Reversible Cyclobutane Formation in a Palladium-mediated Reaction; the *X*-Ray Structure of {2–4-η-(1,2,3,4,5-Pentamethyl-6*R*-phenylbicyclo[3,2,0]-hept-2-enyl)}pentane-2,4-dionatopalladium

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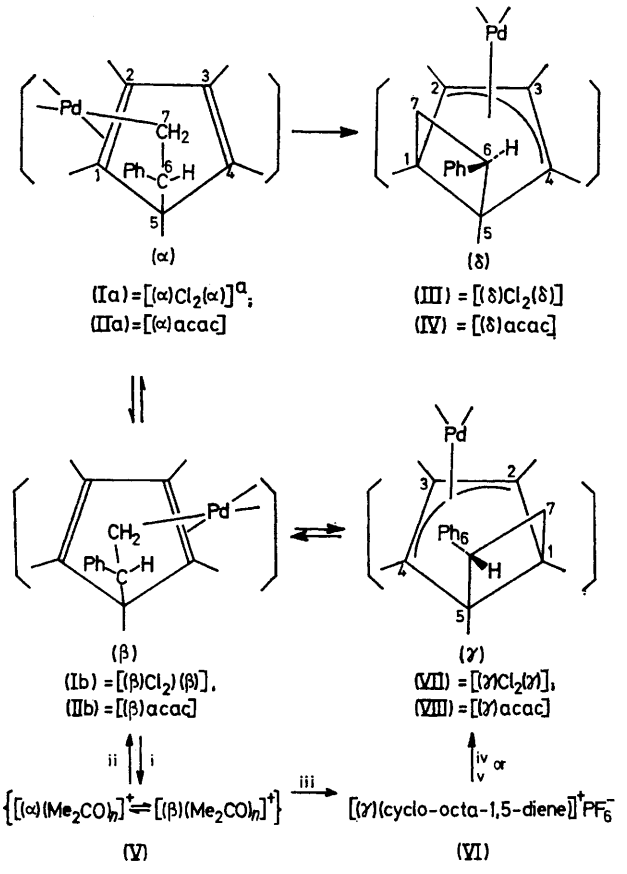
Summary The σ,η-complex (I) undergoes spontaneous reversible ring closure to give the *endo*-phenyl allylic complex (VII), as well as an irreversible ring closure to the thermodynamically most stable *exo*-phenyl allylic isomer (III); the crystal structure of (VIII), the pentanedionato-derivative of (VII), is reported.

REACTIONS involving the transition-metal-mediated cleavage of C–C bonds in cyclic ligands are still rare except for reactions of cyclopropanes.[1] We describe here a reaction wherein a co-ordinated olefin is inserted into a Pd–C σ-bond to give a cyclobutane and which is reversible.

The quantitative rearrangement of (I) [which is composed of the two forms (α) and (β) in dynamic equlibrium with each other] to the *exo*-phenyl allylic complex (III) has been described.[2] When this reaction was followed by ^{1}H n.m.r. spectroscopy (25°; $CDCl_3$) resonances, not due to either (I) or (III), were observed which grew to a maximum over *ca.* 20 h after which they slowly decayed.

The complex (VII) which gave rise to these resonances was obtained preparatively as shown (Scheme). Reaction of complex (I) with $AgPF_6$–acetone gave the somewhat unstable complex (V) from which (I) was regenerated (73% isolated yield) on treatment with LiCl. On reaction of (V)

with cyclo-octa-1,5-diene internal cyclisation to the form (γ) occurred to give the stable cationic complex (VI) (isolated yield 60%). Treatment of (VI) with LiCl gave complex (VII) (47%), or with acetylacetone–base gave (VIII) (60%). The close relationship between (VII) and (III), and between (VIII) and (IV), and the difference between all of these and (I) is most clearly shown by their ^{13}C n.m.r. spectra: (I)† δ 120·7, 129·5 [C(1) and C(2)]; 134·8, 148·5 [C(3) and C(4)]; 65·5 [C(5)], 56·7 [C(6)], and 46·3 [C(7)]; (III) 49·9, 57·4 [C(1) and C(5)]; 99·0, 103·0 [C(2) and C(4)]; 113·4 [C(3)], 44·6 [C(6)], and 31·5 [C(7)]; (IV) 49·3, 56·7 [C(1) and C(5)]; 92·9, 90·0 [C(2) and C(4)]; 112·6 [C(3)], 43·9 [C(6)], and 31·3 [C(7)]; (VI) 52·4, 61·6 [C(1) and C(5)]; 115·6, 122·1 [C(2) and C(4)]; 130·4 [C(3)], 44·0 [C(6)], and 37·4 [C(7)]; (VII)† 48·7 58·4 [C(1) and C(5)]; 96·2, 96·6 [C(2) and C(4)]; 113·3 [C(3)], 42·7 [C(6)], and 33·3 [C(7)]; (VIII) 48·2, 57·9 [C(1) and C(5)]; 87·7, 88·2 [C(2) and C(4)]; 113·8 [C(3)], 43·0 [C(6)], and 32·6 p.p.m. [C(7)].



SCHEME. (i) $AgPF_6$–Me_2CO, 20 °C; (ii) LiCl–Me_2CO; (iii) cyclo-octa-1,5-diene; (iv) LiCl–Me_2CO [to (VII)]; (v) acetylacetone–Na_2CO_3 [to (VIII)].

[a] [(α)Cl_2(α)] represents two units of structure (α) joined by a Pd_2Cl_2 bridge.

The structure of the ligand (γ) and in particular the stereochemistry adopted at C(6) were confirmed by an X-ray crystal structure determination of (VIII).

Crystal data: $C_{23}H_{30}O_2Pd$; the crystals were triclinic with $a = 15{\cdot}35(2)$, $b = 8{\cdot}34(1)$, $c = 14{\cdot}79(2)$ Å, $\alpha = 100{\cdot}5(1)$, $\beta = 141{\cdot}4(1)$, $\gamma = 97{\cdot}3(1)°$; $U = 1043$ Å^3; $Z = 2$, space group $P\bar{1}$. Three dimensional X-ray data were collected with the crystal mounted along the b axis, using Mo-K_α radiation (graphite monochromator) and a Stoe STAD1 2 diffractometer. 4417 Independent reflections were collected with $I_{obs} \geqslant 3\sigma(I_{obs})$; the structure was solved using Patterson and Fourier methods. Block-diagonal least-squares refinement has reduced R to 0·044 allowing anisotropic thermal vibration on all atoms.

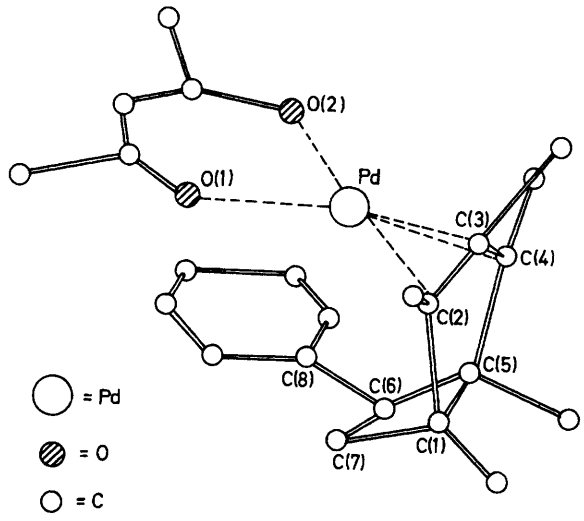


FIGURE. The structure of {2-4-η-(1,2,3,4,5-pentamethyl-6*R*-phenylbicyclo[3,2,0]hept-2-enyl)}pentane-2,4-dionatopalladium. (Hydrogen atoms omitted.) Important bonds lengths are (e.s.d's in parentheses): Pd–O(1) 2·105(4); Pd–O(2) 2·110(4); Pd–C(2) 2·141(5); Pd–C(3) 2·070(5); Pd–C(4) 2·103(5); C(1)–C(2) 1·525(7); C(2)–C(3) 1·425(7); C(3)–C(4) 1·436(7); C(4)–C(5) 1·532(7); C(5)–C(1) 1·570(7); C(5)–C(6) 1·585(7); C(6)–C(7) 1·558(8); C(7)–C(1) 1·562(8); C(6)–C(8) 1·501(7). Bond angles in the cyclobutane ring are 91, 88, 91, and 89°.

The main features of the structure are shown (Figure); bond lengths and bond angles are normal and the crowding that might be expected to arise from the Pd and the phenyl being on the same side of the molecule is relieved by a bending of the cyclopentenyl ring (dihedral angle 31°) and by opening the angle C(8)C(6)C(1) to 142°. The cyclobutane ring is very nearly square planar [dihedral angle between the planes C(1)C(5)C(7) and C(5)C(6)C(7) is 9°] and the angle between the cyclobutane ring and the plane C(2)C(1)-C(5)C(4) is 120°.

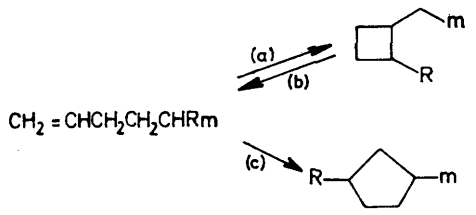
The presence of isomers containing the *endo*-phenyl allylic ligand (γ) during the rearrangement of (I) → (III) was demonstrated by quenching the reaction mixture (after 20 h; 20 °C) by converting the chlorides into the acetylacetonates; the n.m.r. spectrum of the mixture unambiguously showed the presence of (VIII) as well as (II) and (IV). Furthermore, the isolated complex (VII) spontaneously rearranged to (I) and then (III), and (VIII) rearranged to (II) (25°; $CDCl_3$).

It is therefore clear that (VII) is formed reversibly from (I) [probably by internal cyclisation of isomer (Ib)], that the energies of (I) and (VII) are very similar, and that the

† In each case the resonances of the major isomer are given; for (I) this corresponds to (α), while the two isomers observed for (VII) arise from two enantiomers existing in the η^3-allyl ligands.

activation barriers to their interconversions are low. The complex (III) is the thermodynamically favoured end product presumably because it is a less crowded molecule.

Ring opening reactions of this type are likely to be



important in metal-catalysed skeletal rearrangements, particularly since processes such as (a), (b), and (c), are also undergone by magnesium compounds (m = MgX)[3,4]; clearly, there is a whole family of such reactions.

For example, the $[PdCl_2(PhCN)_2]$–$CHCl_3$-catalysed isomerisation of cubane to cuneane[5] can be better understood in terms of a mechanism involving *trans-(exo-)*addition of ClPd–Cl across an edge of cubane, followed by a cyclobutylmethyl-alk-1-en-4-yl rearrangement (b), an alkenylcyclopentyl ring closure (c), and elimination of ClPd–Cl, than *via* a path involving oxidative addition (to Pd^{II}) and carbonium ion intermediates.

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[1] See, for example, D. R. Coulson, *J. Amer. Chem. Soc.*, 1969, **91**, 200; E. Ban, R. P. Hughes, and J. Powell, *J. Organometallic Chem.*, 1974, **69**, 455.
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