Reactions of Co-ordinated Ligands. Part XII.[1] The Preparation and Thermal Rearrangement of η^1-But-3-enyl Complexes of Palladium(II): the Crystal and Molecular Structure of *trans*-Chloro-η^1-[3-chloro-*cis*-1,2-bis-(methoxycarbonyl)but-3-enyl]bis(pyridine)palladium(II)

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The reaction of the η^3-but-3-enyl complexes [Pd(X)CH(CO$_2$Me)CR^1=CHR^1] (X = Cl, hexafluoroacetylacetonate; R^1 = Cl or H, R^2 = H or alkoxy) with pyridine or cyclo-octa-1,5-diene leads to the formation of thermally stable η^1-but-3-enyl complexes of Pd^{II}. A single-crystal *X*-ray diffraction study forms the basis of a discussion as to the origins of the stability of these complexes. Crystals of [PdCl(py)$_2${CH(CO$_2$Me)·CH(CO$_2$Me)·C(Cl):CH$_2$}] are triclinic, $P\bar{1}$, with four molecules in a unit cell of dimensions: a = 14.794(8), b = 11.599(8), c = 13.131(8) Å, α = 89.53(5), β = 113.04(4), γ = 91.50(5)°. The structure has been elucidated by conventional heavy-atom methods from 5 397 diffracted intensities measured on a four-circle diffractometer, and refined to R 0.075. The asymmetric unit thus comprises two crystallographically distinct molecules, and while these do not differ fundamentally in either their geometry or their stereochemistry at the two chiral centres, the ligands adopt different equilibrium positions as a result of free rotation around each ligand axis. The important conclusions of the structure determination are that (i) the two chiral centres have opposite configurations (one *R*, and one *S*), (ii) the groups on the two chiral centres are in a staggered configuration relative to one another, (iii) the hydrogen atoms lie *trans* to one another. Because the space group is centrosymmetric, the crystals comprise equal numbers of *R–S* and *S–R* molecules. Reaction of the η^1-but-3-enyl palladium(II) complexes in refluxing benzene affords π-allylic complexes. The stereochemistry of these is discussed in terms of their ^{1}H n.m.r. spectra and the mechanism of their formation.

THE thermal stability of σ-alkyl complexes of palladium(II) is generally considerably lower than that of their platinum(II) analogues, particularly in the case of alkyl ligands containing β-hydrogen atoms.[2] The facility with which β-hydrogen elimination reactions occur introduces such kinetic instability that many Pd^{II}–alkyl complexes are often difficult to handle.[2] However, the factors affecting the facility of such β-hydrogen elimination reactions are not well understood.

We have previously described the preparation of the substituted η^3-but-3-enyl complexes (1)—(6), from the reactions of *trans*- and *cis*-2,3-dimethoxycarbonylmethylenecyclopropanes with [Pd(MeCN)$_2$Cl$_2$] in either dichloromethane or alcohol solvents. This paper reports the reactions of these η^3-but-3-enyl complexes with pyridine to produce thermally stable η^1-but-3-enyl complexes of palladium(II), also the thermal rearrangements of the η^3-but-3-enyl complexes to produce η^3-propenyl complexes of palladium(II).

RESULTS

Addition of two molar equivalents of pyridine per palladium to a yellow solution of complex (1a) in dichloromethane produced an instantaneous decolourisation, to yield a very pale yellow solution. Evaporation followed by recrystallisation of the residue produced a high yield of air-stable, pale yellow crystals, characterised by microanalysis as a 1 : 2 adduct. The ^{1}H n.m.r. spectrum (Table 1) was entirely consistent with the presence of a but-3-enyl ligand, and integration confirmed the presence of two molecules of pyridine per palladium atom. The nature of the bonding of the but-3-enyl ligand to the metal was deduced from a comparison of the ^{13}C n.m.r. spectrum of the 1 : 2 adduct (Table 2) with that of its η^3-but-3-enyl precursor complex (1a). Particularly diagnostic is the observation that formation of the 1 : 2 adduct causes pronounced downfield shifts of the two olefinic carbon resonances, originally co-ordinated to the metal in (1a) †, to values typical of a free, unco-ordinated chlorovinylidene olefin. The isomeric complex (2) also formed a 1 : 2 adduct with pyridine, which exhibited analogous ^{1}H and ^{13}C n.m.r. spectral features. These isomeric 1 : 2 adducts were therefore structurally formulated as the η^1-but-3-enyl complexes (7a) and (8a) respectively, differing only in the relationship between the absolute configurations at the α and β carbon centres. Similarly the bromo-complex (1c) formed a 1 : 2 adduct (7b) with pyridine.

The ^{1}H n.m.r. spectra of complexes (7a), (7b), and (8a) in CDCl$_3$ solution were temperature invariant from -60 to $+60$ °C. In particular the large coupling constant ($J_{1,2}$ = 12 Hz) between the vicinal protons H^1 and H^2 showed no variation, implying that no differing rate of rotation was occurring about the C^1–C^2 bond within this temperature range. The large value of this vicinal coupling constant[5] can only be rationalised by either a mutually *cis* (dihedral angle 0°) or *trans* (dihedral angle 180°) orientation of H^1 and H^2. Since the former configuration would result in an eclipsed orientation with maximum vicinal steric interactions between bulky groups, the latter staggered configuration with H^1 and H^2 mutually *trans* must be favoured, and is drawn for all complexes (7) and (8).

The mixture of conformational isomers (3a) and (4a) reacted with pyridine to produce a single conformer of the 1 : 2 adduct (7c). The ^{1}H n.m.r. spectrum of (7c) was also temperature invariant from -60 to $+60$ °C, and exhibited an identical value of $J_{1,2}$ to that observed in the spec-

† The upfield shift induced in the ^{13}C n.m.r. spectra of olefins co-ordinated to Pd^{II} is well established.[3,4]

[1] Part XI, M. Green and R. P. Hughes, *J.C.S. Dalton*, preceding paper.

[2] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Vol. 1, Academic Press, New York and London, 1971; and references cited therein.

[3] R. P. Hughes, T. R. Jack, and J. Powell, *J. Organometallic Chem.*, 1973, **63**, 451.

[4] D. G. Cooper, R. P. Hughes, and J. Powell, *J. Amer. Chem. Soc.*, 1972, **94**, 9244.

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

TABLE 1

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

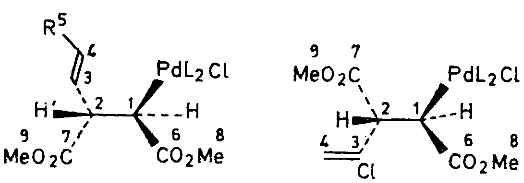
(Complex configuration and numbering as shown in the text)
τ(multiplicity); J Hz

Complex	H¹	H²	Me³ [a]	Me⁴ [a]	R⁵	R⁶	R⁷	L	X
(7a) [b]	6.81(d) $J_{1,2}$ = 12	6.63(d)	6.44(s)	6.29(s)		4.57(d) $J_{6,7}$ = 2	4.90(d)	2.62(m), H_β 2.20(m), H_γ 1.14(m), H_β	
(7b) [b]	6.81(d) $J_{1,2}$ = 11.5	6.60(d)	6.60(d)	6.44(s)		4.55(d) $J_{6,7}$ = 2	4.85(d)	2.62(m), H_γ 2.20(m), H_β 1.14(m), H_γ	
(7c) [b]	6.81(d) $J_{1,2}$ = 11.5	7.36(dd) $J_{2,5}$ = 10	6.50(s)	6.33(s)	5.26(dd) $J_{2,5}$ = 10 $J_{5,6}$ = 12.5	3.60(d)	6.40(s) [a]	2.62(m), H_β 2.20(m), H_γ 1.14(m), H_β	
(7d)	6.83(d) $J_{1,2}$ = 11.5	7.39(dd) $J_{2,5}$ = 10	6.52(s)	6.34(s)	5.22(dd) $J_{2,4}$ = 10	3.67(d) $J_{5,6}$ = 12	6.21(q), CH_2 8.66(t), CH_3 J = 7	2.63(m), H_γ 2.20(m), H_β 1.14(m), H_γ	
(7e)	6.86(d) $J_{1,2}$ = 11.5	7.38(dd) $J_{2,5}$ = 10	6.50(s)	6.32(s)	5.07(dd) $J_{2,5}$ = 10 $J_{5,6}$ = 12	3.80(d)	5.92(m), CH 8.64(d), CH_3 [c] 8.79(d), CH_3 [c]	2.62(n), H_β 2.20(m), H_γ 1.14(m), H_β	
(7f)	6.82(d) $J_{1,2}$ = 11.5	6.70(dd) $J_{2,5}$ = 10	6.50(s)	6.38(s)	5.69(dd) $J_{2,5}$ = 10 $J_{5,7}$ = 6	5.92(m), CH 8.64(d), CH_3 [c] 8.79(d), CH_3 [c]	3.75(d) $J_{5,7}$ = 6	2.62(m), H_γ 2.20(m), H_β 1.14(m), H_γ	
(7g)	6.58(d) $J_{1,2}$ = 11	5.88(d)	6.34(s)	6.30(s)		4.54(d) $J_{6,7}$ = 2	4.58(d)	3.92(s),CH	2.54(m), H_β 2.09(m), H_γ 1.14(m), H_α
(7h)	6.96(d) $J_{1,2}$ = 11.5	6.60(dd) $J_{2,5}$ = 10	6.46(s)	6.40(s)	5.14(dd) $J_{2,5}$ = 10 $J_{5,6}$ = 13	3.54(d)	6.40(s)	4.70(s), CH 8.03(s), CH_3 8.15(s), CH_3	2.62(m), H_β 2.19(m), H_γ 1.20(m), H_α
(7i)	6.56(d) $J_{1,2}$ = 11	5.28(d)	6.32(s)	6.32(s)		4.17(d) $J_{6,7}$ = 2	4.90(d)	7.44(m), CH_2 4.02(m), CH	
(8a) [b]	6.88(d) $J_{1,2}$ = 12	6.74(d)	6.34(s)	6.18(s)		4.86 [d]	4.86 [d]	2.61(m), H_β 2.19(m), H_γ 1.18(m), H_α	
(8b)	6.87(d) $J_{1,2}$ = 11	7.50(dd) $J_{2,5}$ = 10	6.45(s)	6.30(dd)	5.30(dd) $J_{2,5}$ = 10 $J_{5,6}$ = 12	3.60(d)	6.40(s) [a]	2.62(m), H_β 2.19(m), H_γ 1.14(m), H_α	
(8c)	6.77(d) $J_{1,2}$ = 11	5.19(d)	6.31(s)	6.23(s)		4.54(d) $J_{6,7}$ = 2	4.73(d)	7.33(m), CH_2 4.09(m), CH	

[a] Methyl assignments may be reversed; unambiguous assignment impossible. [b] Spectra remain unchanged from −60 to +60 °C in $CDCl_3$ solution. [c] Methyl groups are diastereotopic. [d] Accidently isochronous resonances.

TABLE 2

^{13}C N.m.r. data ($CDCl_3$; 34 °C; 25.15 MHz) for η^1-but-3-enyl complexes (7) and (8a)



(7) (8a)

δ (p.p.m.) downfield from internal $SiMe_4$

Complex	C¹	C²	C³	C⁴	C⁵	C⁶ [a]	C⁷ [a]	C⁸ [a]	C⁹ [a]	L
(7a)	27.77	55.07	139.53	115.86		176.41	169.44	52.10	50.88	125.78, C_α 152.51, C_β 137.83, C_γ
(7b)	30.21	55.03	139.54	116.00		176.19	172.06	52.24	51.02	124.86, C_α 152.89, C_β 137.84, C_γ
(7c)	30.52_1	45.26	149.25	100.59	55.88	176.37	172.98	51.45	50.66	124.86, C_α 152.16, C_β 137.79, C_γ
(7d)	30.40	45.32_1	148.34	101.26	64.61; CH_2 14.44; CH_3	176.37	172.98	51.39	50.60	124.80, C_α 152.16, C_β 137.72, C_γ
(7g)	25.30	53.81	139.66	116.67		175.89	168.67	52.52	51.27	90.40, CH 117.18, CF_3
(8a)	27.46	54.64	136.61	114.41		174.29	171.01	51.91	50.46	124.60, C_α 151.90, C_β 137.64, C_γ

[a] Assignments may be reversed.

trum of (7a) over this temperature range. Similarly, the mixture of conformational isomers (5) and (6) produced the single conformer (8b). The mixture of conformers (3c) and (4c) yielded an analogous 1 : 2 adduct (7d) on reaction with pyridine. The mixture of four isomers (3d), (4d), (3e), and (4e) [two conformational isomers of each geometric isomer] yielded a mixture of two isomeric complexes (7e) and (7f), the geometric isomerism of the isopropoxy-group about the now unco-ordinated olefinic function being maintained in the product mixture.

The monomeric hexafluoroacetylacetonate complex (1e) reacted with only one pyridine molecule per palladium, to yield the η^1-but-3-enyl complex (7g). The ^1H and ^{13}C n.m.r. spectral features of the but-3-enyl ligand were analogous to those of (7a). Similarly, the monomeric acetylacetonate complex mixture (3b) and (4b) reacted to yield the analogous 1 : 1 adduct (7h). A further reaction was observed in the treatment of complexes (1a) and (2) with cyclo-octa-1,5-diene to yield the η^1-but-3-enyl complexes (7i) and (8c) respectively.

It was previously noted that complexes (7a), (7b), (7c), and (8a) exhibited temperature-invariant ^1H n.m.r. spectra up to +60 °C. Indeed these complexes proved to possess remarkable thermal stability. Thus, complexes (7a) and (8a) were recovered unchanged from a refluxing benzene solution after 3 h.

In contrast, the thermal stability of the η^3-but-3-enyl precursors proved to be much lower, under identical conditions. Thus, refluxing a benzene solution of complex (1a) for 2 h yielded a new complex, isomeric with (1a), and formulated on the basis of its ^1H n.m.r. spectrum (Table 3) as the π-allylic complex (9a). The identical complex (9a) was obtained from the thermal rearrangement of complex (21) in refluxing benzene. The ^1H n.m.r. assignments for (9a) were confirmed by formation of the deuteriated complex (9b) from thermolysis of the labelled complex (1b). Notably, complexes (9a) and (9b) exhibited ^1H n.m.r. spectra consistent with the presence of only one of the two possible *syn*/*anti* isomers in $CDCl_3$ solution.

In an analogous thermal rearrangement, the mixture of the conformationally isomeric complexes (3a) and (4a) yielded a mixture of the π-allylic complexes (9c) and (9d); an identical mixture of (9c) and (9d) was also obtained from the thermal rearrangement of the mixture of conformational isomers (5) and (6). Similarly, the conformers (3c) and (4c) thermally rearranged to the π-allylic isomers (9g) and (9h). Thermolysis of the mixture of conformers (3b) and (4b) yielded a mixture of (9e) and (9f); the identical mixture of (9e) and (9f) was obtained by treatment of the isomer mixture of (9c) and (9d) with acetylacetonatothallium. In all the complexes (9c—h) the alkoxy-group was assigned a *syn*-position by virtue of the magnitude of the coupling constant ($J_{1,3}$ = 10 Hz) which is characteristic of a *trans*-coupling constant for an alkoxy-olefin,[5] and consequently, therefore, an alkoxy-allyl ligand.

Reaction of the mixture of isomers (3d), (4d), (3c), and (4c) in refluxing benzene yielded a mixture of the two isomeric π-allylic complexes (9i) and (9j) in which the isopropoxy-group occupies exclusively a *syn*-position. Isomerisation of the *cis*-alkoxy-olefin originally present in the isomers (3c) and (4e) must therefore have occurred.

The ratio of the *syn*/*anti* isomers (1c) : (1d), (9e) : (9f), (9g) : (9h), and (9i) : (9j) was invariably 1 : 2, and was independent of the nature of the alkoxy-group. The assign-

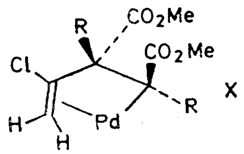
TABLE 3

^1H N.m.r. data ($CDCl_3$; 34 °C; 100 MHz) for η^3-propenyl complexes (9)

(Numbering as shown in the text)

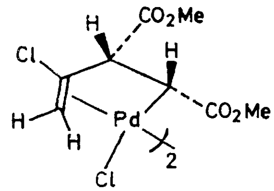
Complex	H[1]	R[2]	R[3]	R[4]	R[5]	X
(9a)	5.44(s) [a]	5.44(s) [a]		6.38(d), 6.78(d) J_{AX} = 17, CH_2; 6.27(s),[a] CO_2Me	6.27(s) [a]	
(9b)	5.44(s) [a]	5.44(s) [a]		6.27(s) [a]	6.27(s) [a]	
(9c)	3.50(d) $J_{1,3}$ = 10	6.30(s) [c]	4.06(d) $J_{1,3}$ = 10	~6.2 [b], 6.70(d) J_{AX} = 17, CH_2; 6.22(s),[c] CO_2Me	6.28(s) [c]	
(9d)	2.78(d) $J_{1,3}$ = 10	6.30(s) [c]	4.80(d) $J_{1,3}$ = 10	6.28(s) [c]	6.68(d), 7.35(d) J_{AX} = 17, CH_2; 6.22(s),[c] CO_2Me	
(9e)	3.71(d) $J_{1,3}$ = 10	6.21(s) [c]	4.00(d) $J_{1,3}$ = 10	~6.2 [b], 6.73(d) J_{AX} = 17, CH_2; 6.25(s),[c] CO_2Me	6.37(s) [c]	4.70(s), CH; 8.08(s), CH_3
(9f)	3.00(d) $J_{1,3}$ = 10	6.20(s) [c]	4.78(d) $J_{1,3}$ = 10	6.30(s) [c]	6.65(d), 7.35(d) J_{AX} = 17, CH_2; 6.30(s),[c] CO_2Me	6.37(s) [c]
(9g)	3.48(d) $J_{1,3}$ = 10	6.20(q), CH_2; 8.68(t), CH_3; J = 7	4.04(d) $J_{1,3}$ = 10	~6.2 [b], 6.72(d) J_{AX} = 17, CH_2; 6.22(s),[c] CO_2Me	6.29(s) [c]	
(9h)	2.76(d) $J_{1,3}$ = 10	6.20(q), CH_2; 8.68(t), CH_3; J = 7	4.80(d) $J_{1,3}$ = 10	6.28(s) [c]	6.66(d), 7.34(d) J_{AX} = 17, CH_2; 6.21(s),[c] CO_2Me	
(9i)	3.46(d) $J_{1,3}$ = 10	5.74(m), CH; 8.65(d), CH_3; 8.70(d), CH_3; J = 7	4.10(d) $J_{1,3}$ = 10	~6.2 [b], 6.74(d) J_{AX} = 17, CH_2; 6.25(s),[c] CO_2Me	6.34(s) [c]	
(9j)	2.65(d) $J_{1,3}$ = 10	5.74(m), CH; 8.65(d), CH_3; 8.70(d), CH_3; J = 7	4.88(d) $J_{1,3}$ = 10	6.30(s)	6.70(d), 7.40(d) J_{AX} = 17, CH_2; 6.34(s),[c] CO_2Me	

[a] Accidently isochronous resonances. [b] Obscured by OMe resonances. Unambiguous assignment between OMe groups is impossible; assignments may therefore be interchanged.



(1)

a; X = Cl, R = H (dimeric)
b; X = Cl, R = D (dimeric)
c; X = Br, R = H (dimeric)
d; X = acetylacetonate, R = H
e; X = hexafluoroacetylacetonate, R = H



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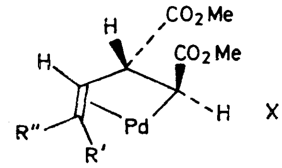
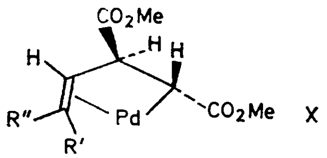


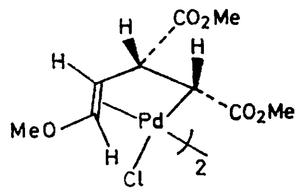
(3)

a; X = Cl, R′ = H, R″ = OMe (dimeric)
b; X = acetylacetonate, R′ = H, R″ = OMe
c; X = Cl, R′ = H, R″ = OEt
d; X = Cl, R′ = H, R″ = OPr^i
e; X = Cl, R″ = H, R′ = OPr^i



(4)

a; X = Cl, R = R′ = H, R″ = OMe
b; X = acetylacetonate R′ = H, R″ = OMe
c; X = Cl, R′ = H, X = OEt
d; X = Cl, R′ = H, R″ = OPr^i
e; X = Cl, R″ = H, R′ = OPr^i



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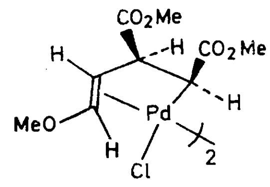

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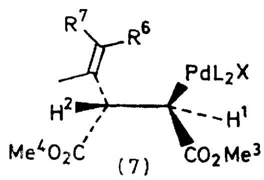
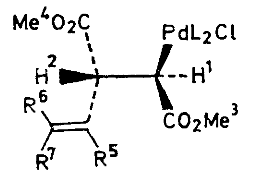


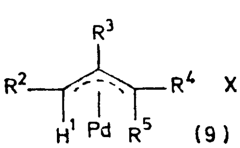
(7)

a; X = R^5 = Cl, R^6 = R^7 = H, L = pyridine
b; X = Br; R^5 = Cl, R^6 = R^7 = H, L = pyridine
c; X = Cl, R^5 = R^6 = H, R^7 = OMe, L = pyridine
d; X = Cl, R^5 = R^6 = H, R^7 = OEt, L = pyridine
e; X = Cl, R^5 = R^6 = H, R^7 = OPr^i, L = pyridine
f; X = Cl, R^5 = R^7 = H, R^6 = OPr^i, L = pyridine
g; X = pyridine, L_2 = hexafluoroacetylacetonate, R^5 = Cl, R^6 = R^7 = H
h; X = pyridine, L_2 = acetylacetonate, R^5 = R^6 = H, R^7 = OMe
i; X = R^5 = Cl, R^6 = R^7 = H, L_2 = cyclo-octa-1,5-diene



(8)

a; R^5 = Cl, R^6 = R^7 = H, L = pyridine
b; R^5 = R^6 = H, R^7 = OMe, L = pyridine
c; R^5 = Cl, R^6 = R^7 = H, L_2 = cyclo-octa-1,5-diene



(9)

a; X = R^3 = Cl, R^2 = H, R^4 = CH_2CO_2Me, R^5 = CO_2Me (dimeric)
b; X = R^3 = Cl, R^2 = H, R^4 = CD_2CO_2Me, R^5 = CO_2Me (dimeric)
c; X = Cl, = R^2 = OMe, R^3 = H, R^4 = CH_2CO_2Me, R^5 = CO_2Me (dimeric)
d; X = Cl, = R^2 = OMe, R^3 = H, R^4 = CO_2Me, R^5 = CH_2CO_2Me (dimeric)
e; X = acetylacetonate, R^2 = OMe, R^3 = H, R^4 = CH_2CO_2Me, R^5 = CO_2Me
f; X = acetylacetonate, R^2 = OMe, R^3 = H, R^4 = CO_2Me, R^5 = CH_2CO_2Me
g; X = Cl, R^2 = OEt, R^3 = H, R^4 = CH_2CO_2Me, R^5 = CO_2Me (dimeric)
h; X = Cl, R^2 = OEt, R^3 = H, R^4 = CO_2Me, R^5 = CH_2CO_2Me (dimeric)
i; X = Cl, R^2 = OPr^i, R^3 = H, R^4 = CH_2CO_2Me, R^5 = CO_2Me (dimeric)
j; X = Cl, R^2 = OPr^i, R^3 = H, R^4 = CO_2Me, R^5 = CH_2CO_2Me (dimeric)

ment of the major isomer as that with the CH_2CO_2Me group in the *anti*-position was based on the observation that protons, and methyl groups, in *anti*-positions on a π-allyl ligand resonate at higher field than do the corresponding groups in *syn*-positions.[6,7] The assignment of the single isomers (9a) and (9b) to their geometries as drawn rests on the similarity of the chemical shifts of the CH_2CO_2Me protons in the spectrum of (9a) to the chemical shifts of the *syn*-CH_2CO_2Me protons in the isomers (9c), (9e), (9g), and (9i).

TABLE 4

Atomic positional (fractional co-ordinates) and thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	10^2U *
Molecule (1)				
Pd	0.002 31(6)	0.241 21(7)	0.273 65(7)	†
Cl(1)	0.010 4(2)	0.447 7(3)	0.261 9(3)	†
Cl(2)	0.160 7(4)	−0.152 0(4)	0.339 6(4)	†
C(1)	0.002 3(9)	0.062 6(10)	0.291 3(9)	5.7(3)
C(101)	−0.096 3(9)	0.030 0(10)	0.284 7(10)	5.8(3)
O(11)	−0.161 5(6)	−0.015 6(8)	0.205 5(7)	†
O(12)	−0.110 0(7)	0.060 5(8)	0.375 5(7)	†
C(102)	−0.209 0(11)	0.047 1(12)	0.372 1(11)	7.9(4)
H(1)	0.053(11)	0.042(12)	0.353(12)	6.00
C(2)	0.027 9(9)	0.002 3(10)	0.205 0(10)	6.1(3)
C(3)	0.044 2(10)	−0.126 9(11)	0.232 1(10)	7.0(3)
C(4)	−0.022 3(10)	−0.210 1(12)	0.174 2(11)	8.0(4)
C(201)	0.113 1(10)	0.055 9(11)	0.182 1(10)	6.4(3)
O(21)	0.167 8(8)	0.133 1(11)	0.233 4(11)	†
O(22)	0.123 8(7)	0.012 8(9)	0.096 9(7)	†
C(202)	0.210 0(11)	0.053 5(13)	0.075 7(12)	8.8(4)
H(2)	−0.037(9)	0.023(10)	0.113(9)	6.00
N(1)	0.105 0(7)	0.248 6(7)	0.430 9(7)	4.9(2)
C(11)	0.075 1(10)	0.254 6(11)	0.513 7(10)	6.9(3)
C(12)	0.138 8(11)	0.268 2(12)	0.625 1(12)	8.2(4)
C(13)	0.239 1(10)	0.276 4(11)	0.648 9(11)	7.5(4)
C(14)	0.271 0(10)	0.267 2(11)	0.567 4(11)	7.2(4)
C(15)	0.200 9(9)	0.254 0(10)	0.456 4(9)	5.9(3)
N(2)	−0.109 8(7)	0.236 1(7)	0.122 0(7)	5.2(2)
C(21)	−0.093 7(10)	0.254 6(11)	0.029 2(10)	6.6(3)
C(22)	−0.171 6(11)	0.264 3(12)	−0.072 9(12)	8.1(4)
C(23)	−0.266 6(11)	0.261 5(12)	−0.080 1(11)	7.8(4)
C(24)	−0.283 7(10)	0.241 5(11)	0.012 0(10)	6.9(3)
C(25)	−0.203 6(9)	0.228 2(10)	0.112 4(10)	6.2(3)
Molecule (2)				
Pd	0.495 51(7)	0.424 70(7)	0.233 78(7)	†
Cl(1)	0.520 2(3)	0.609 3(3)	0.169 0(3)	†
Cl(2)	0.544 1(5)	−0.049 3(5)	0.303 4(7)	†
C(1)	0.462 3(17)	0.261 3(20)	0.285 2(18)	14.4(8)
C(101)	0.484 4(13)	0.288 8(13)	0.419 6(13)	7.9(4)
O(11)	0.421 2(9)	0.339 4(11)	0.432 5(8)	†
O(12)	0.566 4(8)	0.268 9(8)	0.504 2(9)	†
C(102)	0.579 3(11)	0.312 1(13)	0.612 7(12)	8.6(4)
H(1)	0.389(8)	0.214(9)	0.227(9)	6.00
C(2)	0.519 6(17)	0.174 9(19)	0.297 0(18)	14.0(7)
C(3)	0.471 8(12)	0.057 8(14)	0.320 6(13)	9.6(5)
C(4)	0.401 0(10)	0.038 3(11)	0.365 0(10)	7.1(4)
C(201)	0.494 5(14)	0.171 7(13)	0.155 2(13)	8.4(4)
O(21)	0.569 4(8)	0.175 0(9)	0.142 8(8)	†
O(22)	0.409 4(8)	0.152 9(10)	0.078 5(10)	†
C(202)	0.400 9(13)	0.133 6(14)	−0.031 4(14)	10.0(5)
H(2)	0.584(10)	0.213(11)	0.349(10)	6.00
N(1)	0.350 8(7)	0.426 1(8)	0.131 5(7)	5.9(2)
C(11)	0.324 3(10)	0.435 9(11)	0.022 7(11)	7.2(4)
C(12)	0.224 2(11)	0.440 9(12)	−0.045 3(12)	8.1(4)
C(13)	0.152 8(12)	0.440 4(13)	−0.005 2(12)	8.8(4)
C(14)	0.182 1(10)	0.429 1(12)	0.108 1(11)	7.5(4)
C(15)	0.282 6(10)	0.422 6(11)	0.174 7(10)	6.6(3)
N(2)	0.639 0(7)	0.424 9(8)	0.332 8(8)	6.0(3)
C(21)	0.672 5(9)	0.456 7(10)	0.438 1(10)	6.5(3)
C(22)	0.771 3(10)	0.458 7(12)	0.510 1(11)	7.4(4)
C(23)	0.840 0(11)	0.431 0(12)	0.467 8(12)	8.3(4)
C(24)	0.804 9(12)	0.398 2(13)	0.354 1(12)	8.8(4)
C(25)	0.706 5(10)	0.394 4(11)	0.288 8(11)	7.4(4)

TABLE 4 (*Continued*)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule (1)						
Pd	4.37(5)	5.60(6)	5.83(5)	0.43(4)	1.97(4)	−0.27(4)
Cl(1)	6.5(2)	5.8(2)	6.4(2)	0.2(1)	1.6(2)	0.1(1)
Cl(2)	16.8(5)	11.4(4)	9.8(3)	6.0(3)	3.1(3)	0.2(3)
O(11)	6.3(6)	9.6(7)	8.3(6)	−1.0(5)	3.7(5)	−1.1(5)
O(12)	8.8(7)	10.1(7)	8.5(6)	−2.0(6)	6.3(6)	−2.0(5)
O(21)	9.9(9)	15.9(11)	17.1(12)	−4.9(8)	9.1(9)	−9.5(10)
O(22)	8.9(7)	13.3(9)	7.6(6)	−2.8(6)	6.0(6)	−2.3(6)
Molecule (2)						
Pd	6.43(6)	5.19(5)	6.80(6)	0.09(4)	3.58(5)	0.16(4)
Cl(1)	6.7(2)	6.8(2)	8.0(2)	−0.7(2)	1.9(2)	2.0(2)
Cl(2)	17.4(6)	13.1(5)	30.2(9)	4.7(4)	16.3(6)	7.9(5)
O(11)	10.9(9)	13.8(10)	7.0(6)	−0.6(8)	2.4(6)	1.8(6)
O(12)	9.8(8)	8.2(7)	12.2(8)	0.7(6)	7.4(7)	0.5(6)
O(21)	9.5(8)	9.8(7)	7.8(6)	0.3(6)	4.5(6)	−1.2(5)
O(22)	8.7(8)	12.6(9)	12.1(9)	0.0(7)	6.9(7)	−2.7(7)

* $B = 8\pi^2U$ † Anisotropic thermal parameters in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl]\}$, with parameters ($\times 10^2$).

In an attempt to rationalise the remarkable thermal stability of complexes (7) and (8), and the apparent lack of rotation about a carbon–carbon single bond of the η^1-but-3-enyl ligand, and to see if the proposed *trans* conformation of the alkyl chain in these complexes was manifested in the solid state, a single-crystal *X*-ray diffraction study of complex (8a) was undertaken.

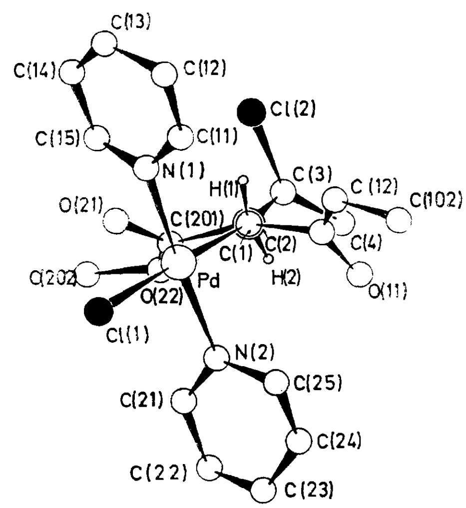


FIGURE 1 Molecule (1) seen in projection along the C(1)–C(2) bond

The overall configuration of the molecule is given in Figure 1; this view, along the C(1)–C(2) bond, shows that C(1) carries a $Pd(py)_2Cl$ group, a CO_2Me group, and a hydrogen atom, while C(2) carries the second CO_2Me group, a $C(CH_2)Cl$ group, and a hydrogen atom. The valencies around C(1) and (C2) are in a staggered conformation with the two hydrogen atoms *trans* to one another. The asymmetric unit of the crystal structure comprises two molecules of $[ClPd(py)_2\{CH(CO_2Me)\cdot C(Cl){:}CH_2\}]$ and the space group symmetry is $P\bar{1}$ ($Z = 4$). For both molecules the two chiral centres, C(1) and C(2), have opposite configurations (R and S or S and R), but because the molecules are required crystallographically to occur in centrosymmetrically-

[6] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1839.
[7] K. Vrieze, A. P. Praat, and P. Cossee, *J. Organometallic Chem.*, 1968, **12**, 533.

related pairs, equal numbers of C(1)*R*, C(2)*S*, and C(1)*S*, C(2)*R* types are present in the crystal. It so happens that the table of atomic co-ordinates (Table 4) refers to one mole-

TABLE 5

Interatomic distances and bond angles

	Molecule (1)	Molecule (2)
(a) Distances		
Pd–Cl(1)	2.405(3)	2.376(4)
Pd–N(1)	2.030(7)	2.036(9)
Pd–N(2)	2.033(8)	2.010(9)
Pd–C(1)	2.086(11)	2.122(24)
C(1)–C(2)	1.51(2)	1.30(3)
C(2)–C(101)	1.53(2)	1.75(3)
C(1)–C(101)	1.47(2)	1.70(3)
C(101)–O(11)	1.22(1)	1.19(2)
C(101)–O(12)	1.34(2)	1.31(2)
O(12)–C(102)	1.46(2)	1.45(2)
C(201)–O(21)	1.21(2)	1.18(3)
C(201)–O(22)	1.29(2)	1.28(2)
O(22)–C(202)	1.48(2)	1.42(2)
C(2)–C(3)	1.54(2)	1.60(3)
C(3)–C(4)	1.36(2)	1.40(3)
C(3)–Cl(2)	1.78(1)	1.73(2)
Pyridine rings		
N(1)–C(11)	1.33(2)	1.33(2)
C(11)–C(12)	1.40(2)	1.40(2)
C(12)–C(13)	1.39(2)	1.35(3)
C(13)–C(14)	1.34(2)	1.39(2)
C(14)–C(15)	1.43(2)	1.40(2)
C(15)–N(1)	1.33(2)	1.34(2)
N(2)–C(21)	1.35(2)	1.33(2)
C(21)–C(22)	1.39(2)	1.39(2)
C(22)–C(23)	1.37(2)	1.38(3)
C(23)–C(24)	1.35(2)	1.43(2)
C(24)–C(25)	1.40(1)	1.37(2)
C(25)–N(2)	1.35(2)	1.39(2)
(b) Angles		
N(1)–Pd–Cl(1)	90.0(2)	90.4(3)
N(2)–Pd–Cl(1)	89.6(3)	88.7(3)
C(1)–Pd–N(1)	87.1(4)	85.4(6)
C(1)–Pd–N(2)	93.4(4)	95.4(6)
Pd–C(1)–C(101)	105.7(8)	100.9(12)
Pd–C(1)–C(2)	112.1(9)	120.9(21)
C(2)–C(1)–C(101)	112.4(9)	100.0(17)
C(1)–C(101)–O(11)	125.8(13)	114.0(13)
C(1)–C(101)–O(12)	112.2(9)	125.7(17)
O(12)–C(101)–O(11)	121.9(13)	120.0(15)
C(101)–O(12)–C(102)	117.0(9)	119.2(14)
C(1)–C(2)–C(3)	110.5(11)	111.3(22)
C(1)–C(2)–C(201)	115.9(10)	91.7(16)
C(3)–C(2)–C(201)	110.9(11)	105.2(14)
C(2)–C(3)–Cl(2)	112.1(8)	104.2(15)
C(2)–C(3)–C(4)	122.3(10)	131.3(17)
Cl(2)–C(3)–C(4)	125.4(10)	123.6(12)
C(2)–C(201)–O(21)	126.7(15)	109.1(13)
C(2)–C(201)–O(22)	114.2(10)	124.9(18)
O(22)–C(201)–O(21)	119.1(15)	125.3(17)
C(201)–O(22)–C(202)	117.1(10)	119.5(16)
(c) Intramolecular contacts		
C(201) ··· Cl(2)	3.08(1)	3.13(2)
O(21) ··· Cl(2)	3.60(1)	3.45(1)
Pd ··· O(11)	3.68(1)	3.35(1)
Pd ··· O(12)	3.24(1)	3.76(1)
Pd ··· O(21)	3.01(1)	3.50(1)
Pd ··· O(22)	>4.0	3.69(1)
O(11) ··· C(25)	3.06(1)	>4.0
O(11) ··· C(15)	>4.0	3.35(1)
O(21) ··· C(25)	>4.0	3.32(2)
O(21) ··· C(15)	3.11(2)	>4.0
C(1) ··· Cl(2)	3.35(1)	3.81(2)
C(4) ··· O(11)	3.23(2)	3.59(2)
O(21) ··· C(1)	>4.0	3.07(3)
(d) Intermolecular contacts <3.4 Å		
$C(14)_1 \cdots C(21^{I})_2$	3.30(2)	
$C(14)_1 \cdots C(22^{I})_2$	3.33(2)	

TABLE 5 (*Continued*)

(d) Intermolecular contracts <3.4 Å	
$C(15)_1 \cdots C(22^{I})_2$	3.36(2)
$C(22)_1 \cdots O(22^{II})_1$	3.36(2)
$C(24)_1 \cdots O(21^{III})_2$	3.34(2)
$C(202)_1 \cdots O(22)_2$	3.13(2)

Subscript 1 refers to molecule 1; 2 to molecule 2. Roman superscripts refer to symmetry operations:

I $1-x, 1-y, 1-z$; II $-x, -y, -z$; III $1+x, y, z$

cule of each kind; molecule (1) (which is illustrated in Figure 1) has chirality C(1)*R*, C(2)*S*, while molecule (2) (which appears together with molecule 1 in the unit cell projection of Figure 2) has chirality C(1)*S*, C(2)*R*.

Although bond lengths and angles in the two molecules agree substantially (Table 5), the structural possibility of free rotation around the Pd–py, C–(CO_2Me), and C–[C(Cl):CH_2] bonds gives rise to considerably different intramolecular contacts for the two molecules. Some of the more significant of these are included in Table 5. It is perhaps easier

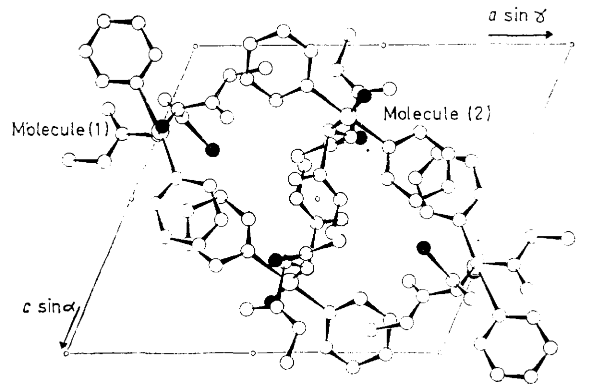


FIGURE 2 The contents of the triclinic unit cell seen in projection down *b* looking towards the origin. In order to bring molecule (1) and molecule (2) uppermost, the cell has been drawn from $-\frac{b}{2}$ to $+\frac{b}{2}$.

to appreciate the differences between molecules (1) and (2), however, by inspection of the angles made between the mean planes of the various ligands and some reference plane E, conveniently taken as the plane defined by atoms Pd, C(1), and C(2). Details are in Table 6. If we label the co-ordination plane of the Pd atom [as defined by Pd, Cl(1), N(1), and N(2)] as A, the planes of the (CO_2Me) groups on C(1) and C(2) as B and C, and the plane of [C(CH_2)Cl] as D, then the angles E–A, E–B, E–C, and E–D for the two molecules are, respectively, (1) 60.7, 69.9, 48.2, and 79.5; (2) 43.9, 80.3, 82.5, and 14.1°; from which it will be seen that the differences are larger for the ligands on C(2) and especially great for ligand D. The pyridine ligands are are also much less nearly co-planar in molecule (2) (21°) than in (1) (11°). For both molecules, ring 2 is taken as that lying *trans* to the H atom on C(1).

Careful comparison of the bond lengths and angles of the two crystallographically distinct molecules not only reveals significant differences but also shows that, where chemically implausible values occur [but only for molecule (2) which is in any case less well defined, see Table 4], these involve the atoms C(1) and C(2). Removal of these atoms, followed by refinement of the rest of the structure and subsequent calculation of an electron-density difference synthesis, gave

TABLE 6

(a) Equations of some unweighted least-squares planes: distances (Å) of relevant atoms from these planes are given in square brackets.

Molecule (1)

Plane (1) (ligand A): Pd, N(1), Cl(1), N(2), C(1)

$$13.621x - 1.025y - 9.439z = 2.830$$

[Pd 0.032, N(1) −0.061, Cl(1) 0.041, N(2) −0.059, C(1) 0.047]

Plane (2) (ligand B): C(1), C(101), O(11), O(12), C(102)

$$-2.431x + 10.415y - 4.257z = -0.638$$

[C(1) 0.045, C(101) −0.027, O(11) −0.007, O(12) −0.063, C(102) 0.052]

Plane (3) (ligand C): C(2), C(201), O(21), O(22), C(202)

$$-6.080x + 7.951y - 5.328z = -1.217$$

[C(2) −0.027, C(201) 0.004, O(21) 0.011, O(22) 0.050, C(202) −0.038]

Plane (4) (ligand D): C(2), C(3), C(4), Cl(12)

$$-11.022x + 0.884y + 11.890z = 2.140$$

[C(2) −0.007, C(3) 0.021, C(4) −0.009, Cl(2) −0.006]

Plane (5) (reference plane E): Pd, C(1), C(2)

$$11.740x + 0.318y + 3.262z = 0.997$$

Plane (6) (pyridine ring 1): Pd, N(1), C(11), C(12), C(13), C(14), C(15)

$$-0.314x + 11.574y - 0.894z = 2.498$$

[Pd 0.049, N(1) −0.038, C(11) −0.034, C(12) 0.004, C(13) 0.046, C(14) 0.003, C(15) −0.029]

Plane (7) (pyridine ring 2): Pd, N(2), C(21), C(22), C(23), C(24), C(25)

$$-1.271x + 11.523y + 1.664z = 3.142$$

[Pd 0.090, N(2) −0.079, C(21) −0.041, C(22) −0.000, C(23) 0.077, C(24) 0.021, C(25) −0.067]

Molecule (2)

Plane (8) (ligand A): Pd, N(1), Cl(1), N(2), C(1)

$$-8.006x + 5.166y + 11.497z = 0.915$$

[Pd −0.001, N(1) −0.011, Cl(1) 0.011, N(2) −0.010, C(1) 0.012]

Plane (9) (ligand B): C(1), C(101), O(11), O(12), C(102)

$$6.561x + 10.177y - 3.906z = 4.530$$

[C(1) 0.048, C(101) −0.052, O(11) −0.002, O(12) −0.047, C(102) 0.053]

Plane (10) (ligand C): C(2), C(201), O(21), O(22), C(202)

$$-1.587x + 11.497y - 0.849z = 0.989$$

[C(2) −0.055, C(201) 0.068, O(21) −0.002, O(22) 0.052, C(202) −0.063]

Plane (11) (ligand D): C(2), C(3), C(4), Cl(2)

$$4.649x + 0.801y + 9.819z = 5.452$$

[C(2) 0.020, C(3) −0.064, C(4) 0.027, Cl(2) 0.017]

Plane (12) (reference plane E): Pd, C(1), C(2)

$$2.199x + 2.937y + 10.768z = 4.854$$

Plane (13) (pyridine ring 1) Pd, N(1), C(11), C(12), C(13), C(14), C(15)

$$-0.112x + 11.574y + 0.916z = 5.042$$

[Pd 0.032, N(1) −0.029, C(11) −0.012, C(12) −0.006, C(13) 0.034, C(14) 0.003, C(15) −0.022]

Plane (14) (pyridine ring 2) Pd, N(2), C(21), C(22), C(23), C(24), C(25)

$$2.444x + 11.037y - 3.897z = 4.972$$

[Pd 0.016, N(2) −0.017, C(21) 0.005, C(22) −0.011, C(23) 0.016, C(24) 0.011, C(25) −0.018]

TABLE 6 (*Continued*)

(b) Angles (°) between least-squares planes

Molecule (1)		Molecule (2)	
(5)–(1)	60.7	(12)–(8)	43.9
(5)–(2)	70.0	(12)–(9)	80.3
(5)–(3)	48.2	(12)–(10)	82.5
(5)–(4)	79.5	(12)–(11)	14.1
(6)–(7)	11.2	(13)–(14)	21.3

new (and better) positions resulting in amendment of certain molecular characteristics as follows:

	x	y	z
C(1)	0.4795	0.2693	0.3045
C(2)	0.5154	0.1711	0.2916

Re-refinement, however, shifted these atoms back to the positions given in Table 4, and we have no explanation for this. In any case, arguments pertaining to the chirality and stereochemistry of the molecules are unaffected.

DISCUSSION

The molecular structure of complex (8a) confirms, in the solid state, the staggered configuration with H^1 and H^2 vicinally *trans* which must also be the single conformation in solution up to +60° C. In addition, the observed relationship between the absolute configurations of C^1 and C^2 confirms that the initial Pd^{II}-promoted ring-opening of *cis*-2,3-dimethoxycarbonylmethylenecyclopropane to produce complex (2), the immediate η^3-bonded precursor of (8a), must occur with retention of configuration at the carbon atom which becomes σ-bonded to the metal.

The stability of the η^1-but-3-enyl complexes towards β-hydrogen elimination reactions is also explained if the conformation shown in Figure 1 is that existing in solution. In order to achieve the normally assumed transition state for such a reaction,[8] with Pd, C^1, C^2, and H^2 all coplanar, a 60° rotation about the C^1–C^2 bond must occur. The energy barrier for this rotation must be high due to the vicinal interactions between the bulky substituents on C^1 and C^2.

The proposed mechanism for the rearrangement of the η^3-but-3-enyl complexes (1)—(6) into their corresponding η^3-allyl products is outlined in the Scheme, using the rearrangement of the conformational isomer (3a) into a mixture of isomers (9c) and (9d) as a representative example. Completely analogous schemes can be drawn for the rearrangements of any other η^3-but-3-enyl complex.

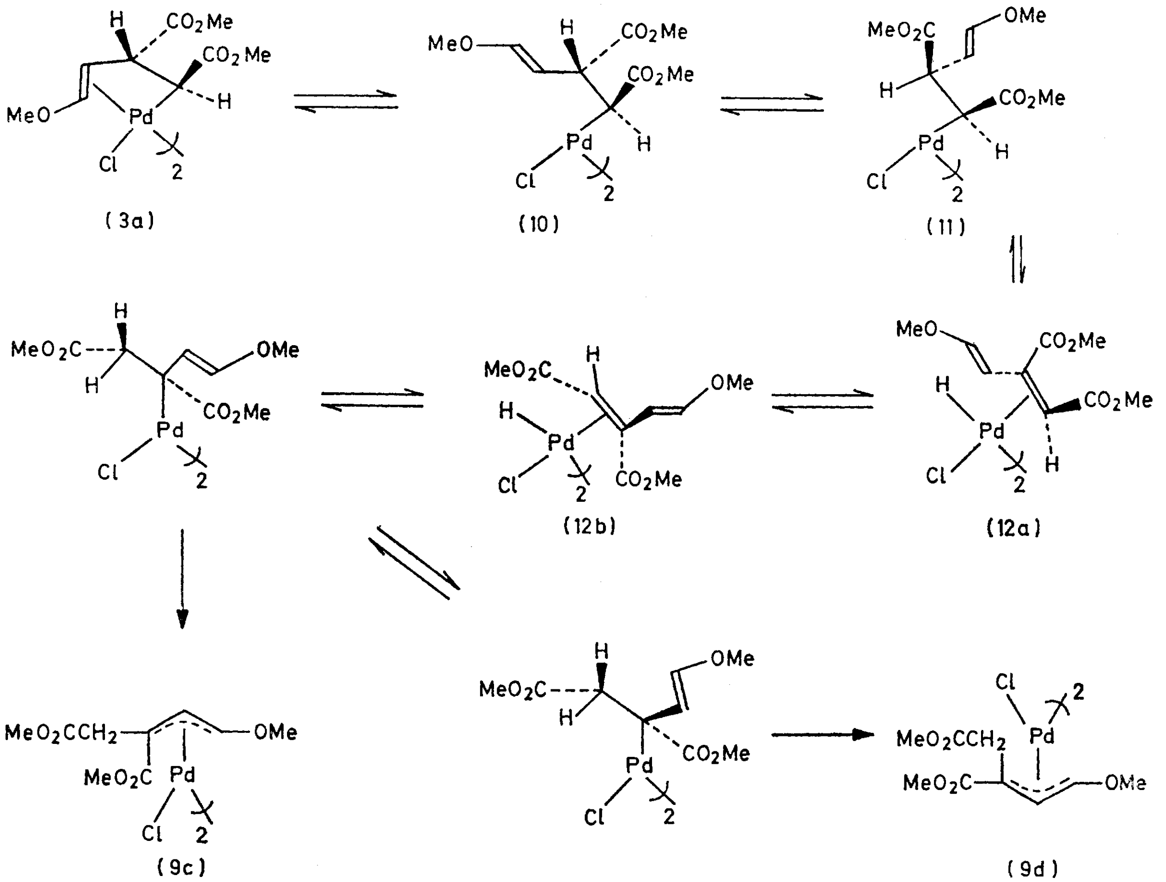
Dissociation of the η^3-but-3-enyl ligand in (3a) to its η^1-bonded form (10) must be a low-energy process, even at ambient temperatures, since the dissociation, followed by rotation about the C^2–C^3 bond and reformation of the metal–olefin bond, interchanges conformational isomers: *e.g.* complex (3a) and complex (4a). It has previously been established that this process of conformer interconversion is ready at room temperature.[1]

However, rotation about the C^1–C^2 bond in intermediate (10) to give a species (11) in which Pd, C^1, C^2, and

[8] B. L. Shaw, *Chem. Comm.*, 1968, 464.

H^2 are all co-planar, and all lie in the square plane of co-ordination, must be a much higher energy process as discussed above. The structural requirements of intermediate (11) are based on the assumption that, according to the principle of microscopic reversibility, the transition-state geometries for β-hydrogen elimination and the *cis*-insertion of an olefin into a metal–hydrogen bond should be identical. Consequently, a vacant *cis*-co-ordination site must also be available on the metal, to accommodate the migrating hydrogen atom. β-Hydrogen elimination from (11) generates (12a) in which the axis of the newly formed olefin lies in the co-ordination plane. Olefin rotation in (12a) generates (12b) and presents the *cis*-hydrogen ligand with the terminal olefinic carbon atom. *cis*-Insertion generates an η^1-allylic species which can collapse to an η^3-allylic complex to produce either isomer (9c) or (9d). It is noteworthy that olefin dissociation in intermediates (12a,b) must be slow compared to the rate of rotation and insertion, since no products derived from Pd–H addition to the unco-ordinated alkoxy-olefin are observed.

The reluctance of the η^1-but-3-enyl complexes (7a) and (8a) to undergo an analogous rearrangement is presumably due to the fact that in such complexes rotation about the C^1–C^2 bond is not sufficient to generate the required transition-state geometry; dissociation of a pyridine ligand to generate a vacant *cis*-co-ordination site is also required. An alternative pathway involves formation of a five-co-ordinate species which, apparently, in the case of these Pd^{II} complexes, does not represent a low-energy route.



SCHEME

The η^3-allylic complexes (9a) and (9b), which contain a Cl atom in the R^3 position, exist as only one isomer in solution, whereas all other complexes (9c—j) which have no substituent at R^3 exist as a mixture of isomers. With no substituent at R^3 the CO_2Me and CH_2CO_2Me are free to occupy either *syn*-(R^4) or *anti*-(R^5) positions; some preference is shown by the CO_2Me group for the *syn*-position. However, there must be a significantly greater interaction between a Cl atom at R^3 with a *syn*-CO_2Me group than with a *syn*-CH_2CO_2Me group; the CO_2Me group is thus forced into an *anti*-(R^5) position. Similar effects have been noted for the η^3-but-3-enyl complexes (1) and (2), which exist as only one conformer in solution, and the complexes (3) and (4), and (5) and (6), which exist as mixtures of conformers.[1]

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.

Complexes (1)—(6) were prepared as described previously.[1]

Preparation of η^1-*But-3-enyl Complexes of Palladium*(II).—A solution of complex (1a) (0.123 g, 0.35 mmol) in dichloromethane (5 cm^3) was treated with pyridine (0.06 g, 0.76 mmol). The resultant pale yellow solution was evaporated to dryness and the residue was crystallised from dichloromethane–pentane (−30 °C) to yield *complex* (7a) as pale yellow *prisms* (0.17 g, 95%), m.p. 120—122 °C (decomp.) (Found: C, 42.7; H, 4.1; N, 5.5. $C_{18}H_{20}Cl_2N_2O_4Pd$ requires C, 42.7; H, 4.0; N, 5.5%).

A similar reaction of complex (2) (0.20 g, 0.57 mmol) in dichloromethane (5 cm^3) with pyridine (0.09 g, 1.2 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), *complex* (8a) as yellow *prisms* (0.27 g, 93%), m.p. 146—148 °C (decomp.) (Found: C, 42.5; H, 3.9; N, 5.5. $C_{18}H_{20}Cl_2N_2O_4Pd$ requires C, 42.7; H, 4.0; N, 5.5%).

A similar reaction of complex (1b) (0.20 g, 0.51 mmol) in dichloromethane (50 cm^3) with pyridine (0.09 g, 1.2 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), *complex* (7b) as pale yellow *prisms* (0.27 g, 96%), m.p. 131—133 °C (decomp.) (Found: C, 39.0; H, 3.7; N, 5.4. $C_{18}H_{20}BrClN_2O_4Pd$ requires C, 39.3; H, 3.7; N, 5.1%).

A similar reaction of conformational isomers (3a) and (4a) (0.09 g, 0.26 mmol) in dichloromethane (5 cm^3) with pyridine (0.05 g, 0.63 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), *complex* (7c) as pale yellow *prisms* (0.12 g, 93%), m.p. 111—114 °C (decomp.) (Found: C, 45.8; H, 4.8; N, 5.8. $C_{19}H_{23}ClN_2O_5Pd$ requires C, 45.5; H, 4.6; N, 5.6%).

A similar reaction of the mixture of conformational isomers (5) and (6) (0.09 g, 0.26 mmol) in dichloromethane (5 cm^3) with pyridine (0.05 g, 0.63 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), *complex* (8b) as pale yellow *prisms* (0.11 g, 84%), m.p. 119—121 °C (decomp.) (Found: C, 45.6; H, 4.7; N, 5.6. $C_{19}H_{23}ClN_2O_5Pd$ requires C, 45.5; H, 4.6; N, 5.6%).

A similar reaction of the mixture of conformational isomers (3c) and (4c) (0.20 g, 0.56 mmol) in dichloromethane (5 cm^3) with pyridine (0.09 g, 1.2 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), *complex* (7d) as pale yellow *prisms* (0.26 g, 90%), m.p. 104—107 °C (decomp.) (Found: C, 46.8; H, 4.8; N, 5.5. $C_{20}H_{25}ClN_2O_5Pd$ requires C, 46.6; H, 4.9; N, 5.4%).

A similar reaction of the mixture of conformational and geometric isomers (3d), (4d), (3e), and (4e) (0.26 g, 0.70 mmol) in dichloromethane (10 cm^3) with pyridine (0.42 g, 1.5 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), a mixture of the geometrically isomeric complexes (7e) and (7f) as pale yellow *prisms* (0.33 g, 89%), m.p. 123—125 °C (decomp.) (Found: C, 47.9; H, 5.1; N, 5.3. $C_{21}H_{27}ClN_2O_5Pd$ requires C, 47.7; H, 5.1; N, 5.3%).

A similar reaction of complex (1e) (0.20 g, 0.38 mmol) in dichloromethane (5 cm^3) with pyridine (0.03 g, 0.38 mmol) yielded, after recrystallisation from pentane (−30 °C), complex (7g) as yellow *prisms* (0.21 g, 91%), m.p. 79—81 °C (Found: C, 36.5; H, 2.9; N, 2.4. $C_{18}H_{16}ClF_6NO_6Pd$ requires C, 36.1; H, 2.7; N, 2.3%).

A similar reaction of a mixture of the conformationally isomeric complexes (3b) and (4b) (0.14 g, 0.34 mmol) in dichloromethane (5 cm^3) with pyridine (0.03 g, 0.37 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), complex (7h) as pale yellow *prisms* (0.15 g, 90%), m.p. 99—102 °C (decomp.) (Found: C, 46.7; H, 5.0; N, 2.8. $C_{19}H_{25}NO_7Pd$ requires C, 47.0; H, 5.2; N, 2.9%).

A similar reaction of complex (1a) (0.25 g, 0.72 mmol) in dichloromethane (5 cm^3) with cyclo-octa-1,5-diene (0.50 g, 4.6 mmol) yielded, after recrystallisation from dichloromethane–pentane, complex (7i) as pale yellow *prisms* (0.24 g, 73%), decomp. 140 °C (Found: C, 41.7; H, 4.9. $C_{16}H_{22}Cl_2O_4Pd$ requires C, 42.1; H, 4.9%).

A similar reaction of complex (2) (0.10 g, 0.29 mmol) in dichloromethane (5 cm^3) with cyclo-octa-1,5-diene (0.50 g, 4.6 mmol) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), complex (8c) as yellow *prisms* (0.10 g, 77%), m.p. 140—142 °C (decomp.) (Found: C, 42.2; H, 4.9; Cl, 15.9. $C_{16}H_{22}Cl_2O_4Pd$ requires C, 42.1; H, 4.9; Cl, 15.6%).

Attempted Thermal Rearrangement of Complexes (7a) *and* (8a).—A solution of complex (7a) (0.40 g, 0.79 mmol) in benzene (50 cm^3) was refluxed for 3 h. Evaporation of the solution yielded only unchanged complex (7a), as evidenced by the ^{1}H n.m.r. spectrum of the residue.

A similar reaction of complex (8a) yielded only unchanged starting material.

Thermal Rearrangements of η^3-*But-3-enyl Complexes of Palladium*(II).—A solution of complex (1a) (0.50 g, 1.4 mmol) in benzene (50 cm^3) was refluxed for 3 h. Evaporation of the solution and recrystallisation of the residue from dichloromethane–pentane (−30 °C) yielded complex (9a) as yellow *crystals* (0.45 g, 90%), m.p. 100—102 °C (decomp.) (Found: C, 27.8; H, 3.0. $C_8H_{10}Cl_2O_4Pd$ requires C, 27.7; H, 2.9%).

An analogous reaction of complex (2) (0.50 g, 1.4 mmol) in benzene (50 cm^3) yielded an identical sample of complex (9a), identified by its ^{1}H n.m.r. spectrum.

Similarly, thermal rearrangement of complex (1b) (0.50 g, 1.4 mmol) in refluxing benzene (50 cm^3; 3 h) yielded, after recrystallisation from dichloromethane–pentane, complex (9b) as yellow *crystals* (0.43 g, 86%), m.p. 100—102 °C (decomp.) (Found: C, 27.7; H, 3.0. $C_8H_8D_2Cl_2O_4Pd$ requires C, 27.5; H, 2.9%).

Similarly, thermal rearrangement of the mixture of conformationally isomeric complexes (3a) and (4a) (0.50 g, 1.4 mmol) in refluxing benzene (50 cm^3; 3 h) yielded, after recrystallisation from dichloromethane–pentane, a mixture of complexes (9c) and (9d) as yellow *prisms* (0.41 g, 82%), m.p. 112—114 °C (decomp.) (Found: C, 31.4; H, 4.0. $C_9H_{13}ClO_5Pd$ requires C, 31.5; H, 3.8%).

An identical mixture of complexes (9c) and (9d) (80%), identified by their ^{1}H n.m.r. spectrum, was obtained by the thermal rearrangement of the mixture of conformationally isomeric complexes (5) and (6) (0.50 g, 1.4 mmol) in refluxing benzene (50 cm^3, 3 h).

A mixture of complexes (9c) and (9d) (0.20 g, 0.58 mmol) in dichloromethane (10 cm^3) was treated with acetylacetonatothallium (0.20 g, 0.66 mmol) and stirred (3 h). Pentane (50 cm^3) was added and the resultant suspension was filtered through a Kieselguhr plug. The filtrate was evaporated to dryness, and recrystallisation of the residue from dichloromethane–pentane (−30 °C) afforded pale yellow *crystals* (0.23 g; 97%), m.p. 98—100 °C (decomp.), shown by ^{1}H n.m.r. spectroscopy to be a mixture of the isomeric complexes (9e) and (9f) (Found: C, 41.3; H, 5.0. $C_{14}H_{20}O_7Pd$ requires C, 41.3; H, 5.0%).

An identical mixture of complexes (9e) and (9f) (89%), identified by its ^{1}H n.m.r. spectrum, was obtained from the thermal rearrangement of the conformationally isomeric pair of complexes (3b) and (4b) (0.50 g, 1.2 mmol) in refluxing benzene (50 cm^3; 3 h).

Similarly, thermal rearrangement of the mixture of conformationally isomeric complexes (3c) and (4c) (0.50 g, 1.4 mmol) in refluxing benzene (50 cm^3; 3 h) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), a mixture of complexes (9g) and (9h) as yellow *prisms* (0.40 g, 80%), m.p. 103—107 °C (decomp.) (Found: C, 33.4; H, 4.2. $C_{10}H_{15}ClO_5Pd$ requires C, 33.6; H, 4.2%).

Similarly, thermal rearrangement of the mixture of conformational and geometric isomers (3d), (4d), (3e), and (4e) (0.50 g, 1.3 mmol) in refluxing benzene (50 cm^3; 3 h) yielded, after recrystallisation from dichloromethane–pentane (−30 °C), a mixture of complexes (9i) and (9j) as yellow *prisms* (0.43 g, 86%), m.p. 107—109 °C (decomp.) (Found: C, 35.8; H, 4.7. $C_{11}H_{17}ClO_5Pd$ requires C, 35.6; H, 4.6%).

Crystal Structure Determination.—The crystal, 0.025 × 0.026 × 0.023 cm^3, was characterised and the intensities were collected on a Syntex P2_1 four-circle diffractometer; the unit cell was defined by inspection of the real-space vectors produced by the autoindexing program from 15 randomly chosen reflections (with $17° < 2\theta < 22°$); data collection (with equatorial bisecting geometry and a θ—2θ scan in 96 steps) employed graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å); $2.9° \leqslant 2\theta \leqslant 50.0°$. The scan rate = 0.00134 C, where C was a preliminary 2 s peak count (for $25 \leqslant C \leqslant 750$); for $C \leqslant 25$, scan rate = 0.03° s^{-1}, and for $C > 750$, scan rate = 1.0° s^{-1}; scan interval: 1° below θ for $K_{\alpha1}$ to 1° above θ for $K_{\alpha2}$; background count (before and after each scan): to give total background time = scan time; 3 check reflections periodically (every 30 reflections) showed no significant variance over the 56-h X-ray exposure. Number of reflections measured: 6 279; number observed 5 397 [according to the criterion $I > 2.5\sigma(I)$].

Crystal Data—$C_{18}O_4H_{20}N_2Cl_2Pd$, M = 505.66, Triclinic, a = 14.794(8), b = 11.599(8), c = 13.131(8)Å, α = 89.53(5), β = 113.04(4), γ = 91.50(5)°, space group $P\bar{1}$, Z = 4, D_c = 1.615 g cm^{-3}, D_m (flotation) = 1.61 g cm^{-3}, $F(000)$ = 254, μ(Mo-K_α) = 11.6 cm^{-1}. The small crystal and low μ (11.6 cm^{-1}) did not require an X-ray absorption correction to be made. The structure was solved by conventional heavy-atom methods and has been refined to R = 0.075 with anisotropic thermal parameters for Pd, Cl, and O.

Individual weights were applied according to the scheme: $1/w = (x.y)$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, and $y = F_o/a$ if $F_o > a$, $y = 1$ if $F_o \leqslant a$, in which a = 50.0 and b = 3.0. All computational work was carried out with the 'X-Ray System'.[9] Atomic scattering factors are those of ref. 10 (Pd), ref. 11 (C, N, O, Cl), and ref. 12 (H). Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21795 (22 pp., 1 microfiche).*

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* For details, see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

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