δ)	78—81	45.9 (46.1)	5.3 (5.1)	5.3 (4.9)N	36
(5δ)	128—130	50.9 (51.3)	6.5 (6.2)		84
(6δ)	129—131	52.7 (52.5)	5.5 (5.2)		73
(7δ)	130—132	51.0 (50.8)	5.7 (5.4)	18.9 (18.8)Br	65

Solvate Complexes (3αβ) *and* (4αβ).—[Pd(α- $\rightleftharpoons$ β-$C_5Me_5CHPhCH_2$)$(MeCN)_2$][PF_6], (3αβ). Solid silver hexafluorophosphate (0.23 g, 0.9 mmol) was added to a stirred solution of compound (1) (0.34 g, 0.9 mmol) in acetonitrile (15 ml) at

−37 °C. Stirring was continued for 15 min after which the solution was allowed to warm up to +20 °C and the silver choride was filtered off. The solvent was removed *in vacuo* and the residual oil was crystallised by addition of diethyl ether and cooling to −10 °C. The resulting yellow-green crystalline solid (0.28 g, 0.49 mmol, 54%) was purified by filtration of an acetonitrile solution through a cellulose column and recrystallised from acetonitrile–diethyl ether to yield the analytically pure bright yellow crystals of compound (3).

$[Pd(\alpha\text{-} \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)(Me_2CO)_2][PF_6]$, (4αβ).

The acetone complex $[Pd(\alpha\text{-} \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)(Me_2CO)_2][PF_6]$ (4αβ) was made in acetone solution in the same way, but all attempts to isolate it resulted in decomposition. Attempts to prepare the dichloromethane-solvate complex were unsuccessful and only the decomposition products, α- and β-pentamethylcyclopentadienylstyrene and palladium metal, were isolated.

Addition of lithium chloride (0.16 g, 3.7 mmol) to a freshly prepared solution of the acetone-solvate complex (4αβ) {from (1αβ) (0.22 g, 0.58 mmol) and $Ag[PF_6]$ (0.15 g, 0.6 mmol) in acetone (10 ml)} regenerated complex (1αβ) (73% yield).

$[Pd(\alpha\text{-} \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)(acac)]$, (2αβ).—Addition of pentane-2,4-dione (0.25 g, 2.5 mmol) and sodium carbonate (0.4 g, 4 mmol) to a freshly prepared filtered solution of (4αβ) {from (1αβ) (0.39 g, 1.0 mmol) and $Ag[PF_6]$ (0.28 g, 1.1 mmol) in acetone (35 ml)} at 20 °C gave, after work-up and crystallisation from methanol, pale yellow crystals of (2αβ) (0.25 g, 55%).

At −40 °C the ^{13}C n.m.r. spectrum showed the presence of two isomers; the major isomer was identified as the α-form {δ 122.1, 128.9 [C(1), C(2)], 134.1, 147.0 [C(3), C(4)], 66.4 [C(5)], 55.2 [C(6)], 41.1 [C(7)], and 142.4 [C(8)]} and the minor as the β-form {δ 119.3 [C(1), C(2) merged], 135.4, 145.4 [C(3), C(4)], 63.8 [C(5)], 51.9 [C(6)], 39.4 [C(7)], and 140.4 [C(8)]}.

$[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)(cod)][PF_6]$, (5γ).—Silver hexafluorophosphate (0.20 g, 0.86 mmol) was added to a stirred solution of (1αβ) (0.30 g, 0.79 mmol) and cyclo-octa-1,5-diene (0.12 g, 1.1 mmol) in acetone (30 ml) at 20 °C. The reaction mixture was filtered to remove AgCl, and the solvent removed from the filtrate to leave a greenish oil which was crystallised from acetone–diethyl ether to give (5γ) as colourless crystals (0.33 g, 70%).

The above preparation in dichloromethane in place of acetone gave a higher yield (78%) and this route was the one more generally used. After isolation of (5γ), crystallisation of the mother-liquors from dichloromethane–diethyl ether yielded a white crystalline complex identified as $[Pd(\delta\text{-}C_5Me_5CHPhCH_2)(cod)][PF_6]$, (5δ), in 8% yield.

$[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)(cot)][PF_6]$ (6γ) was prepared in an identical manner from cyclo-octatetraene in 78% yield. The mother liquors again yielded 9% of $[Pd(\delta\text{-}C_5Me_5CHPhCH_2)(cot)][PF_6]$.

$[\{Pd(\gamma\text{-}C_5Me_5CHPhCH_2)X\}_2]$, (1γ, X = Cl), (7γ, X = Br), *and* (8γ, X = I).—Lithium chloride (0.35 g, 9 mmol) was added to a solution of $[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)(cod)][PF_6]$ (5γ) (0.84 g, 1.4 mmol) in acetone (50 ml) at 20 °C. After the solution had been stirred for 20 min the solvent was removed *in vacuo*, the residue washed with water, air-dried, and crystallised from chloroform–methanol to give yellow crystals of (1γ) (0.25 g, 47%). Crystallisation was also effected from benzene–light petroleum or dichloromethane–light petroleum, and in each case the ^1H n.m.r. spectrum showed the presence of solvent of crystallisation.

The same reaction on the cot complex (6γ) was investigated by ^1H n.m.r. spectroscopy and was shown to give only (1γ), cot, and some (6γ).

The bromo- and iodo-complexes (7γ) and (8γ) were prepared in the same way using lithium bromide and iodide respectively.

The far-i.r. spectra showed bridging ν(Pd–Cl) 244, 252 cm^{-1}, (1γ), ν(Pd–Br) 158 cm^{-1}, (7γ), and ν(Pd–I) 146 cm^{-1}, (8γ), and were consistent with their formulation as halide-bridged η^3-allylic dimers.

$[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)(acac)]$ (2γ).—The $[Pd(\gamma\text{-}C_5Me_5CHPhCH_2)(cod)][PF_6]$ complex (5γ) (1.2 g, 2.1 mmol) was added in small portions during 10 min to a stirred solution of pentane-2,4-dione (1 g, 10 mmol) in acetone (150 ml) at 20 °C containing sodium carbonate (2.2 g, 18 mmol). The solution was stirred for a further 10 min, after which it was filtered and the filtrate evaporated *in vacuo*. The residue was extracted with light petroleum, the solvent was removed, and the complex (2γ) was obtained as pale yellow crystals (0.45 g, 60%) after crystallisation from methanol. The complex (2γ) could also be prepared by reaction of (1γ) with pentanedionatothallium(I); ^1H n.m.r. spectroscopy showed it to be the only product.

Complexes of the $Pd(\delta\text{-}C_5Me_5CHPhCH_2)$ *Form*, (1δ), (2δ), (3δ), (5δ), (6δ), *and* (7δ).—The chloro-complex (1δ) was prepared in 80% yield by the literature method by isomerisation of (1αβ). The acetonitrile-solvate complex (3δ) was prepared from (1δ) in the same manner as (3αβ) from (1αβ). Again here, although a fairly stable solution of the acetone-solvate complex, $[Pd(\delta\text{-}C_5Me_5CHPhCH_2)(Me_2CO)_2][PF_6]$, could be obtained, attempts to isolate a solid always resulted in decomposition. The cod and cot complexes (5δ) and (6δ) were obtained from (1δ) by the route used for (5γ) and (6γ). Reaction of the cod complex (5δ) with lithium halide in acetone gave the chloride (1δ) (55%) and the bromide (7δ) (65%) respectively. The pentanedionato-complex (2δ) was also prepared from (5δ).

Quenching of the Isomerisation Reactions (1αβ $\rightleftharpoons$ (1γ); (1αβ) $\longrightarrow$ (1δ).—A solution of $[\{Pd(\alpha\text{-} \rightleftharpoons \beta\text{-}C_5Me_5CHPhCH_2)Cl\}_2]$ (1αβ) (0.18 g, 0.47 mmol) in [^{2}H]chloroform (0.5 ml) was kept at +20 °C for 20 h. Pentanedionatothallium (0.14 g, 0.47 mmol) was then added to the mixture which was well shaken and then centrifuged to remove TlCl. The 100 MHz ^1H n.m.r. spectrum clearly showed the presence of the pentanedionato-complexes (2αβ), (2γ), and (2δ) in the approximate ratios of 70 : 15 : 15 (see text).

We thank the S.R.C. for support of this work, I.C.I. Ltd. for a grant towards the purchase of chemicals, and Drs. P. M. Bailey and B. E. Mann for helpful discussion.

[6/721 *Received, 12th April*, 1976]