Reactions of Co-ordinated Ligands. Part XI.[1] The Ring Opening of Methylenecyclopropanes by Palladium(II)–Nucleophile Systems; Formation of Substituted η^3-But-3-enyl Complexes of Palladium(II)

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trans- and *cis*-2,3-Dimethoxycarbonylmethylenecyclopropanes react with $[Pd(MeCN)_2Cl_2]$ in dichloromethane to yield isomeric, ring-opened η^3-[3-chloro-1,2-bis(methoxycarbonyl)but-3-enyl]palladium(II) complexes, *via* $[Pd(\eta^2\text{-methylenecyclopropane})Cl_2]$ intermediates. Analogous reactions in methanol, ethanol, isopropyl alcohol, and t-butyl alcohol solvents yield isomeric η^3-[4-alkoxy-1,2-bis(methoxycarbonyl)but-3-enyl]palladium(II) complexes. ^1H and ^{13}C N.m.r. data for these, and derived, complexes are reported and discussed in terms of conformational isomerism within the chelating but-3-enyl ring. The mechanisms of these ring-opening reactions are discussed in terms of substituted cyclopropylmethyl-palladium intermediates, and the implications with respect to the mechanisms of chloropalladation and alkoxypalladation reactions of olefins are also reviewed.

TRANSITION-METAL promoted reactions of methylenecyclopropanes have aroused considerable recent interest, particularly as to the role of the metal in promoting opening reactions of the cyclopropane ring.[2-5] We have previously established that methylenecyclopropane (1a), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane

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[2] R. Noyori, T. Octagi, and H. Takaya, *J. Amer. Chem. Soc.*, 1970, **92**, 5780.

[3] R. Noyori, T. Ishigana, N. Hayashi, and H. Takaya, *J. Amer. Chem. Soc.*, 1973, **95**, 1674.

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(1b), and *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (1c) form a variety of stable η^2-bonded complexes with Rh^I, Ir^I, Pt^0, and Pt^{II} systems.[6] These η^2-bonded complexes proved to have remarkable stability, the cyclopropane ring remaining intact after prolonged thermolysis and u.v. irradiation.[6]

Previous reports have demonstrated that methylenecyclopropane (1a) and 2,2-diphenylmethylenecyclopropane (1e) reacted with $[Pd(PhCN)_2Cl_2]$ to yield the η^3-allylic complexes (2) and (3) respectively, in which the cyclopropane ring had opened.[7] It therefore seemed potentially fruitful to examine the reactions of the *trans*- and *cis*-disubstituted methylenecyclopropanes (1b), (1c), and (1d) with Pd^{II} systems. A preliminary account of this work has appeared.[8]

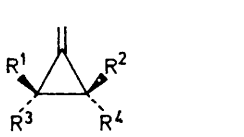
RESULTS

Prolonged stirring of an equimolar solution of $[Pd(MeCN)_2Cl_2]$ and *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (1b) in dichloromethane resulted in a colour change from deep orange-brown to golden yellow. Evaporation yielded a sparingly soluble yellow material of empirical formula $PdCl_2(C_8H_{10}O_4)$. The ^1H n.m.r. spectrum (Table 1) of this complex exhibited six resonances at τ 6.26 and 6.30 (CO_2Me groups), 5.01 and 5.24 (characteristic of a vinylidene olefin co-ordinated to Pd^{II}),[9] and at 5.38 and 8.42. A large coupling constant of 10 Hz was observed between the latter two proton resonances. An identical reaction of $[Pd(MeCN)_2Cl_2]$ with *trans*-2,3-dimethoxycarbonyl-2,3-dideuterio-methylenecyclopropane (1c) yielded an analogous complex, the ^1H n.m.r. spectrum of which showed no resonances at τ 5.38 and 8.42. The large coupling constant observed between these two resonances in the protio-complex strongly implied that the cyclopropane ring has been ruptured across the 1,2-bond, since the largest coupling previously observed between these two protons in simple η^2-bonded transition-metal complexes of (1b) was only 3—4 Hz.[6]

The most plausible structures for the protio- and deuterio-complexes were thus formulated as (4a) and (4b) respectively, in which the cyclopropane ring had undergone a ring-opening reaction, with migration of a chloride ligand from the metal to the organic moiety, yielding a substituted but-3-enyl species η^3-bonded to palladium.

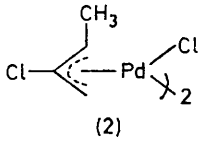
In agreement with this formulation, only one Cl atom per metal atom in (4a) proved to be metathetically replaceable. Thus complex (4a) reacted with an excess of lithium bromide in acetone to afford the analogous bromide-bridged complex (4c). Similarly, treatment of (4a) with acetylacetonatothallium, hexafluoroacetylacetonatothallium, or cyclopentadienylthallium, yielded the pentane-soluble, monomeric complexes (4d), (4f), and (4g) respectively. Treatment of the deuterio-complex (4b) with acetylacetonatothallium afforded the monomeric complex (4e). The ^1H n.m.r. (Table 1) and ^{13}C n.m.r. (Table 2) of these complexes were in complete agreement with their formulation as substituted η^3-but-3-enyl complexes of Pd^{II}.

If the reaction between $[Pd(MeCN)_2Cl_2]$ and (1b) was

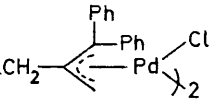


(I)

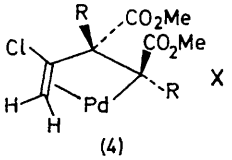
a; $R^1=R^2=R^3=R^4=H$
b; $R^1=R^4=CO_2Me$; $R^2=R^3=H$
c; $R^1=R^4=CO_2Me$; $R^2=R^3=D$
d; $R^1=R^2=CO_2Me$; $R^3=R^4=H$
e; $R^1=R^3=Ph$; $R^2=R^4=H$



(2)

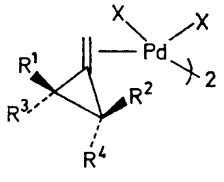


(3)



(4)

a; X=Cl; R=H (dimer)
b; X=Cl; R=D (dimer)
c; X=Br; R=H (dimer)
d; X=acetylacetonate; R=H
e; X=acetylacetonate; R=D
f; X=hexafluoroacetylacetonate; R=H
g; $X=\eta^5-C_5H_5$



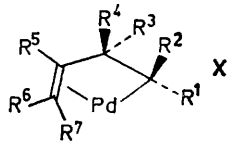
(5)

a; X=Cl; $R^1=R^4=CO_2Me$; $R^2=R^3=H$
b; X=Br; $R^1=R^4=CO_2Me$; $R^2=R^3=H$

[6] M. Green, J. A. K. Howard, R. P. Hughes, S. C. Kellett, and P. Woodward, *J.C.S. Dalton*, 1975, 2007.
[7] R. Noyori and H. Takaya, *Chem. Comm.*, 1969, 525.
[8] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1974, 686.
[9] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1973, **60**, 387.

TABLE 1

^{1}H N.m.r. data for η^3-but-3-enyl complexes of palladium(II) ($CDCl_3$; 34 °C; 100 MHz)



Complex	X	R^1	R^2	R^3	R^4	R^5	R^6	R^7	τ(multiplicity), J/Hz R^1	R^2	R^3	R^4	R^6	R^7	X
(4a)	Cl	H	CO_2Me	CO_2Me	H	Cl	H	H	8.42 (d) $J_{1,4}$ = 10	6.26 (s)	6.30 (s)	5.38 (d) $J_{1,4}$ = 10		5.24 (d) $J_{6,7}$ = 1	5.04 (d)
(4b)	Cl	D	CO_2Me	CO_2Me	D	Cl	H	H		6.26 (s)	6.30 (s)			5.24 (d) $J_{6,7}$ = 1	5.01 (d)
(4c)	Br	H	CO_2Me	CO_2Me	H	Cl	H	H	8.40 (d) $J_{1,4}$ = 10	6.20 (s)	6.30 (s)	5.40 (d) $J_{1,4}$ = 10		5.25 (d) $J_{6,7}$ = 1	5.00 (d)
(4d)	acac	H	CO_2Me	CO_2Me	H	Cl	H	H	8.43 (d) $J_{1,4}$ = 9	6.24 (s)	6.28 (s)	5.32 (d) $J_{1,4}$ = 9 $J_{4,6}$ = 1		5.36 (dd) $J_{4,6}$ = 1 $J_{6,7}$ = 1	5.18 (d)	8.02 (s), CH_3 8.07 (s), CH_3 4.68 (s), CH
(4e)	acac	D	CO_2Me	CO_2Me	D	Cl	H	H		6.24 (s)	6.28 (s)			5.36 (d) $J_{6,7}$ = 1	5.18 (d)	8.02 (s), CH_3 8.07 (s), CH_3 4.68 (s), CH
(4f)	hfacac	H	CO_2Me	CO_2Me	H	Cl	H	H	8.25 (d) $J_{1,4}$ = 9	6.25 (s)	6.26 (s)	5.28 (dd) $J_{1,4}$ = 9 $J_{4,6}$ = 1		5.10 (dd) $J_{4,6}$ = 1 $J_{5,6}$ = 2	5.04 (d)	3.86 (s), CH
(4g)	C_5H_5	H	CO_2Me	CO_2Me	H	Cl	H	H	8.38 (d) $J_{1,4}$ = 9	6.25 (s)	6.37 (s)	5.38 (dd) $J_{1,4}$ = 1 $J_{4,6}$ = 1		5.86 (dd) $J_{5,6}$ = 2	6.46 (d)	4.36 (s) C_5H_5
(8a)	Cl	CO_2Me	H	CO_2Me	H	Cl	H	H	6.30 (s)	6.89 (d) $J_{2,4}$ = 10	6.39 (s)	5.87 (dd) $J_{2,4}$ = 10 $J_{4,6}$ = 2		5.11 (dd) $J_{4,6}$ = 2 $J_{5,6}$ = 2	4.49 (d)	
(8b)	acac	CO_2Me	H	CO_2Me	H	Cl	H	H	6.30 (s)	7.01 (d) $J_{2,4}$ = 10	6.43 (s)	5.87 (dd) $J_{2,4}$ = 10 $J_{4,6}$ = 2		5.24 (dd) $J_{4,6}$ = 2 $J_{5,6}$ = 2	4.57 (d)	7.96 (s), CH 8.06 (s), CH_3 4.66 (s), CH
(8c)	C_5H_5	CO_2Me	H	CO_2Me	H	Cl	H	H	6.35 (s)	6.55 (d) $J_{2,4}$ = 10	6.52 (s)	6.09 (dd) $J_{2,4}$ = 10 $J_{4,6}$ = 2		5.70 (dd) $J_{4,6}$ = 2 $J_{5,6}$ = 2	5.80 (d)	4.26 (s) C_5H_5
(6a)	Cl [a]	H	CO_2Me	CO_2Me	H	H	OMe	H	8.53 (d) $J_{1,4}$ = 9	6.20 (s)	6.23 (s)	5.93 (dd) $J_{1,4}$ = 9 $J_{4,5}$ = 10	5.70 (dd) $J_{5,7}$ = 10 $J_{4,5}$ = 10	6.34 (s)	2.39 (d) $J_{5,7}$ = 10	
(7a)	Cl [a]	CO_2Me	H	H	CO_2Me	H	OMe	H	6.14 (s)	7.84 (d) $J_{2,3}$ = 6	*ca.* 6.2	6.35 (s)	5.70 (dd) $J_{3,5}$ = 10 $J_{5,7}$ = 10	6.34 (s)	2.69 (d) $J_{5,7}$ = 10	
(6b)	Cl [a]	D	CO_2Me	CO_2Me	D	H	OMe	H		6.20 (s)	6.23 (s)		5.70 (d) $J_{5,7}$ = 10	6.34 (s)	2.39 (d) $J_{5,7}$ = 10	
(7b)	Cl [a]	CO_2Me	D	D	CO_2Me	H	OMe	H	6.14 (s)			6.35 (s)	5.70 (d) $J_{5,7}$ = 10	6.34 (s)	2.69 (d) $J_{5,7}$ = 10	
(6c)	Br [a]	H	CO_2Me	CO_2Me	H	H	OMe	H	8.52 (d) $J_{1,4}$ = 9	6.20 (s)	6.21 (s)	5.90 (dd) $J_{1,4}$ = 9 $J_{4,5}$ = 10	5.75 (dd) $J_{4,5}$ = 10 $J_{5,7}$ = 10	6.30 (s)	2.35 (d) $J_{5,7}$ = 10	
(7c)	Br [a]	CO_2Me	H	H	CO_2Me	H	OMe	H	6.14 (s)	7.80 (d) $J_{2,3}$ = 6	*ca.* 6.2 [b]	6.30 (s)	5.70 (dd) $J_{4,5}$ = 10 $J_{5,7}$ = 10	6.34 (s)	2.70 (d) $J_{5,7}$ = 10	
(6d)	acac [c]	H	CO_2Me	CO_2Me	H	H	OMe	H	8.53 (d) $J_{1,4}$ = 8	6.21 (s)	6.24 (s)	6.00 (dd) $J_{1,4}$ = 9 $J_{4,5}$ = 10	5.71 (dd) $J_{4,5}$ = 10 $J_{5,7}$ = 10;	6.35 (s)	2.47 (d) $J_{5,7}$ = 10	8.02 (s), CH_3 8.15 (s), CH_3 4.74 (s), CH
(7d)	acac [c]	CO_2Me	H	H	CO_2Me	H	OMe	H	6.27 (s)	7.86 (d) $J_{2,3}$ = 6	*ca.* 6.2 [b]	6.30 (s)	5.71 (dd) $J_{4,5}$ = 10 $J_{5,7}$ = 10	6.35 (s)	2.74 (d) $J_{5,7}$ = 10	8.06 (s), CH_3 8.15 (s), CH_3 4.74 (s), CH
(6e)	Cl	H	CO_2Me	CO_2Me	H	H	OCH_2Me	H	8.52 (d) $J_{1,4}$ = 9	6.21 (s)	6.24 (s)	5.91 (dd) $J_{1,4}$ = 9 $J_{4,5}$ = 10	5.72 (dd) $J_{4,5}$ = 10 $J_{5,7}$ = 10	6.21 (q), CH_2 J = 7	2.40 (d) 8.66 (t), CH_3 $J_{5,7}$ = 10	
(7e)	Cl	CO_2Me	H	H	CO_2Me	H	OCH_2Me	H	6.13 (s)	7.82 (d) $J_{2,3}$ = 6	*ca.* 6.2 [b]	6.33 (s)	5.70 (dd) $J_{3,5}$ = 10 $J_{5,7}$ = 10	6.20 (q), CH_2 J = 7	2.70 (d) 8.64 (t), H_3 $J_{5,7}$ = 10	
(6f)	Cl	H	CO_2Me	CO_2Me	H	H	$OCHMe_2$	H	8.40 (d) $J_{1,4}$ = 8	6.26 (s)	6.38 (s)	6.02 (dd) $J_{1,4}$ = 9 $J_{4,5}$ = 10	5.70 (dd) $J_{4,5}$ = 10 $J_{5,7}$ = 11	5.50 (m), CH 8.59 (d), CH_3 J = 6	2.33 (d) $J_{5,7}$ = 11 8.68 (d), CH_3	
(7f)	Cl	CO_2Me	H	H	CO_2Me	H	$OCHMe_2$	H	6.30 (s)	7.87 (d) $J_{2,3}$ = 6	*ca.* 6.2 [b]	6.38 (s)	5.72 (dd) $J_{3,5}$ = 10 $J_{5,7}$ = 11	5.50 (m), CH 8.59 (d), CH_3 8.68(d), CH_3 J = 6	2.63 (d) $J_{5,7}$ = 11	
(6g)	Cl	H	CO_2Me	CO_2Me	H	H	H	$OCHMe_2$	8.20 (d) $J_{1,4}$ = 8	6.38 (s)	6.40 (s)	6.02 (dd) $J_{1,4}$ = 8 $J_{4,5}$ = 10	5.75 (dd) $J_{4,5}$ = 10 $J_{5,6}$ = 5	5.50 (m), CH 8.59 (d), CH_3	3.30 (d) $J_{5,6}$ = 4	
(7g)	Cl	CO_2Me	H	H	CO_2Me	H	H	$OCHMe_2$	6.38 (s)	8.18 (d) $J_{2,3}$ = 6	*ca.* 6.2 [b]	6.40 (s)	5.70 (dd) $J_{3,5}$ = 10 $J_{5,6}$ = 4	5.50 (m), CH 8.59 (d), CH_3 8.68 (d), CH_3	3.28 (d) $J_{5,6}$ = 4	
(6h)	Cl	H	CO_2Me	CO_2Me	H	H	H	$OCMe_3$	8.30 (d) $J_{1,4}$ = 8	6.35 (s)	6.42 (s)	6.00 (dd) $J_{1,4}$ = 8 $J_{4,5}$ = 10	5.75 (dd) $J_{4,5}$ = 10 $J_{5,6}$ = 4	8.90 (s)	3.30 (d) $J_{5,6}$ = 4	
(7h)	Cl	CO_2Me	H	H	CO_2Me	H	H	$OCMe_3$	6.38 (s)	8.00 (d) $J_{2,3}$ = 6	*ca.* 6.2 [b]	6.40 (s)	5.70 (dd) $J_{3,5}$ = 10 $J_{5,6}$ = 4	8.89 (s)	3.26 (d) $J_{5,6}$ = 4	
(9a)	Cl	CO_2Me	H	CO_2Me	H	H	OMe	H	6.30 (s)	6.89 (d) $J_{2,4}$ = 10	6.39 (s)	5.87 (dd) $J_{2,4}$ = 10 $J_{4,5}$ = 9	5.70 (dd) $J_{4,5}$ = 9 $J_{5,7}$ = 11	6.35 (s)	2.40 (d) $J_{5,7}$ = 11	
(10a)	Cl	H	CO_2Me	H	CO_2Me	H	OMe	H	7.32 (d) $J_{1,3}$ = 9	6.30 (s)	5.86 (dd) $J_{1,3}$ = 9 $J_{3,5}$ = 10	6.40 (s)	5.70 (dd) $J_{3,5}$ = 10 $J_{5,7}$ = 11	6.34 (s)	2.13 (d) $J_{5,7}$ = 11	
(9b)	Cl	CO_2Me	H	CO_2Me	H	H	$OCMe_3$	H	6.30 (s)	6.90 (d) $J_{2,4}$ = 10	6.40 (s)	5.85 (dd) $J_{2,4}$ = 10 $J_{4,5}$ = 9	5.70 (dd) $J_{4,5}$ = 9 $J_{5,7}$ = 11	8.90 (s)	2.38 (d) $J_{5,7}$ = 11	
(10b)	Cl	H	CO_2Me	H	CO_2Me	H	$OCMe_3$	H	7.30 (d) $J_{1,3}$ = 9	6.32 (s)	5.84 (dd) $J_{1,3}$ = 9 $J_{3,5}$ = 10	6.42 (s)	5.70 (dd) $J_{3,5}$ = 10 $J_{5,7}$ = 11	8.88 (s)	2.15 (d) $J_{5,7}$ = 11	

[a] Ratio of isomers (6a) : (7a), (6b) : (7b), (6c) : (7c), (6e) : (7e) is *ca.* 2 : 1 by integration. [b] Obscured by CO_2Me resonances. [c] Ratio of isomers (6d) : (7d) is 1 : 1 by integration.

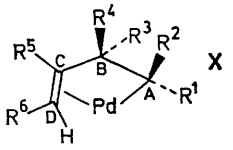
worked up after only 1 h, instead of allowing the solution to attain its final golden yellow colour, a brown, sparingly soluble solid was obtained, which was shown by microanalysis to be isomeric with (4a). This complex proved too insoluble for ^1H and ^{13}C n.m.r. spectra to be recorded, but it reacted rapidly with an excess of pyridine in dichloromethane to yield $[Pd(pyridine)_2Cl_2]$ and unchanged (1b).* The brown complex was therefore formulated as the dimeric η^2-bonded olefin complex (5a). A suspension of (5a) in a large volume of dichloromethane yielded, after prolonged stirring, a yellow solution from which complex (4a) could be isolated.

Similarly, reaction of $[Pd(MeCN)_2Br_2]$ with (1b) in dichloromethane solution resulted in the precipitation of an insoluble brown solid which reacted with pyridine to yield $[Pd(pyridine)_2Br_2]$ and (1b); this complex was therefore formulated as (5b). No reaction of (5b) to yield a ring-opened product analogous to (4a) could be effected by prolonged stirring in dichloromethane.

Reaction of equimolar amounts of $[Pd(MeCN)_2Cl_2]$ and (1b) in methanol solution, in the presence of sodium carbonate, rapidly produced a golden yellow solution, from which yellow crystals of stoicheiometry $PdCl(OCH_3)(C_8H_{10}O_4)$ were isolated; no traces of complex (4a) were observed. The solution nature of this complex was assigned, on the basis of ^1H and ^{13}C n.m.r. spectroscopy, as a mixture of the isomeric forms (6a) and (7a), differing in the conformation of the CO_2Me groups with respect to the co-ordinated olefin.† Similarly, the deuteriated (1c) yielded a mixture of isomers (6b) and (7b).

TABLE 2

^{13}C N.m.r. data for η^3-But-3-enyl complexes of palladium(II) ($CDCl_3$; 34 °C; 25.15 MHz)



Complex	X	R^1	R^2	R^3	R^4	R^5	R^6	δ(p.p.m. downfield from internal $SiMe_4$) CA	CB	CC	CD	R^1	R^2	R^3	R^4	R^6	X
(4d)	acac	H	CO_2Me	CO_2Me	H	Cl	H	7.70	55.57	90.95	78.63		175.64 [a] *C*=O; 52.42 [a] OCH_3	170.85 [a] *C*=O; 51.39 [a] OCH_3			188.51 184.99 C=O; 27.54 26.39 CH_3; 99.81 *C*H
(4f)	hfacac	H	CO_2Me	CO_2Me	H	Cl	H	8.01	55.45	91.98	80.15		175.89 [a] *C*=O 52.72 [a] OCH_3	619.88 [a] *C*=O 52.00 [a] OCH_3			176.67 J_{C-F} = 34 C=O; 117.37 J_{C-F} = 285 CF_3; 90.40 *C*H
(8a)	Cl	CO_2Me	H	CO_2Me	H	Cl	H	8.05	55.98	89.90	78.33	172.35 [a] *C*=O 52.34 OCH_3		168.54 [a] *C*=O; 52.34 OCH_3			
(8c)	η^5-C_5H_5	CO_2Me	H	CO_2Me	H	Cl	H	−9.18	55.98	77.82	62.47	176.90 [a] *C*=O; 51.55 [a] OCH_3		170.77 *C*=O; 51.06 [a] OCH_3			97.21
(6a)	Cl	H	CO_2Me	CO_2Me	H	H	OMe	−2.55	44.29	43.14	143.31		174.80 [a] *C*=O; 52.42 [a] OCH_3	170.73 [a] *C*=O; 52.06 [a] OCH_3		60.19	
(7a)	Cl	CO_2Me	H	H	CO_2Me	H	OMe	6.87	38.71	41.32	141.85	175.00 [a] *C*=O; 52.40 [a] OCH_3			172.98 [a] *C*=O; 51.33 [a] OCH_3	60.55	
(6e)	Cl	H	CO_2Me	CO_2Me	H	H	OCH_2Me	−2.79	44.2	43.14	142.70		174.86 [a] *C*=O; 52.36 [a] OCH_3	170.79 [a] *C*=O; 51.99 [a] OCH_3		69.35 CH_2; 14.13 CH_3	
(7e)	Cl	CO_2Me	H	H	CO_2Me	H	OMe	6.67	38.34	41.07	141.06	174.80 [a] *C*=O; 52.36 [a] OCH_3			173.03 *C*=O; 51.20 [a] OCH_3	69.83 CH_2; 14.13 CH_3	

[a] The assignment of individual *C*=O and OCH_3 resonances between individual isomers is not unambiguous. Some assignments may therefore prove to be revised.

The η^2-bonded olefin complex (5b) reacted smoothly in methanol in the presence of Na_2CO_3, to afford the corresponding bromide-bridged complex, shown by ^1H n.m.r. spectroscopy to exist as a mixture of (6c) and (7c). The isomeric mixture of (6a) and (7a) reacted with acetylacetonatothallium to afford the corresponding acetylacetonato-system, which was also shown by ^1H n.m.r. spectroscopy to exist as a conformationally isomeric pair (6d) and (7d).

Reaction of $[Pd(MeCN)_2Cl_2]$ with (1b) in ethanol, in the presence of Na_2CO_3, yielded the conformationally isomeric pair of complexes (6e) and (7e). In all the complexes (6a—e) and (7a—e) the substituent geometry of the co-ordinated olefinic function was shown to be exclusively *trans* by ^1H n.m.r. spectroscopy, the coupling constant of 10 Hz being characteristic of a *trans*-disubstituted alkoxy-olefin.[11]

The reaction of $[Pd(MeCN)_2Cl_2]$ with (1b) in isopropyl alcohol, however, gave rise to an analogous ring-opening reaction but yielded a mixture of four isomeric products; these were the conformationally isomeric pair of complexes (6f) and (7f), in which the substituent geometry of the

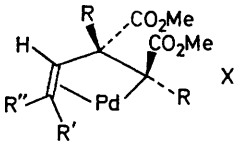
* η^3-But-3-enyl complexes of Pd^{II} react with two molar equivalents of pyridine to yield stable η^1-but-3-enyl complexes.[10]

† That these are indeed conformational isomers is demonstrated by the reaction of the isomeric mixture with pyridine, to yield a single, preferred conformational isomer of the η^1-bonded ligand complex.[10]

[10] R. Goddard, M. Green, R. P. Hughes, and P. Woodward, *J.C.S. Dalton*, following paper.

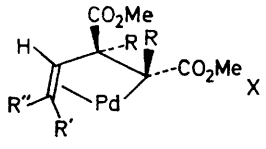
co-ordinated alkoxy-olefin was shown to be *trans* by virtue of the coupling constant of 10 Hz between the two olefinic protons, and the conformationally isomeric pair of complexes (6g) and (7g), in which the co-ordinated alkoxy-olefin was shown to have a *cis*-geometry, the corresponding coupling constant [11] being only 4 Hz.*

this solution yielded a yellow complex, formulated on the basis of microanalysis, ^1H, and ^{13}C n.m.r. spectra as the single isomer (8a), isomeric with (4a). Treatment of complex (8a) with acetylacetonatothallium, or cyclopentadienylthallium, yielded the monomeric, pentane-soluble, complexes (8b) and (8c) respectively.



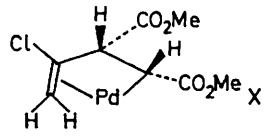
(6)

a; X=Cl; R=R'=H; R''=OMe(dimer)
b; X=Cl; R=D; R'=H; R''=OMe(dimer)
c; X=Br; R=R'=H; R''=OMe(dimer)
d; X=acac; R=R'=H; R''=OMe
e; X=Cl; R=R'=H; R''=OEt (dimer)
f; X=Cl; R=R'=H; R''=OPr^i(dimer)
g; X=Cl; R=R''=H; R'=OPr^i(dimer)
h; X=Cl; R=R''=H; R'=OBu^t(dimer)



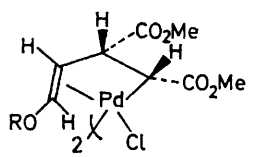
(7)

a; X=Cl; R=R'=H; R''=OMe(dimer)
b; X=Cl; R=D; R'=H; R''=OMe(dimer)
c; X=Br; R=R'=H; R''=OMe(dimer)
d; X=acac; R=R'=H; R''=OMe
e; X=Cl; R=R'=H; R''=OEt(dimer)
f; X=Cl; R=R'=H; R''=OPr^i(dimer)
g; X=Cl; R=R''=H; R'=OPr^i(dimer)
h; X=Cl; R=R''=H; R'=OBu^t(dimer)



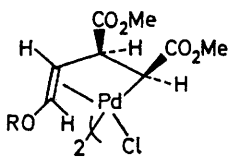
(8)

a; X=Cl (dimer)
b; X=acac
c; X=η^5-C_5H_5



(9)

a; R=Me
b; R=Bu^t



(10)

a; R=Me
b; R=Bu^t

In contrast, reaction of $[Pd(MeCN)_2Cl_2]$ with (1b) in t-butyl alcohol yielded the conformationally isomeric pair of complexes (6h) and (7h), in which the geometry of the co-ordinated alkoxy-olefin was shown by ^1H n.m.r. spectroscopy to be exclusively *cis*.

Analogous reactions of $[Pd(MeCN)_2Cl_2]$ with *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (1d) in dichloromethane and alcoholic solvents were also investigated. Thus, reaction of $[Pd(MeCN)_2Cl_2]$ with an equimolar amount of (1d) in dichloromethane solution resulted in a much faster reaction than was observed with (1b), yielding a golden yellow solution in less than 1 h. Evaporation of

Reaction of $[Pd(MeCN)_2Cl_2]$ with (1d) in methanol solution, in the presence of sodium carbonate, yielded a mixture of the conformationally isomeric pair of complexes (9a) and (10a), in which the geometry of the co-ordinated alkoxy-olefin was shown to be exclusively *trans*, in agreement with the observations concerning the analogous reaction of (1b). However, in t-butyl alcohol solution $[Pd(MeCN)_2Cl_2]$ and (1d) reacted smoothly to produce only a mixture of the conformational isomeric pair of complexes (9b) and (10b), in which the geometry of the co-ordinated alkoxy-olefin was shown to be exclusively *trans*, in contrast to the corresponding reaction of (1b) which produced an exclusively *cis*-alkoxy-olefin.

* Reaction of this mixture of four isomers with pyridine yields an isomeric mixture of two η^1-bonded complexes, the only observable isomerism being that about the now unco-ordinated alkoxy-olefin.[10]

[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford 1966, vol. 2.

DISCUSSION

The Pd^{II}-promoted ring-opening of both *trans*- and *cis*-2,3-dimethoxycarbonylmethylenecyclopropane, (1b), and (1c), occurs stereospecifically in dichloromethane solution, to yield the isomeric, substituted η^3-but-3-enyl complexes (4a) and (8a) respectively. In the reaction of the *trans*-diester (1b), an intermediate η^2-bonded olefin complex can be isolated from an interceptory work-up of the reaction mixture. That (5a) is indeed a key intermediate is evidenced from the observation that a suspension of (5a) in dichloromethane slowly rearranges to yield (4a). However, the ring-opening reaction of the *cis*-diester (1c), after co-ordination to Pd^{II}, is much more rapid than that of (1b), and no η^2-bonded complex intermediate analogous to (5a) was observed.

The ring-opening reaction in dichloromethane is stereospecific in two respects; the migrating chloride ligand becomes attached exclusively to the internal olefinic carbon atom, generating a co-ordinated vinylidene olefin, and the ring-opening proceeds with retention, rather than inversion, of configuration at the cyclopropane carbon atom which finally becomes σ-bonded to palladium.*

In alcoholic solution both the *trans*- and *cis*-diesters (1b) and (1c) undergo an analogous ring-opening reaction with $[Pd(MeCN)_2Cl_2]$, yielding an analogous η^3-but-3-enyl skeleton, but no chloride is incorporated into the organic ligand. Instead, alkoxide is incorporated exclusively at the terminal olefinic carbon atom, generating a disubstituted alkoxy-olefin.

All the η^3-but-3-enyl complexes produced in alcoholic solution, *i.e.* complexes (6), (7), (9), and (10), exhibit conformational isomerism within the chelating but-3-enyl ring in solution. However, complexes (4) and (8), which have a chlorine atom in the 3-position of the but-3-enyl ligand, exhibit ^1H and ^{13}C n.m.r. spectra consistent with the presence of only one of the two possible ring conformers.

In complexes (4) and (8), molecular models strongly suggest that the dominant steric interaction is between the chlorine atom in the 3-position and the CO_2Me substituent in the 2-position. To minimise this interaction it is necessary for the 2-CO_2Me substituent to occupy a pseudo-*exo*-position as drawn for both (4) and (8). The 1-CO_2Me group in complexes (4) must therefore occupy a pseudo-*syn*-position as drawn, and that in complexes (8) a pseudo-*anti*-position † as drawn, since their geometric orientation with respect to the 2-CO_2Me group is predetermined by the *trans*- or *cis*-configurations of the diester precursors. It is noteworthy that the chemical shifts of the protons in the 1-position of complexes (4) and (8) (Table 1) exhibit the same trend as that shown in η^3-propenyl complexes [12,13] in that the pseudo-*anti*-proton in complexes (4) resonates at much higher field than its pseudo-*syn*-counterpart in complexes (8).

In the alkoxy-olefin complexes (6), (7), (9), and (10), there is no substituent in the 3-position to interact sterically with the 2-CO_2Me group. This group can therefore occupy a pseudo-*exo* [as in isomers (6)] or pseudo-*endo* [as in isomers (7)] position, giving rise to conformational isomers. The ^1H n.m.r. assignments for each isomer are based on the assignments for the single conformational isomers observed in complexes (4) and (8). The ratio of conformational isomers must be thermodynamically determined, and is dependent upon the other ligands present on the metal. Thus, the ratio of (6a) : (7a), (6b) : (7c), and (6e) : (7e) is 2 : 1 in $CDCl_3$ solution, but the ratio in the acetylacetonate complexes (6d) : (7d) is 1 : 1. The equilibrium between conformational isomers must therefore be dynamic since a 2 : 1 ratio of (6a) : (7a) converts into a 1 : 1 ratio of (6d) : (7d). Interconversion of conformational isomers can only be achieved by dissociation of the co-ordinated olefin, rotation about the 2–3 bond of the now η^1-but-3-enyl ligand, and reformation of the olefin–metal bond.

The reaction of $[Pd(MeCN)_2Cl_2]$ with the *trans*-diesters (1b) in alcoholic solution also gives rise, in some cases, to geometrically isomeric products, differing in the geometry, *trans* or *cis*, of the substituents on the co-ordinated alkoxy-olefin. Whether the geometry is *trans* or *cis*, or a mixture of both, is apparently dependent upon the bulkiness of the alkoxide substituent. Thus, for methoxide and ethoxide, the olefin geometry is exclusively *trans*, for isopropoxide a mixture of *trans* : *cis* in the ratio of *ca.* 1 : 1 is obtained, and for t-butoxide the geometry is exclusively *cis*. The reaction of $[Pd(MeCN)_2Cl_2]$ with the *cis*-diester (1d) in either methanol or t-butyl alcohol shows no variations with alkoxide bulk, exclusively *trans*-olefin geometries being obtained in both cases. Some steric discrimination must, therefore, occur in the reaction pathway for the *trans*-diester which is not manifested in the corresponding reaction of the *cis*-diester.

Any mechanistic interpretation must, therefore, account for the differences in product geometries, the different site of attachment of chloride and alkoxide to the ring-opened skeleton, and the much faster rate of ring-opening observed for the *cis*-diester compared to the *trans*-diester in dichloromethane solution, together with the generally faster rates of reaction in alcohol solvents compared to dichloromethane.

The simplest mechanism for formation of complex (4a) from $[Pd(MeCN)_2Cl_2]$ and the *trans*-diester (1b), *via* the intermediacy of (5a), is depicted in Scheme 1. Chloropalladation of the co-ordinated olefin as shown generates a substituted cyclopropylmethyl-palladium species, which is expected to ring-open in a concerted, low-energy fashion as shown. This palladium(II)-promoted cyclopropylmethyl to but-3-enyl interconversion is completely analogous to the well-defined nortricyclenyl to norbornenyl

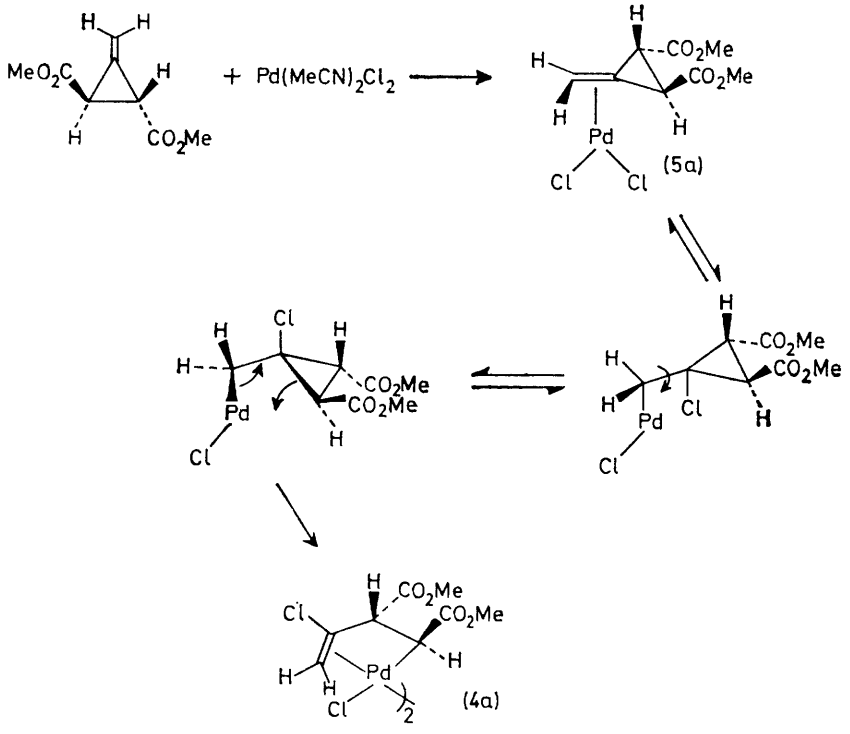
* Retention is confirmed in a crystal structure of the η^1-bonded complex derived from reaction of complex (8a) with pyridine.[10]

† The *syn* and *anti* terminology refers, respectively, to whether the 1-CO_2Me group points in the same, or opposite, direction to that of the Cl atom in the 3-position, by analogy with η^3-propenyl ligand systems.[12,13]

[12] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

[13] H. C. Dehm and J. C. W. Chien, *J. Amer. Chem. Soc.*, 1960, **82**, 4429.

interconversion.[14] It should be noted that in the cyclopropylmethyl intermediate derived from the *trans*-diester there are two distinct bonds in the cyclopropane ring which may be cleaved in the ring-opening process. The one depicted in Scheme 1 leads directly to the preferred conformation of the product (4a). Alternative cleavage of the other 1,2-bond would lead to a conformational isomer of (4a), which would then rearrange by a dissociative route. It is impossible to distinguish which, if any, bond is preferentially cleaved.



SCHEME 1

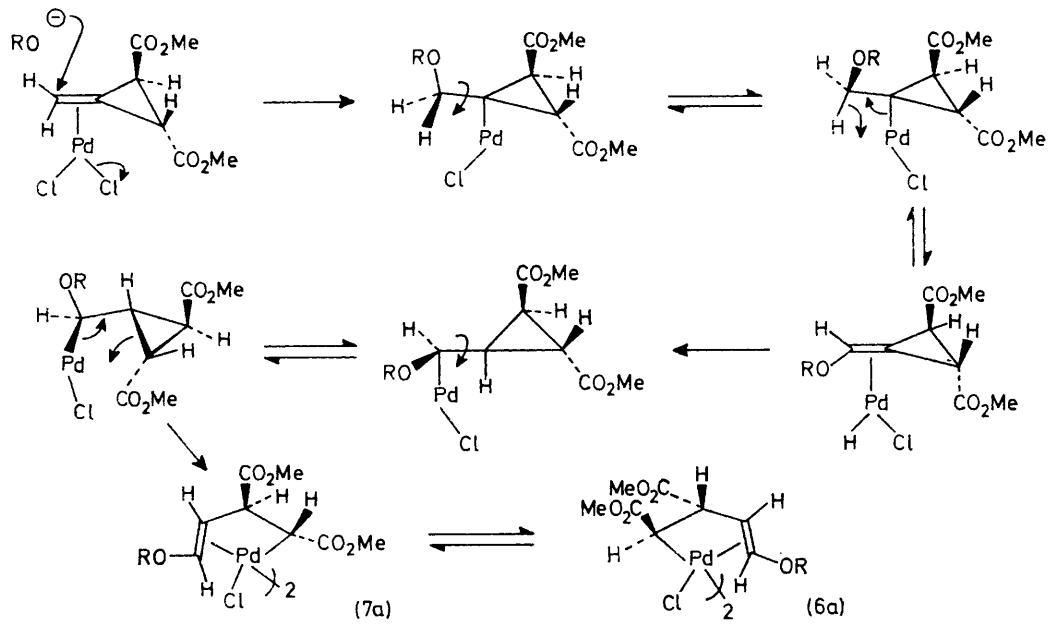
The same reaction product arises whether the initial chloropalladation occurs in a *cis*-fashion, *i.e.* a *cis*-ligand migration reaction, or in a *trans*-fashion by nucleophilic attack by external chloride ion. Definitive examples of both processes have been recently reported.[15-17] However, the following arguments strongly imply a *cis*-chloropalladation reaction.

A prerequisite for a *cis*-ligand migration reaction to a co-ordinated olefin is normally considered to involve a propeller-type olefin rotation around the metal–olefin bonding axis, to generate a planar four-centre intermediate in which the axis of the olefin lies in the square-plane of co-ordination of the metal.[18,19] It has previously been shown that propeller rotation of the olefinic ligand in η^2-bonded complexes of Rh^I and Ir^I with the *trans*-diesters (1b) is sterically impeded by interaction of the *endo*-CO_2Me group with ligands *cis* to itself. However, in the analogous η^2-bonded complexes of the *cis*-diester (1d), in which both CO_2Me groups are presumably *exo* with respect to the metal, propeller rotation was shown to be fast at ambient temperature.[6] By analogy, therefore, propeller rotation of the *trans*-diester ligand in (5a) is expected to be a relatively high-energy reaction; consequently the planar four-centre intermediate required for *cis*-chloropalladation is not readily achieved. Such an intermediate should readily be obtainable in a Pd^{II} complex of the *cis*-diester, with both CO_2Me groups *exo*, since propeller rotation should be a low-energy process. This argument explains the markedly faster rate of production of ring-opened complexes (8a) from (1c), compared to that of (4a) from (1b), and also the stability of (5a), and strongly implies that chloropalladation is the rate-determining step for the overall reaction sequence.[20]

An interesting corollary to this argument is that, in this system, *cis*-chloropalladation, where sterically possible, must be a far faster process than *trans*-chloropalladation.[20] It is notable that examples of *trans*-chloropalladation were only found in systems where the required transition state geometry for *cis*-chloropalladation is sterically forbidden;[16,17] indeed, *trans*-chloropalladation of intermediate (5a) cannot be definitely excluded.

[14] E. Bau, R. P. Hughes, and J. Powell, *J. Organometallic Chem.*, 1974, **69**, 455; and references cited therein.
[15] B. E. Mann, P. M. Bailey, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1975, **97**, 1275; and references cited therein.
[16] W. T. Wipke and G. L. Goeke, *J. Amer. Chem. Soc.*, 1974, **96**, 4244.
[17] G. Wiger, G. Albels, and M. F. Rettig, *J.C.S. Dalton*, 1974, 2242.
[18] B. L. Shaw, *Chem. Comm.*, 1968, 464.
[19] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, London, vol. 1, p. 137.
[20] P. M. Henry, *J. Org. Chem.*, 1972, **37**, 2443.

The reaction of the *trans*-diester (1b) with $[Pd(MeCN)_2Cl_2]$ in alcoholic solvents proceeds much faster than in dichloromethane, to yield a mixture of ring-opened conformers. The proposed mechanism is depicted in Scheme 2, and presumably proceeds *via* the intermediacy



SCHEME 2

of (5a). *trans*-Alkoxypalladation of (5a) must be fast, compared to the *cis*-chloropalladation process, since products derived from the latter reaction are not observed. This is not surprising since there is an infinite concentration of external solvent nucleophile available, and also since no olefin rotation is required to achieve the transition-state geometry for *trans*-alkoxypalladation.

It is also remarkable that the external alkoxide nucleophile must attack exclusively at the terminal olefinic carbon atom, in order to achieve the observed product structure, whereas the internally derived chlorine in the *cis*-chloropalladation reaction attacks exclusively at the internal carbon. The reasons for such selectivity are as yet unknown, yet precedence can be found in the reaction of allene with palladium halides in benzene or methanol.[21,22] The remarkable similarity in the nature of bonding of allene and methylenecyclopropane to transition metals has been discussed elsewhere;[6] we now find a parallel in their chemical reactions.

Attack of alkoxide on the terminal carbon atom of coordinated (1b) requires a subsequent 1,2-hydrogen shift, presumably *via* the metal as shown, to generate the cyclopropylmethyl-palladium species which provides a low-energy ring-opening route. The steric discrimination with increasing alkoxide bulk, leading to *trans*- or *cis*-olefin geometries in the final products derived from (1b), must arise in an unsymmetrical transition state, provided the alkoxide is sufficiently bulky to sense the asymmetry, thereby giving rise to a kinetically controlled *cis*-olefin geometry. In the reaction of the *trans*-diester depicted in Scheme 2, such asymmetry can arise either in the transition state(s) for the 1,2-hydrogen shift, or in the ring-cleavage step, or in both. It is therefore not possible to identify the exact nature of this remarkable steric control. However, both these transition states for the corresponding reaction of the *cis*-diester are symmetrical, in that both CO_2Me groups are on the same side of the cyclopropane ring. The chosen reaction path therefore leads to the more thermodynamically stable *trans*-olefin geometry in the product.

[21] R. G. Schultz, *Tetrahedron*, 1964, **20**, 2809.
[22] M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1687.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

^1H N.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer at 100 MHz. ^{13}C N.m.r. spectra were recorded on a Jeol JNM-PFT-100 spectrometer, operating in the Fourier-transform mode, at 25.15 MHz.

trans-2,3-Dimethoxycarbonylmethylenecyclopropane,[23] and *trans*-2,3-dimethoxycarbonyl-2,3-dideuteriomethylenecyclopropane [24] were prepared by literature methods.

Reactions of $[Pd(MeCN)_2Cl_2]$ *with* trans-2,3-*Dimethoxycarbonylmethylenecyclopropane*, (1b).—(a) *In dichloromethane*. A solution of $[Pd(MeCN)_2Cl_2]$ (1.53 g, 5.9 mmol) and *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (1.00 g, 5.9 mmol) in dichloromethane (150 cm^3) was stirred (21 °C; 48 h), after which time the initial orange solution had faded to a pale golden-yellow colour. The solution was reduced in volume to *ca.* 50 cm^3 and pentane (200 cm^3) was added

[23] I. S. Krull, *J. Organometallic Chem.*, 1973, **57**, 363, and references cited therein.
[24] A. T. Bottini and J. D. Roberts, *J. Org. Chem.*, 1956, **21**, 1169.

slowly to precipitate *complex* (4a) as pale yellow *needles* (2.00 g, 98%), m.p. 135—139 °C (decomp.) [Found: C, 28.0; H, 3.0. $(C_8H_{10}Cl_2O_4Pd)_2$ requires C, 27.7; H, 2.9%]. Work-up of this reaction mixture after only 1 h yielded an insoluble solid complex (5a) (90%), m.p. 110—115 °C (decomp.) [Found: C, 28.0; H, 3.0. $(C_8H_{10}O_4Pd)_2$ requires C, 27.7; H, 2.9%].

Prolonged stirring (48 h) of a suspension of complex (5a) (0.50 g, 3.5 mmol) in dichloromethane (100 cm³) resulted in a golden-yellow solution. Volume reduction to *ca.* 20 cm³ followed by addition of pentane (100 cm³) yielded *complex* (4a) (0.49 g, 98%), identified by its ^{1}H n.m.r. spectrum.

A suspension of complex (5a) (0.20 g, 1.4 mmol) in deuteriochloroform (1 cm³) was treated with pyridine (0.22 g, 2.8 mmol). The resultant mixture was stirred (0.5 h) and filtered to yield a golden yellow solid, identified by its i.r. spectrum as $[Pd(pyridine)_2Cl_2]$. The ^{1}H n.m.r. spectrum of the filtrate showed it to contain only unchanged *trans*-2,3-dimethoxycarbonylmethylenecyclopropane. Similarly, prolonged stirring (48 h, 21 °C) of a solution of $[Pd(MeCN)_2Cl_2]$ (0.50 g, 1.9 mmol) and *trans*-2,3-dimethoxycarbonyl-2,3-dideuteriomethylenecyclopropane (0.33 g, 1.9 mmol) in dichloromethane (50 cm³) yielded, after an identical work-up procedure, *complex* (4b) (0.65 g, 96%), m.p. 134—138 °C (decomp.) [Found: C, 27.8; H, 3.0. $(C_8H_8Cl_2D_2O_4Pd)_2$ requires C, 27.5; H, 2.9%].

A solution of complex (4a) (0.50 g, 1.4 mmol) and lithium bromide (2.50 g, 28.7 mmol) in acetone (50 cm³) was stirred (0.5 h, 21 °C), and then evaporated to dryness. Extraction of the residue with dichloromethane (3 × 50 cm³), concentration of the combined extracts to *ca.* 20 cm³, followed by addition of pentane (100 cm³) precipitated complex (4c) as golden yellow *needles* (0.50 g, 89%), m.p. 120—122 °C (decomp.) (Found: C, 24.7; H, 2.7. $C_8H_{10}BrClO_4Pd$ requires C, 24.5; H, 2.6%).

A solution of complex (4a) (0.50 g, 1.4 mmol) and acetylacetonatothallium(I) (0.48 g, 1.6 mmol) in dichloromethane (20 cm³) was stirred (1 h; 21 °C). Pentane (50 cm³) was added, and the precipitated thallium(I) chloride was removed by filtration through a plug of Kieselguhr. The resultant pale yellow solution was evaporated to dryness and the residue recrystallised from pentane (−30 °C) to yield complex (4d) as pale yellow *needles* (0.50 g, 84%), m.p. 80—82 °C (decomp.) (Found: C, 38.2; H, 4.4; Cl, 9.0. $C_{13}H_{17}ClO_6Pd$ requires C, 38.0; H, 4.2; Cl, 8.6%).

Similarly, complex (4b) (0.20 g, 0.6 mmol) and acetylacetonatothallium (0.20 g, 0.7 mmol) yielded *complex* (4e) as pale yellow *needles* (0.18 g, 76%), m.p. 80—82 °C (decomp.) (Found: C, 37.9; H, 4.1. $C_{13}H_{15}ClD_2O_6Pd$ requires C, 37.8; H, 4.1%).

A solution of complex (4a) (0.50 g, 1.4 mmol) and hexafluoroacetylacetonatothallium (0.60 g, 1.4 mmol) in dichloromethane (20 cm³) was stirred (1 h; 21 °C). Pentane (50 cm³) was added and the resultant suspension was filtered through a Kieselguhr plug. Evaporation of the filtrate and recrystallisation of the residue from pentane (−30 °C) yielded *complex* (4f) as cream *prisms*, m.p. 69—70 °C (decomp.) (Found: C, 29.7; H, 2.3; Cl, 7.1; F, 21.9. $C_{13}H_{11}ClF_6O_6Pd$ requires C, 30.0; H, 2.1; Cl, 6.8; F, 22.0%).

A mixture of complex (4a) (0.30 g, 0.8 mmol) and cyclopentadienylthallium (0.30 g, 1.1 mmol) in dichloromethane (20 cm³) was stirred (2 h; 21 °C), and filtered. Evaporation of the resultant solution to dryness and recrystallisation of the residue from pentane (−30 °C) yielded complex (4g) as red prisms (0.25 g, 77%), m.p. 110—111 °C (decomp.) (Found: C, 41.6; H, 4.2; Cl, 9.8. $C_{13}H_{15}ClO_4Pd$ requires C, 41.1; H, 4.0; Cl, 9.4%).

(b) *In methanol.* A solution of $[Pd(MeCN)_2Cl_2]$ (1.00 g, 3.8 mmol) and *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.70 g, 4.1 mmol) in methanol (50 cm³) was treated with sodium carbonate (0.21 g, 2.0 mmol), and stirred (10 h; 21 °C). The resultant golden-yellow solution was evaporated to dryness and the residue was extracted with dichloromethane (3 × 20 cm³). The filtered extracts were combined and evaporated to dryness. Recrystallisation of the residue from dichloromethane–pentane (−30 °C) yielded yellow *prisms* (1.15 g, 87%), m.p. 106—108 °C (decomp.), shown by ^{1}H n.m.r. to consist of a mixture of conformationally isomeric *complexes* (6a) and (7a) [Found: C, 31.7; H, 3.9; Cl, 10.6. $(C_9H_{13}ClO_5Pd)_2$ requires C, 31.5; H, 3.8; Cl, 10.3%].

A similar reaction between $[Pd(MeCN)_2Cl_2]$ (0.50 g, 1.9 mmol), *trans*-2,3-dimethoxycarbonyl-2,3-dideuteriomethylenecyclopropane (0.33 g, 1.9 mmol), and sodium carbonate (0.11 g, 1.0 mmol) in methanol (20 cm³) yielded, after identical work-up, yellow *prisms* (0.60 g, 90%), m.p. 107—108 °C (decomp.), shown by ^{1}H n.m.r. to consist of a mixture of conformationally isomeric *complexes* (6b) and (7b) [Found: C, 31.5; H, 3.9. $(C_9H_{11}ClD_2O_5Pd)_2$ requires C, 31.3; H, 3.8%].

A solution of complexes (6a) and (7a) (0.20 g, 0.6 mmol) and acetylacetonatothallium (0.20 g, 0.7 mmol) in dichloromethane (20 cm³) was stirred (1 h; 21 °C). Pentane (50 cm³) was added and the resultant suspension was filtered through a Kieselguhr plug. Evaporation of the filtrate to dryness, and recrystallisation of the residue from pentane (−30 °C) yielded cream *needles* (0.21 g, 89%), m.p. 80—81 °C (decomp.), shown by ^{1}H n.m.r. to consist of a mixture of the conformationally isomeric complexes (6d) and (7d) (Found: C, 41.6; H, 4.9. $C_{14}H_{20}O_7Pd$ requires C, 41.3; H, 5.0%).

(c) *In ethanol.* A mixture of $[Pd(MeCN)_2Cl_2]$ (1.00 g, 3.8 mmol), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.80 g, 4.7 mmol), and sodium carbonate (0.21 g, 2.0 mmol) in ethanol (50 cm³) was stirred (10 h; 21 °C). The resultant golden-yellow solution was evaporated to dryness and the residue was extracted with dichloromethane (3 × 20 cm³). The filtrate extracts were evaporated to dryness, and the residue recrystallised from dichloromethane–pentane (−30 °C) to yield yellow prisms (1.10 g, 80%), m.p. 97—99 °C (decomp.), shown by ^{1}H n.m.r. to consist of a mixture of the conformationally isomeric *complexes* (6e) and (7e) [Found: C, 33.4; H, 4.2. $(C_{10}H_{15}ClO_5Pd)_2$ requires C, 33.6; H, 4.2%].

(d) *In isopropyl alcohol.* A similar reaction of $[Pd(MeCN)_2Cl_2]$ (1.0 g, 3.8 mmol), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.80 g, 4.7 mmol), and sodium carbonate (0.21 g, 2.0 mmol) in isopropyl alcohol (100 cm³) yielded after identical work-up, yellow *prisms* (1.24 g, 87%), m.p. 96—97 °C (decomp.), shown by ^{1}H n.m.r. to consist of a mixture of the isomeric *complexes* (6f), (6g), (7f), and (7g) [Found: C, 35.5; H, 4.7. $(C_{11}H_{17}ClO_5Pd)_2$ requires C, 35.6; H, 4.6%].

(e) *In t-butyl alcohol.* A similar reaction of $[Pd(MeCN)_2Cl_2]$ (1.00 g, 3.8 mmol), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.80 g, 4.7 mmol), and sodium carbonate (0.21 g, 2.0 mmol) in t-butyl alcohol (70 cm³), yielded after identical work-up, yellow *prisms* (1.20 g, 81%), m.p. 91—93 °C (decomp.), shown by ^{1}H n.m.r. to consist of a mixture of the conformationally isomeric complexes (6h) and (7h) [Found: C, 37.6; H, 5.0. $(C_{12}H_{19}ClO_5Pd)_2$ requires C, 37.4; H, 4.9%].

Reactions of $[Pd(MeCN)_2Br_2]$ *with* trans-2,3-*Dimethoxycarbonylmethylenecyclopropane*.—(a) *In dichloromethane*. *trans*-2,3-Dimethoxycarbonylmethylenecyclopropane (0.50 g, 2.9 mmol) was added, with stirring, to a solution of $[Pd(MeCN)_2Br_2]$ (1.0 g, 2.8 mmol) in dichloromethane (50 cm³). The resultant precipitate was filtered off, washed with dichloromethane and pentane, and dried under vacuum to afford *complex* (5b) as an amorphous, dark brown powder (1.10 g, 88%), m.p. 103—105 °C (decomp.) [Found: C, 21.8; H, 2.1. $(C_8H_{10}Br_2O_4Pd)_2$ requires C, 22.0; H, 2.3%].

(b) *In methanol*. A solution of $[Pd(MeCN)_2Br_2]$ (1.00 g, 2.8 mmol), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.50 g, 2.9 mmol), and sodium carbonate (0.15 g, 1.4 mmol) was stirred (8 h; 21 °C). The resultant golden-yellow solution was evaporated to dryness and extracted with dichloromethane (3 × 20 ml). The filtered extracts were evaporated to dryness and the residue was recrystallised from dichloromethane–pentane to yield yellow *needles* (1.00 g, 90%), m.p. 97—99 °C (decomp.), shown by ^1H n.m.r. spectroscopy to consist of a mixture of the conformationally isomeric complexes (6c) and (7c) [Found: C, 28.0; H, 3.4. $(C_9H_{13}BrO_5Pd)_2$ requires C, 27.9; H, 3.4%].

An identical mixture of *complexes* (6c) and (7c) was prepared by treatment of a suspension of complex (5b) (0.50 g, 1.1 mmol) in methanol (50 cm³) with sodium carbonate (0.06 g, 0.6 mmol). The mixture was stirred (8 h; 21 °C) and worked up as above to yield the *product mixture* as yellow *needles* (85%), identified by ^1H n.m.r. spectroscopy.

Reactions of $[Pd(MeCN)_2Cl]$ *with* cis-2,3-*Dimethoxycarbonylmethylenecyclopropane*.—(a) *In dichloromethane*. A solution of $[Pd(MeCN)_2Cl_2]$ (3.00 g, 11.6 mmol) and *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (2.00 g, 11.8 mmol) was stirred (1 h; 21 °C). The initial orange-yellow solution rapidly faded to a pale golden yellow. Evaporation, and recrystallisation of the residue from dichloromethane–pentane yielded *complex* (8a) as fine yellow *needles* (3.80 g, 94%), m.p. 145—149 °C (decomp.) [Found: C, 27.8; H, 3.0. $(C_8H_{10}O_4Pd)_2$ requires C, 27.7; H, 2.9%].

A solution of complex (8a) (0.18 g, 0.5 mmol) and acetylacetonatothallium (0.18 g, 0.6 mmol) in dichloromethane (20 cm³) was stirred (1 h; 21 °C). Pentane (50 cm³) was added and the resultant suspension was filtered through a Kieselguhr plug. The resultant filtrate was evaporated to dryness and the residue recrystallised from pentane (−30 °C) to afford *complex* (8b) as pale yellow needles (0.17 g, 80%), m.p. 75—77 °C (decomp.) (Found: C, 38.0; H, 4.1. $C_{13}H_{17}ClO_6Pd$ requires C, 38.0; H, 4.1%).

A solution of complex (8a) (0.30 g, 0.8 mmol) and cyclopentadienylthallium (0.30 g, 1.1 mmol) in dichloromethane (20 cm³) was stirred (3 h; 21 °C), and filtered. Evaporation of the filtrate to dryness, and recrystallisation of the residue from pentane (—30 °C) yielded *complex* (8c) as red *prisms* (0.22 g, 68%), m.p. 121—123 °C (decomp.) [Found: C, 41.5; H, 4.1; Cl, 9.8. $C_{13}H_{15}ClO_4Pd$ requires C, 41.4; H, 4.1; Cl, 9.4%]

(b) *In methanol*. A mixture of $[Pd(MeCN)_2Cl_2]$ (1.00 g, 3.8 mmol), *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (0.70 g, 4.1 mmol), and sodium carbonate (0.21 g, 2.0 mmol) in methanol (50 cm³) was stirred (0.5 h; 21 °C). The resultant golden yellow solution was evaporated to dryness and the residue was extracted with dichloromethane (3 × 20 cm³). The filtered extracts were evaporated to dryness, and the residue was recrystallised from dichloromethane–pentane to afford yellow *needles* (1.10 g, 83%), m.p. 122—125 °C (decomp.), shown by ^1H n.m.r. spectroscopy to consist of a mixture of the conformationally isomeric *complexes* (9a) and (10a) [Found: C, 31.6; H, 3.8; Cl, 10.5. $(C_9H_{13}ClO_5Pd)_2$ requires C, 31.5; H, 3.8; Cl, 10.3%].

(c) *In t-butyl alcohol*. A similar reaction of $[Pd(MeCN)_2Cl_2]$ (1.0 g, 3.8 mmol), *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (0.70 g, 4.1 mmol), and sodium carbonate (0.21 g, 2.0 mmol) in t-butyl alcohol (50 cm³) yielded, after an identical work-up, yellow *prisms* (1.00 g, 67%), m.p. 106—108 °C (decomp.), shown by ^1H n.m.r. spectroscopy to consist of a mixture of the conformationally isomeric complexes (9b) and (10b) [Found: C, 37.5; H, 5.0. $(C_{12}H_{19}ClO_5Pd)_2$ requires C, 37.4; H, 4.9%].

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