Synthesis and Thermal Decomposition of Palladacyclopentane Derivatives of the Type $[\overline{\mathrm{Pd(CH_2CHRCHRC}}\mathrm{H_2)L_2}]$ (R = H or Me). *X*-Ray Crystal Structure of $[\overline{\mathrm{Pd(CH_2CH_2CH_2C}}\mathrm{H_2)(bipy)}]$†

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A series of new palladacyclopentane derivatives of formula $[\overline{\mathrm{Pd(CH_2CHRCHRC}}\mathrm{H_2)L_2}]$ [L_2 = $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$ (dcpe) or $Ph_2P(CH_2)_4PPh_2$ (dppb), R = H; L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe), 2,2′-bipyridyl (bipy), or $Me_2NCH_2CH_2NMe_2$ (tmen), R = Me] has been prepared. The first *X*-ray crystal structure determination of a palladacyclopentane derivative is reported: the compound $[\overline{\mathrm{Pd(CH_2CH_2CH_2C}}\mathrm{H_2)(bipy)}]$ gives crystals belonging to the *C*2/*c* space group: a = 16.643(9), b = 11.174(4), c = 7.451(3) Å, β = 116.05(9)°, and Z = 4; R = 0.0340 for 826 observed reflections. The metal co-ordination is square planar and the molecules lie on a two-fold axis. The palladacyclopentane ring shows a half-chair conformation with the two-fold axis running through Pd and the middle of the C(β)–C(β′) bond. A study of the thermal decomposition of the palladacyclopentanes has been carried out: $[\overline{\mathrm{Pd(CH_2CH_2CH_2C}}\mathrm{H_2)L_2}]$ (L = PPh_3; L_2 = dppe, tmen, bipy, dcpe, or dppb) gives butenes as the major products; cyclobutane (L = PPh_3) and ethylene (L_2 = dppe or dcpe) are also formed as minor products. By comparing these results with those for the decomposition of some methyl-substituted palladacyclopentanes, it is shown that the presence of ethylene is not attributable to fragmentation of the metallacyclic skeleton, but rather to the rupture of the P–C bonds of the diphosphine ligands. The decomposition of palladacyclopentanes is also induced by $Bu^n_2O\cdot BF_3$: linear C_4 hydrocarbons are formed.

A major contribution to the advancement of organometallic chemistry coming from the study of the reactivity of metallacyclopentanes is certainly the discovery of a multiplicity of decomposition patterns. Indeed these systems show a variety of decomposition modes such as β-hydrogen elimination, reductive elimination, and C–C bond rupture.[1] These modes can be taken as modelling a number of transition-metal-catalysed reactions, including linear dimerization of olefins, cyclobutanation, and isomerization of strained rings.

Because transition-metal complexes of the nickel triad are particularly active in such reactions, metallacyclopentane derivatives of these metals (in particular Ni and Pt) have been intensively studied.[1] A few simple palladacyclopentane derivatives have been reported,[2] but so far their thermal decomposition reactions in solution have been investigated only in a preliminary way.[3] In this paper a study of the thermal decomposition of these and other new palladacyclopentanes is reported.

Results

Synthesis of Palladacyclopentanes.—The Scheme outlines the reactions employed for the preparation of the palladacyclopentane derivatives (**1**)—(**9**). Compounds (**1**)—(**4**) have already been described;[2] all the other palladacyclopentanes are new complexes. Two types of procedure have been followed: dialkylation of the appropriate dichloro complex [route (i), Scheme], and substitution of the tmen ligand from the corresponding palladacyclopentane derivative [route (ii), Scheme].

In Table 1 we report the analytical and the ^1H n.m.r. data of the new complexes. In some cases, when the ^1H n.m.r. spectra were of little help for the structural assignment, protonolysis was carried out with HCl; n-butane was the predominant product (>95%). In the course of the preparative work well formed crystals of $[\overline{\mathrm{Pd(CH_2CH_2CH_2C}}\mathrm{H_2)(bipy)}]$ (**3**) were obtained by crystallization from acetone. Since no structural information on palladacyclopentanes had been reported in the literature and in general there is a paucity of information on structures of simple tetramethylenemetal moieties,[4] we decided to carry out a diffractometric study on (**3**).

Crystal-structure Analysis of Compound (**3**).—Table 2 gives the atomic co-ordinates, and in Table 3 the relevant interatomic distances and bond angles are compared with those of $[\overline{\mathrm{Ni(CH_2CH_2CH_2C}}\mathrm{H_2)(bipy)}]$[4c] which gives isostructural crystals.‡ The thermal motion analysis, carried out by considering the whole molecule as a rigid body and applying the

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† (2,2′-Bipyridyl)(butane-1,4-diyl)palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ The published lattice parameters[4c] are a = 16.600(3), b = 10.837(2), c = 14.815(2) Å, and β = 153.05(1)°. In order to have the same choice of unit cell as that assumed for the palladium derivative (**3**), it is necessary to apply the following transformation matrix to the above parameters:

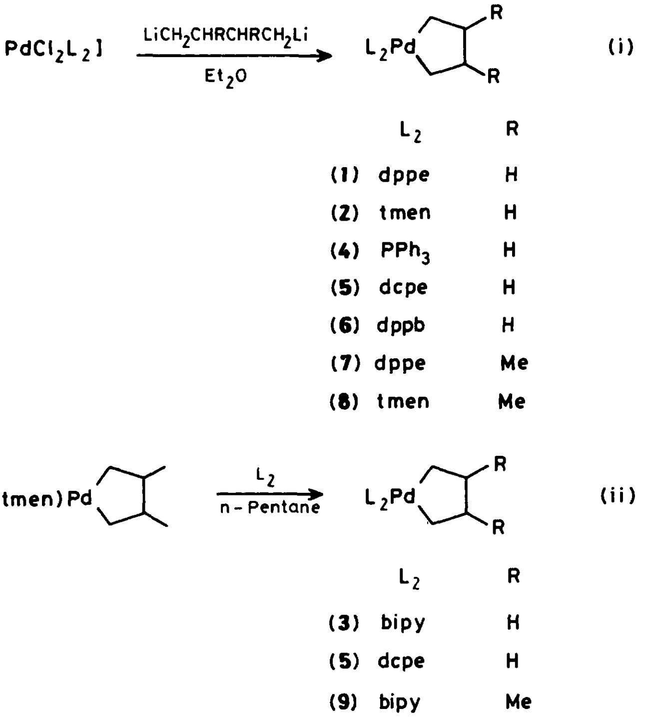
$$\begin{pmatrix} \bar{1} & 0 & \bar{2} \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$$

and translate the origin to $\frac{1}{4}$ a, $\frac{1}{4}$ b, $\frac{1}{2}$ c, giving: a = 16.632(4), b = 10.837(2), c = 7.523(1) Å, and β = 117.03(1)°.

Table 1. Analytical and spectroscopic data

Compound	Colour	Analysis (%)[a] C	Analysis (%)[a] H	^{1}H N.m.r. data[b]
(**5**) $[\mathrm{Pd(CH_2CH_2CH_2CH_2)(dcpe)}]$	Yellow	61.45 (61.6)	10.05 (9.65)	0.88—2.60 (56, br m)[c]
(**6**) $[\mathrm{Pd(CH_2CH_2CH_2CH_2)(dppb)}]$	White	65.55 (65.25)	6.05 (6.15)	1.72—2.49 (16, br m, CH_2), 7.04—7.49 (20, m, Ph)[c]
(**7**) $[\mathrm{Pd(CH_2CHMeCHMeCH_2)(dppe)}]$	White	65.15 (65.3)	6.20 (6.10)	1.42 (6, m, Me), 1.86 (4, m, P–CH_2), 2.19 (2, m, CH), 2.82 (4, m, Pd–CH_2), 6.75—7.80 (20, m, Ph)[d]
(**8**) $[\mathrm{Pd(CH_2CHMeCHMeCH_2)(tmen)}]$	White	48.3 (47.6)	8.40[e] (8.95)	1.30 (6, m, C–Me),[d] 1.52 (2, m, CH), 1.85 (4, m, Pd–CH_2), 2.18 (16, m, N–Me and N–CH_2)
(**9**) $[\mathrm{Pd(CH_2CHMeCHMeCH_2)(bipy)}]$	Orange	56.1 (55.6)	5.65 (5.80)	0.92 (6, br s, Me), 1.18 (2, m, CH), 1.79 (4, br, d, *J* 6 Hz, Pd–CH_2), 7.45 (2, m, bipy), 8.01 (4, m, bipy), 8.67 (2, m, bipy)[f]
(**10**) $[\mathrm{Pd(CH_2CMe_3)_2(dcpe)}]$	White	64.6 (64.4)	10.85 (10.5)	0.95—2.07 (48, br m, dcpe), 1.56 (18, s, Me), 2.25 [4, dd, $J(\mathrm{PH})_{cis}$ 7, $J(\mathrm{PH})_{trans}$ 12 Hz, Pd–CH_2][d]

[a] Calculated values are given in parentheses. [b] Given as chemical shift (δ), relative intensity, multiplicity, assignment; br = broad, m = multiplet, d = doublet, and s = singlet. [c] In C_6D_6. [d] In C_5D_5N. [e] N, 8.95 (9.15)%. [f] In CH_2Cl_2.



Scheme. dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$, tmen = $\mathrm{Me_2NCH_2CH_2NMe_2}$, dcpe = $\mathrm{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2}$, dppb = $\mathrm{Ph_2P(CH_2)_4PPh_2}$, and bipy = 2,2′-bipyridyl

LTS method of Schomaker and Trueblood,[5] gives a quite satisfactory fit as indicated by the low value of the index $R_U = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{\frac{1}{2}} = 0.056$, where $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$. The root-mean-square values of the eigenvalues of the tensors *L* (4.4, 2.5, 2.3°) and *T* (0.210, 0.204, 0.158 Å) in the directions of the minimum, medium, and maximum inertia moments respectively gives a quite reasonable description of the overall librational motion of the molecule.

Table 2. Fractional co-ordinates (× 10^4) for compound (**3**) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0	1 819.8(6)	2 500
N	−833(3)	333(5)	2 262(6)
C(1)	−461(3)	−759(5)	2 390(8)
C(2)	−939(6)	−1 773(8)	2 345(10)
C(3)	−1 798(6)	−1 697(9)	2 128(11)
C(4)	−2 165(5)	−630(11)	1 973(12)
C(5)	−1 682(4)	399(7)	2 051(9)
C(6)	849(5)	3 198(7)	2 743(11)
C(7)	504(5)	4 353(7)	3 167(12)

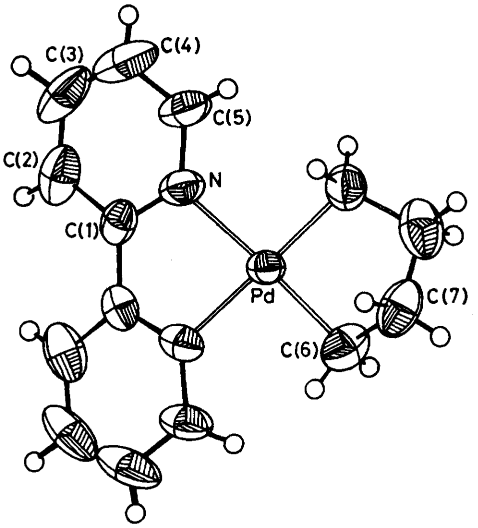


Figure. ORTEP drawing of a molecule of $[\mathrm{Pd(CH_2CH_2CH_2CH_2)(bipy)}]$ (**3**) showing thermal ellipsoids at 40% probability

The Figure shows an ORTEP drawing of the molecule which exhibits a crystallographic two-fold symmetry along a direction running through the metal atom and the mid-points of the C(1)–C(1′) and C(7)–C(7′) bonds. The co-ordination around Pd is not significantly distorted from planarity, and excluding the C(7)–C(7′) atoms the entire molecule is planar. From the distances and angles quoted in Table 3 it appears that, as expected, the major differences between the structures of the palladium and nickel metallacycles involve essentially the

Table 3. Comparison of selected distances (Å) and angles (°) in the complexes $[\overline{\mathrm{M(CH_2CH_2CH_2CH_2}})(\mathrm{bipy})]$ (M = Ni or Pd). Values corrected for rigid-body thermal motion are given in square brackets*

	M = Pd	M = Ni		M = Pd	M = Ni
M–N	2.121(5) [2.129]	1.958(4)	N–M–N′	76.8(2)	81.4(1)
M–C(6)	2.044(8) [2.051]	1.948(6)	C(6)–M–C(6′)	82.2(3)	83.9(1)
C(6)–C(7)	1.502(12) [1.507]	1.516(5)	N–M–C(6′)	100.5(3)	97.4(1)
C(7)–C(7′)	1.529(14) [1.535]	1.489(21)	C(1)–N–C(5)	118.7(6)	117.4(3)
N–C(1)	1.353(8) [1.358]	1.344(5)	N–C(1)–C(2)	119.9(7)	122.2(3)
N–C(5)	1.353(8) [1.358]	1.361(8)	N–C(5)–C(4)	121.0(8)	123.0(4)
C(1)–C(2)	1.376(11) [1.382]	1.387(7)	C(1)–C(2)–C(3)	121.0(8)	119.1(3)
C(4)–C(5)	1.390(14) [1.395]	1.374(8)	C(5)–C(4)–C(3)	120.5(10)	118.9(4)
C(2)–C(3)	1.369(15) [1.374]	1.385(14)	C(2)–C(3)–C(4)	119.0(10)	119.4(4)
C(3)–C(4)	1.321(16) [1.326]	1.365(8)	N–C(1)–C(1′)	115.6(5)	114.0(3)
C(1)–C(1′)	1.468(11) [1.474]	1.459(11)	C(2)–C(1)–C(1′)	124.6(6)	123.8(3)
C(6) ··· C(6′)	2.69(2)	2.60(1)	M–N–C(1)	116.0(4)	115.2(2)
N ··· N′	2.64(1)	2.55(1)	M–N–C(5)	125.3(5)	127.4(2)
C(2) ··· C(2′)	3.03(2)	3.00(2)	M–C(6)–C(7)	110.7(6)	111.9(2)
C(5) ··· C(6′)	3.40(2)	3.15(1)	C(6)–C(7)–C(7′)	106.0(6)	106.0(4)

* Primes indicate the equivalent position $x, y, \frac{1}{2} - z$. The values for the nickel complex have been recalculated from the published co-ordinates using the PARST program.

Table 4. Volatile products from the thermal decomposition of the palladacyclopentanes (**1**)—(**4**)[a]

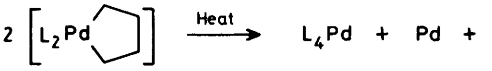
		Distribution of decomposition products (%)[b]							
Compound	Time (h)	Ethylene	Propane	Cyclobutane	1-Butene	n-Butane	2-Butene *cis*	2-Butene *trans*	Butadiene
(**1**)[c]	15	5.7	1.0	0.4	85.9		3.4	3.6	
(**2**)[d]	2.5		0.3		8.7	14.9	27.3	48.8	
(**3**)[d]	5				22.5	16.9	26.9	33.7	
(**3**)[d,e]	5			15.4	31.6	8.5	5.3	12.1	27.1
(**4**)[c]	5			17	79.5				3.5
(**4**)[c,e]	5			21.7	67.2				11.1

[a] Solvent, toluene; reaction temperature, 60 °C, apart from the case of compound (**1**) (95 °C). [b] Concentrations are referred to the total volatile products. [c] Initial concentration, 8×10^{-3} mol dm^{-3}. [d] Initial concentration, 16×10^{-3} mol dm^{-3}. [e] In the presence of air.

distances and angles at the metal atom, the other distances and angles showing differences less than 3σ. The increase in the M–N distance on going from Ni to Pd is significantly larger than that of the M–C distance: Δ(M–C) = 0.096(10), Δ(M–N) = 0.163(6) Å. It is worth noticing that, with increasing size of the metal and consequently with the increasing M–C and M–N distances, the angles N–M–N′ and C–M–C′ decrease but not as much as if the bites of the two chelating ligands had remained unchanged. Indeed these N ··· N′ and C(6) ··· C(6′) bite distances increase by the same amount [0.09(2) Å] with increasing size of the metal.

The five-membered metallacyclopentane rings are puckered with an exact half-chair conformation required by the two-fold symmetry of the molecule. The values of the total puckering amplitudes,[6] 0.464(8) and 0.422(7) Å for the palladium and nickel derivatives respectively, indicate that the puckering is a little more pronounced in the palladacycle as a consequence of the increased M–C distance.

Thermal Decomposition of Compounds (**1**)—(**4**).—Thermal decomposition studies were carried out by dissolving desired amounts of the freshly crystallized palladacyclopentane derivatives in the appropriate solvent (toluene in most cases), and then heating the solution by use of a thermostatted bath. The decomposition is accompanied by the formation of a mirror of palladium metal in the case of compounds (**2**) and (**3**), and by the precipitation of massive amounts of solid (not solely palladium metal) in the case of (**1**) and (**4**). Reaction (1) is probably occurring in the last two cases.



(1)

L_2 = dppe (**1**), L = PPh_3 (**4**)

The volatile organic products formed in the reaction were collected by distillation into a trap cooled at −180 °C and then analysed (Table 4). In all cases the major products are 1- and 2-butene, but while 1-butene predominates when the ancillary ligand is a phosphine, 2-butenes are the major products in the other two cases. By assuming that 1-butene is formed by simple β-hydrogen elimination and then is in part isomerized to 2-butenes, most of the isomerization in the case of compounds (**2**) and (**3**) could be associated with the formation of a palladium mirror which could catalyse the isomerisation of 1-butene to 2-butenes.[7] In addition to butenes significant amounts of other products are present. In the case of compound (**1**), ethylene has been found which could be a product of fragmentation of the metallacycle carbon skeleton[1c,d] and therefore be of special significance in connection with the important field of C–C bond activation (see the following paragraph). In the case of compounds (**2**) and (**3**), butane (*ca.* 15%) was found which could reflect the involvement of intermolecular reactions of the

Table 5. Influence of the solvent on the composition of the volatile products from thermal decomposition of $[Pd(CH_2CH_2CH_2CH_2)(PPh_3)_2]$ (**4**)[a]

	Distribution of decomposition products (%)					
Solvent	Ethylene	Cyclobutane	1-Butene	2-Butene *cis*	2-Butene *trans*	Butadiene
Toluene		17	79.5			3.5
Pyridine			92.0			8.0
Dimethylformamide[b]		10.8	68.9	0.7	1.8	16.9
Acetonitrile	0.4	0.6	95.5	0.3	0.5	2.7
Dimethyl sulphoxide		2.8	91.2	1.7	1.3	3.0

[a] Reaction conditions: temperature, 60 °C; time, 5 h; initial concentration of compound (**4**), 8 × 10^{-3} mol dm^{-3}. [b] Propane (0.9%) is also present.

Table 6. Volatile products from thermal decomposition of the palladacyclopentanes

					n-C_4 Distribution (%)				
Run	Compound	Time (h)	C_2H_4 (%)	n-C_4 (%)	n-Butane	1-Butene	2-Butene *cis*	2-Butene *trans*	Butadiene
1	(**1**)[b]	15	5.7	9.29		85.9	3.4	3.6	
2	(**1**)	70	36.3	63.7		58.7	2.5	2.5	
3	(**6**)	23	0.5	99.5		93.1	1.3	0.3	4.8
4	(**6**)[c]	70		100	0.8	88.9	3.3	2.8	4.2
5	(**5**)	23	20.2	79.8	4.6	8.0	20.9	46.3	
6	(**5**)[c]	70	97.8	2.2	0.1	0.4	0.6	1.1	
7	(**5**)	70	60.6	39.4	4.0	4.8	10.0	20.6	
8	(**5**)[d]	120		100	6.4	33.5	21.6	38.5	

[a] Solvent, toluene; reaction temperature, 95 °C, if not otherwise stated. [b] Other minor products: propane (1%) and cyclobutane (0.4%). [c] Analysis carried out on the same sample examined after 23 h. [d] Reaction temperature, 19 °C.

palladacycle with a hydridopalladium(II) species or, alternatively, the abstraction of hydrogen atoms from the solvent molecules. In addition to linear C_4 hydrocarbons, the phosphine-containing palladacycles (**1**) and (**4**) give cyclobutane as a minor product. The formation of cyclobutane, which in the case of (**4**) amounts to 17%, can easily be accommodated within the scheme proposed previously[8,9] in order to rationalize the reductive elimination of alkanes from d^8 transition-metal dialkyls. Indeed, kinetic studies[8] and theoretical analysis[9] indicate that in the case of palladium dialkyls the elimination is preceded by a dissociative step and involves a three-co-ordinated complex. It can therefore be foreseen that the production of cyclobutane is favoured only when the ancillary ligand dissociates easily, as is probably the case in (**4**).

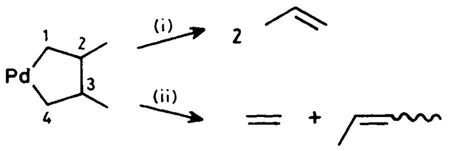
To substantiate better this interpretation, the effect of the solvent and the presence of free phosphine upon the nature of the decomposition product of (**4**) was investigated. As shown in Table 5, 1-butene and 2-butenes are in all cases the major constituents of the volatile product mixture, but the cyclobutane content is significant when poorly co-ordinating solvents (toluene and dimethylformamide) are used and drops to low levels when highly co-ordinating solvents (pyridine, acetonitrile, and dimethyl sulphoxide) are used. The general effect is similar to that observed in reactions where free phosphine is added: indeed only 1-butene is formed (the formation of cyclobutane being completely suppressed) when the reaction is carried out in the presence of free phosphine [ratio of PPh_3:(**4**) = 1:1, toluene as the solvent]. The presence of dioxygen also influences the nature of the decomposition products (see Table 4), the formation of cyclobutane being strongly favoured: for instance compound (**3**) gives cyclobutane (*ca.* 15%), while in the absence of O_2 only linear C_4 products are produced. Such an effect of oxidizing agents on the reductive-elimination reactions of dialkyl derivatives of d^8 transition metals and in particular of a nickelacyclopentane derivative was observed previously.[1b]

Thermal Decomposition of Diphosphine-containing Palladacyclopentanes.—As we have already pointed out, the presence of ethylene in the decomposition products of compound (**1**) deserves special attention. The formation of ethylene upon thermolysis of metallacyclopentanes can be indicative of a carbon–carbon bond cleavage of the ring and has special relevance to some transition-metal-catalysed reactions.[10] However in our case ethylene has been observed only in the case of (**1**) and, in principle, the diphosphine skeleton could also afford ethylene *via* P–C bond rupture, as had been observed in the thermogravimetric analysis of (**1**) and of $[PdBu^n_2(dppe)]$.[3] Moreover tertiary phosphines, which are extensively used in organometallic chemistry and in catalysis, have been shown to be less stable than they were thought to be and evidence on P–C activation has recently been accumulated.[11]

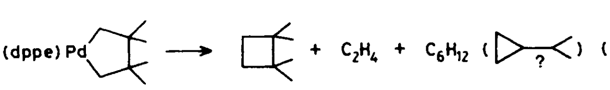
In order to elucidate this crucial point we have studied the thermal decomposition in solution of compounds (**5**) and (**6**) which are characterized by the presence of diphosphine ligands different from dppe, and of compound (**7**) which is the methyl-substituted analogue of (**1**). The results of this study, compared with those of the decomposition of (**1**), are reported in Table 6. Considering the two unsubstituted palladacycles $[Pd(CH_2CH_2CH_2CH_2)(dppb)]$ (**6**) and $[Pd(CH_2CH_2CH_2CH_2)(dcpe)]$ (**5**), one can observe that butenes are formed almost exclusively in the case of (**6**) (run 3), while in the case of (**5**) (run 5) ethylene (20%) is formed in addition to butenes. In no case was cyclobutane detected. If the ethylene were derived from the metallacyclic moiety, it is difficult to explain why the two compounds behave so differently. In contrast, we are inclined to believe that some P–C bond rupture occurs to give ethylene (from dppe and dcpe) and butenes (from dppb), in accord with the data on the decomposition of compound (**5**) at different reaction times. On going from 23 to 70 h of heating, the percentage of ethylene in the volatile products increases from 20 to 60% (runs 5 and 7). However, by distilling off the gases after 23 h of heating (run 5) and then examining the composition of the gases distilled after 47 h of further heating (run 6) (70 h in total), it is found that ethylene comprises 97.8% of the mixture. A similar behaviour is observed in the case of compound (**1**): when long reaction times are adopted, the amounts of ethylene increase.

Although there may be alternative explanations of these facts, we prefer prevalent decomposition of the metallacyclic ring in the initial period of heating and prevalent P–C bond rupture during the second period of heating. The relative robustness of the P–C bond could be the reason for the absence of ethylene when compound (**5**) is decomposed at low temperature (run 8). This interpretation is reinforced by the results of thermolysis of $[Pd(CH_2CMe_3)_2(dcpe)]$ (**10**) whose alkyl groups could not easily give ethylene by decomposition: thermolysis under the same experimental conditions as for (**5**) gives significant amounts (10%) of ethylene in addition to 2,2,5,5-tetramethylhexane which is the main product.

Finally, the overall picture of the thermal decomposition of methyl-substituted palladacycles is also consistent with the hypothesis that ethylene originates from P–C bond rupture of the diphosphine ligand. The decomposition of the dimethyl-substituted palladacycle (**7**) (15 h, 95 °C) is particularly significant in this respect. G.l.c. analysis of the volatile products reveals the presence of 2,3-dimethyl-1-butene (75%) and ethylene (25%). Now the normal mode of C–C bond fragmentation of metallacyclopentanes occurs invariably *via* breaking of the C^2–C^3 bond. If this also occurred in our case, the only decomposition product should be propylene [route (i) in equation (2)]. On the other hand by admitting that the alternative route (ii) might occur, two products in equimolar amounts should be obtained, *i.e.* ethylene and 2-butene. Since neither propylene nor butenes have been observed, it must be concluded that no metallacyclic fragmentation is occurring. The results of thermolysis of the tetramethyl-substituted palladacycle $[Pd(CH_2CMe_2CMe_2CH_2)(dppe)]$ point to the same conclusion. As already reported,[12] the major decomposition pattern is reductive elimination of 1,1,2,2-tetramethylcyclobutane, no β-hydrogen atoms being present. We have now investigated the volatile products by g.l.c. analysis and ethylene has been detected in addition to smaller amounts of another product which has been shown by mass spectrometry to be C_6H_{12} [equation (3)]. This product is not 2,3-dimethyl-1-butene. It could be isopropylcyclopropane although it is not clear how this would be formed. The two possible modes of C–C fragmentation should give 2-methylpropene, or alternatively ethylene plus 2,3-dimethyl-2-butene; none of these is substantiated by the experimental results. Therefore, also in this case the presence of ethylene is due to some fragmentation of the diphosphine ligand.



(2)



(3)

Table 7. Decomposition of the palladacyclopentanes (**1**)—(**4**) induced by $Bu^n{}_2O\cdot BF_3$ *

				n-C₄ Distribution (%)			
Compound	C_2H_4 (%)	C_3H_8 (%)	n-C_4 (%)	1-Butene	n-Butane	2-Butene *cis*	2-Butene *trans*
(**1**)	0.3		99.7	1.6	47.9	11.2	39.0
(**2**)	0.2		99.8	1.7	50.0	12.1	36.0
(**3**)		2.4	97.6	3.2	20.9	15.4	58.1
(**4**)			100	4.7	4.2	20.9	70.2

* Reaction conditions: *ca.* 70 mg of palladacycle in toluene (10 cm³), ratio of $Bu^n{}_2O\cdot BF_3$:Pd = 2:1, 2 h at room temperature.

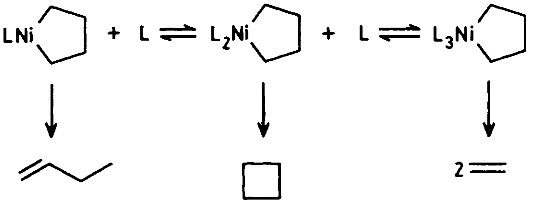
Decomposition of the Palladacyclopentanes (**1**)—(**4**) *induced by* $Bu^n{}_2O\cdot BF_3$.—This study was prompted by the observation that rhoda- and irida-cyclopentane derivatives react with $Bu^n{}_2O\cdot BF_3$ to give hydrogen-abstraction reactions from the β-position of the metallacyclic moiety.[13] With the aim of extending such investigations to palladacyclopentanes we treated the complexes (**1**)—(**4**) with $Bu^n{}_2O\cdot BF_3$ and, unexpectedly, found that a fast decomposition reaction occurred. The reactants were mixed at −78 °C and then the reaction mixture was warmed to room temperature. In all cases as soon as $Bu^n{}_2O\cdot BF_3$ was added the colour of the solution changed to deep red with subsequent formation of a palladium mirror in the case of compounds (**2**) and (**3**). It should be borne in mind that relatively high temperatures and long reaction times are needed for the thermal decomposition to occur.

The gases evolved in the decomposition of the metallacycles were examined and the most significant result was that linear C_4 hydrocarbons were always predominant (Table 7); minor amounts of C_2 and C_3 products were present in some cases. Also of note is the extensive isomerization to 2-butenes, which is obviously connected with the Lewis-acid character of BF_3. When the reaction of compound (**4**) with $Bu^n{}_2O\cdot BF_3$ was carried out in the presence of triphenylphosphine [molar ratio PPh_3:(**4**) = 1:1] the rate of decomposition was markedly slower (14 h). In addition, the extent of isomerization was considerably decreased.

These facts can easily be explained if one thinks of the BF_3 as removing (by abstracting H^- or by simply assisting) a hydrogen atom from one of the β-positions of the ring and then transferring it to an α-position with the consequent formation of 1-butene. The effect of the presence of triphenylphosphine could be due to its preferred co-ordination with respect to H^- by the boron.

Conclusions

As has been shown above, palladacyclopentanes decompose essentially to n-butenes, with the remarkable exception of the triphenylphosphine-containing palladacycle (**4**) where cyclobutane is also formed as a major product. It is perhaps useful to recall the results of the thermal decomposition of the nickel and platinum analogues.[1a,b] In the case of nickel, three decomposition patterns may occur depending on its co-ordination number, leading to the formation of n-butenes, ethylene, or cyclobutane, respectively [equation (4)].[1b] In the case of



(4)

platinacyclopentanes, n-butenes are the major products unless some intervention of the solvent causes the formation of platinum(IV) species which then eliminate cyclobutane.[1a] Palladacyclopentanes exhibit a behaviour which is different from that of the other metallacycles of the nickel triad. Ethylene is not formed, probably because of the greater reluctance of palladium to achieve five-co-ordination which, according to the mechanistic scheme developed by Hoffmann for nickelacyclopentanes and in general for d^8 transition-metal metallacycles,[10] is a prerequisite for the otherwise symmetry-forbidden formation of ethylene. Cyclobutane is formed preferentially from a three-co-ordinated species as the decomposition reactions of compound (**4**) carried out in the presence of free phosphine and in different solvents seem to indicate; moreover, all the experimental and theoretical work on reductive-elimination reactions from palladium(II) dialkyls confirm that a three-co-ordinated species is involved. As for the formation of butenes, the complexity of several possible multistep pathways makes it difficult to draw conclusions (recently an intermolecular reaction pathway for the decomposition of platinacyclopentanes has been ascertained[14]), but it seems that both four- and three-co-ordinated species could give butenes.

Experimental

Reactions and manipulations were carried out under dinitrogen or argon. The solvents were dried and distilled. The compounds (**1**)—(**4**),[2] (**10**),[12] $Li(CH_2CH_2CH_2CH_2)Li$,[1a] and $Li(CH_2CMe_3)$[15] were prepared as described. The adduct $Bu^n{}_2O{\cdot}BF_3$ was prepared from $Et_2O{\cdot}BF_3$ (Carlo Erba) and di-n-butyl ether by distillation of diethyl ether.

Proton n.m.r. spectra were recorded using a Varian T60 spectrometer. Microanalyses were by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. Infrared spectra were obtained on a Perkin-Elmer 225 instrument, mass spectra with a gas chromatograph–Hewlett-Packard model 5995A mass spectrometer. G.l.c. analyses were performed on a Perkin-Elmer Sigma 3B instrument equipped with flame-ionization detectors and using 3% silicone gum rubber on Chromosorb AW-DMCS (80—100 mesh) (SE 30) for C_2 hydrocarbons and 0.19% picric acid on Carbopack C (80—100 mesh) for C_4 hydrocarbons. Melting or decomposition points were determined on a Kofler hot-stage apparatus and are uncorrected.

[1,2-*Bis*(*dicyclohexylphosphino*)*ethane*]*dichloropalladium*(II).—To a stirred solution of $[PdCl_2(PhCN)_2]$ (0.59 g, 1.53 mmol) in benzene (10 cm^3) was added 1,2-bis(dicyclohexylphosphino)ethane (0.64 g, 1.53 mmol) causing an almost immediate precipitation of a white solid. After 2 h of stirring, pentane (30 cm^3) was added. The solid was filtered off, washed repeatedly with pentane, and dried under vacuum (0.89 g, 97%), m.p. 311 °C (decomp.) (Found: C, 52.2; H, 7.95. Calc. for $C_{26}H_{48}Cl_2P_2Pd$: C, 52.05; H, 8.05%).

[1,2-*Bis*(*dicyclohexylphosphino*)*ethane*](*butane*-1,4-*diyl*)-*palladium*(II) (**5**).—*Method* (*A*). To a stirred solution of $[\overline{Pd(CH_2CH_2CH_2CH_2})(tmen)]$ (**2**) (0.14 g, 0.49 mmol) in pentane (20 cm^3) was added a solution of 1,2-bis(dicyclohexylphosphino)ethane (0.19 g, 0.49 mmol) in pentane (20 cm^3). After 2 h of stirring, the solvent was removed under reduced pressure, and the solid residue was extracted with pentane. The product was crystallized from pentane at −30 °C as golden-yellow crystals (0.06 g, 21%), m.p. 144 °C (decomp.).

Method (*B*). 1,4-Dilithiobutane (3.6 cm^3 of a 0.42 mol dm^{-3} diethyl ether solution, 1.50 mmol) was slowly added (15 min) to a suspension of $[PdCl_2(dcpe)]$ (0.3 g, 0.5 mmol) in diethyl ether at −78 °C. The reaction mixture was stirred for 2 h, then warmed to room temperature and stirred for 2 h. The mixture was hydrolysed with water at 0 °C and the ether layer was separated and dried over anhydrous Na_2SO_4. After removal of the volatile materials the solid residue was extracted with pentane (80 cm^3). The pentane solution was concentrated to *ca.* 20 cm^3 and cooled at −30 °C overnight to give golden yellow crystals (0.14 g, 46%).

[1,2-*Bis*(*cyclohexylphosphino*)*ethane*]*dineopentylpalladium*-(II) (**10**).—The compound $[PdCl_2(dcpe)]$ (0.31 g, 0.52 mmol), neopentyl-lithium (0.68 g, 1.56 mmol), and diethyl ether (15 cm^3) were introduced into a Schlenk tube at −78 °C. The suspension was stirred at this temperature for 15 min, then the temperature was raised to 25 °C and stirred for 5 h. The volatile materials were removed at reduced pressure and the residue was extracted with toluene (20 cm^3): after hydrolysis with water at 0 °C and drying over Na_2SO_4, the solution was filtered, concentrated to 10 cm^3, and added slowly to pentane (50 cm^3). After some hours white crystals were formed, filtered off, and dried *in vacuo* (0.13 g, 39%), m.p. 162 °C (decomp.).

[1,2-*Bis*(*diphenylphosphino*)*butane*](*butane*-1,4-*diyl*)-*palladium*(II) (**6**).—The compound $[PdCl_2(dppb)]$ (0.31 g, 0.52 mmol) in diethyl ether (30 cm^3) was treated with 1,4-dilithiobutane (3.7 cm^3 of a 0.42 mol dm^{-3} diethyl ether solution, 1.56 mmol). The mixture was stirred at −78 °C for 1 h, then at room temperature for 3 h. The solid formed was separated from the solution, dried *in vacuo* and extracted with toluene (40 cm^3), and the solution filtered and concentrated to 10 cm^3. Pentane (30 cm^3) was added to the filtrate and cooling at −30 °C overnight gave white crystals (0.07 g, 23%), m.p. 142 °C (decomp.).

[1,2-*Bis*(*diphenylphosphino*)*ethane*](2,3-*dimethylbutane*-1,4-*diyl*)*palladium*(II) (**7**).—The compound $[PdCl_2(dppe)]$ (0.61 g, 1.06 mmol) in diethyl ether (50 cm^3) was treated with 1,4-dilithio-2,3-dimethylbutane (5.5 cm^3 of a 0.61 mol dm^{-3} diethyl ether solution, 3.18 mmol) at −78 °C for 1 h and at room temperature for 4 h. After hydrolysis at 0 °C the ether solution was dried over Na_2SO_4, then filtered and evaporated to dryness. The solid residue was extracted with acetone (20 cm^3). The acetone solution was concentrated to 5 cm^3 and cooled at −30 °C overnight to give white crystals (0.22 g, 35%), m.p. 133 °C (decomp.).

(2,3-*Dimethylbutane*-1,4-*diyl*)(NNN′N′-*tetramethylethylenediamine*)*palladium*(II) (**8**).—The compound $[PdCl_2(tmen)]$ (0.61 g, 2.07 mmol) in diethyl ether (50 cm^3) was treated with 1,4-dilithio-2,3-dimethylbutane (6.8 cm^3 of a 0.61 mol dm^{-3} diethyl ether solution, 4.14 mmol) at −78 °C for 1 h and at room temperature for 1 h. After evaporation of the solvent, the remaining solid residue was extracted with pentane (60 cm^3) and hydrolysed at 0 °C. After drying over Na_2SO_4 the pentane solution was filtered, concentrated to 10 cm^3, and then cooled to −78 °C to give white crystals (0.25 g, 40%), m.p. 85 °C (decomp.).

(2,2′-*Bipyridyl*)(2,3-*dimethylbutane*-1,4-*diyl*)*palladium*(II) (**9**).—To a stirred solution of compound (**8**) (0.10 g, 0.33 mmol) in pentane (10 cm^3) was added a solution of 2,2′-bipyridine (0.06 g, 0.33 mmol) in pentane (10 cm^3). An orange solid precipitated immediately. After 2 h of stirring the solid was separated, washed with pentane, recrystallised from acetone, and dried *in vacuo* (0.07 g, 60%), m.p. 136 °C (decomp.).

Thermal Decomposition.—General procedure. Thermolysis reactions were carried out in sealed tubes with a sealed side-arm,

Table 8. Experimental data for the crystallographic analysis of compound (3)

Formula	$C_{14}H_{16}N_2Pd$	Formula	$C_{14}H_{16}N_2Pd$
M	318.7	θ range/°	3—27
Space group	$C2/c$	h range	19—17
a/Å	16.643(9)	k range	0—13
b/Å	11.174(4)	l range	0—8
c/Å	7.451(3)	Standard reflection	441
β/°	116.05(9)	Intensity variation	None
U/Å^3	1 244.9(9)	Scan mode	ω—2θ
Z	4	No. of measured reflections	2 294
D_c/mg m^{-3}	1.700	Observed reflections $[I > 3\sigma(I)]$	826
F(000)	640	$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.0398
T/K	294	Max shift to error ratio	0.002
Crystal size/mm	0.08 × 0.13 × 0.45	Min., max. height in final difference map, $\Delta\rho$/e Å^{-3}	−0.05, 0.06
Diffractometer	Philips PW 1100		
μ/mm^{-1}	1.449	No. of refined parameters	110
Scan speed/° s^{-1}	0.10	$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0340
Scan width/°	1.60	$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0320
Radiation	Mo-K_α	$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$	1.57
		w	$1/\sigma^2(F_o)$

by using a solution of *ca.* 0.05 g of the palladacyclic compound in toluene (10 cm^3) under argon. The solution was heated for the desired time at the decomposition temperature by using an oil-bath (±1 °C). After decomposition the tubes were cooled and connected through the side-arm to a trap cooled at −196 °C and to a water pump. The sealed side-arm was broken and the gases were distilled, collected, and analysed by g.l.c. The extent of the decomposition was determined by adding a known amount of propane to the gases. The yields were in the range 45—55%.

Reactions of Palladacyclopentanes.—With $Bu^n{}_2O{\cdot}BF_3$. The palladacyclopentane (*ca.* 0.15 g) in toluene (15 cm^3) was treated under argon at −78 °C with freshly prepared $Bu^n{}_2O{\cdot}BF_3$ (0.02 cm^3). The solution was stirred at −30 °C for 0.5 h and then at room temperature for 2 h. After the decomposition was complete, the gases were distilled and analysed following the above procedure.

With HCl. In a typical experiment the starting material (*ca.* 0.1 g) was dissolved in benzene (10 cm^3) at room temperature. Pure dry HCl was then bubbled through the solution. The evolved gases were trapped at −196 °C and then analysed by g.l.c.

Crystal Structure Analysis of $[\overline{Pd(CH_2CH_2CH_2CH_2})(bipy)]$ (3).—Details of the lattice parameters, data collection, and structure refinement are summarised in Table 8. The unit-cell dimensions and estimated standard deviations (e.s.d.s) were determined by least-squares fitting[16] of the θ angles of 27 intense reflections chosen from diverse regions of reciprocal space in the range θ 14.7—21.4° using Mo-K_{α_1} radiation (λ = 0.709 300 Å) and the Nelson and Riley[17] extrapolation function. The reflection intensities were corrected for Lorentz and polarization effects. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares using the SHELX 76 program.[18] All the hydrogen atoms were located from a Fourier difference synthesis and refined isotropically. The atomic scattering factors and anomalous scattering coefficients were taken from ref. 19. The calculations were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma. In addition to the quoted program, PARST,[20] THMV,[21] ORTEP,[22] and PLUTO[23] were used.

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