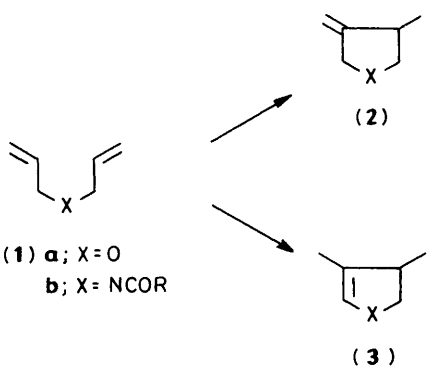
Palladium- and Rhodium-catalysed Cyclisation of 1,6-, 1,7- and 1,8-Dienes to Cyclopentenes and Methylenecyclopentenes. Crystal Structure of Dichloro(4,4-diacetylhepta-1,6-diene)platinum(II)

Ronald Grigg,* John F. Malone, Thomas R. B. Mitchell, Ashok Ramasubbu, and Ronald M. Scott
Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

Hepta-1,6-dienes disubstituted at C-4 with certain carbonyl-containing groups cyclise, in good yield, to the corresponding 4,4-disubstituted 1,2-dimethylcyclopent-2-enes when treated with a catalytic amount of palladium acetate in chloroform containing hydrogen chloride. Changing the catalyst precursor to chlorotris(triphenylphosphine)rhodium(I) led to the formation of the corresponding 1-methyl-2-methylenecyclopentanes which, in turn, isomerised to 1,2-dimethylcyclopent-1-enes in ethanolic hydrogen chloride containing the rhodium complex. The effect of terminal substitution of the dienes with methyl groups was examined. 1,7- and 1,8-Dienes give rise to mixtures of five-membered ring products. Possible mechanisms for the catalytic processes are discussed. The *X*-ray crystal structure analysis of dichloro(4,4-diacetylhepta-1,6-diene)platinum(II) is reported.

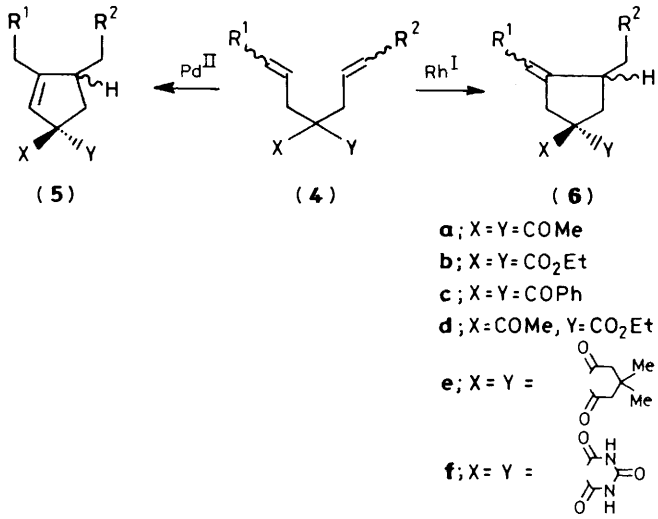
In recent years there has been a rapid increase in reports of applications of transition metal complexes to the stoicheiometric and catalytic construction of carbocyclic and heterocyclic systems. The potential of these processes is further enhanced by the observation that the usual rules for ease of cyclisation of linear precursors need not necessarily apply and that the medium-sized rings, accessible only with difficulty, may be obtained by application of transition metal complexes.[1] The majority of the recently developed syntheses depend on functional group activation of olefinic,[2] aromatic,[3] or allylic[4] systems for the ring-forming processes.

Although intermolecular oxidative and non-oxidative coupling of olefins has been widely studied,[5,6] there have been few reports of the corresponding intramolecular processes that do not involve the presence of activating groups. In 1971 Shaw *et al.*[7] reported the non-oxidative cyclisation of diallyl ether (**1a**) to (**2a**) catalysed by rhodium trichloride. We have investigated the scope of this cyclisation and find it is not very tolerant of substitution. Of a number of alkyl-substituted diallyl ethers only 1,3'-dimethyl diallyl ether could be cyclised.[8,9] Schmitz *et al.*[10] have observed similar reactions (**1b**)→(**2b**) and (**1b**)→(**3b**) with rhodium trichloride and palladium chloride respectively.



We have described briefly[11,12] the cyclisation of some 1,6-dienes substituted with two carbonyl-containing groups at C-4 such as (**4a**—**f**; $R^1 = R^2 = H$) to cyclopentenes (**5a**—**f**; $R^1 = R^2 = H$) catalysed by palladium(II) and to methylenecyclopentanes (**6a**—**c**; $R^1 = R^2 = H$) by rhodium(I) and now report on these reactions in detail.

Reactions promoted by Palladium(II) *Acetate and Palladium*(II) *Chloride.*—Initial experiments involved heating compounds of



type (**4**) with 5 mol % palladium(II) acetate or chloride in chloroform at 60 °C in an autoclave under an air pressure of 25 atm (type A reaction conditions). Products (**5**) were obtained in fair yield (Table 1). Carbon tetrachloride was also suitable as a solvent, but not benzene, dimethylformamide, cyclohexane, or ethyl acetate. The reaction was inhibited by addition of carbon monoxide (under pressure), dimethyl acetylenedicarboxylate, sodium acetate, cupric acetate, or ethanol.

Subsequently the use of an autoclave was found to be unnecessary provided that hydrogen chloride was passed through the solvent before beginning the reaction (type B reaction conditions). Now merely boiling the chloroform solution under reflux led to both faster reaction and better yields. Still later it was found that the reaction was further facilitated by removal of the ethanol stabiliser from the chloroform by passage through a column of alumina (type C conditions). The ethanol reduces the palladium(II) salts to the metal which is catalytically inactive. No reaction occurred when (**4b**; $R^1 = R^2 = H$) was refluxed in chloroform containing hydrogen chloride in the absence of palladium salts. The diene (**4b**; $R^1 = R^2 = H$) also failed to react in chloroform containing hydrogen chloride and the radical initiators benzoyl peroxide or α,α-azoisobutyronitrile. Thus the reaction is neither purely thermal nor radical in nature.

The cyclisation of compounds in which the terminal olefinic groups are unsubstituted (**4**; $R^1 = R^2 = H$) proceeds readily in

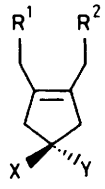
Table 1. Cyclisation of (**4**) to (**5**) using palladium catalysts under various conditions*

Entry	Starting material	Catalyst precursor	A		B		C	
			Time (h)	Yield (%)[e]	Time (h)	Yield (%)[e]	Time (h)	Yield (%)[e]
1	(**4a**; $R^1 = R^2 = H$)	$Pd(OAc)_2$	12	39	8	58		
2	(**4a**; $R^1 = R^2 = H$)	$PdCl_2$	36	62				
3	(**4b**; $R^1 = R^2 = H$)	$Pd(OAc)_2$	14	46	6	87.5	0.17	87
4	(**4b**; $R^1 = R^2 = H$)	$PdCl_2$			8	80[a]		
5	(**4c**; $R^1 = R^2 = H$)	$Pd(OAc)_2$	72	28	8	60	0.25	63
6	(**4d**; $R^1 = R^2 = H$)	$Pd(OAc)_2$	75	40[b]	8	72[b]		
7	(**4e**; $R^1 = R^2 = H$)	$Pd(OAc)_2$[c]			6	51		
8	(**4f**; $R^1 = R = H$)	$Pd(OAc)_2$			10	80		
9	(**4a**; $R^1 = Me$, $R^2 = H$)	$Pd(OAc)_2$	72	36	14	81		
10	(**4b**; $R^1 = Me$, $R^2 = H$)	$Pd(OAc)_2$						N.R.
11	(**4a**; $R^1 = R^2 = Me$)	$Pd(OAc)_2$	216	15	36	68		
12	(**4a**; $R^1 = R^2 = Me$)	$PdCl_2$	96	21				
13	(**4b**; $R^1 = R^2 = Me$)	$Pd(OAc)_2$					5	82

* A, Autoclave, 25 atm air, $CHCl_3$, 5 mol % Pd compound, 60 °C; B, $CHCl_3$, HCl bubbled for 3—5 min, reflux, 5 mol % Pd compound; C, $CHCl_3$ (ethanol free), HCl bubbled for 3—5 min, reflux 5 mol % Pd compound.

[a] 75% Yield in 8 h if no HCl used. [b] Two stereoisomers in ratio 2:1 formed. [c] 10 Mol% $Pd(OAc)_2$ used. [d] Reaction temperature 70 °C. [e] Isolated yields.

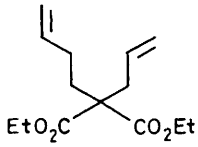
very good yield (Table 1, entries 1—8). No trace of any compound of type (**6**) could be detected in the products, but in some cases, *e.g.* where X = Y = Ac, CO_2Et, g.l.c. analysis indicated that 6—8% of the product was of type (**7**; $R^1 = R^2 = H$). The proportion of (**7**) did not change as the reaction



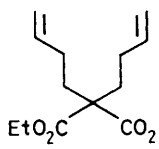
(**7**) a; X = Y = COMe
b; X = Y = CO_2Et

progressed indicating that it was not formed from (**5**). Ethyl diallylacetoacetate (**4d**; $R^1 = R^2 = H$) gave two stereoisomers of type (**5**) in the ratio 2:1, but the configuration of the major isomer was not established. When palladium chloride is used as catalyst (precursor) the addition of hydrogen chloride is not necessary (Table 1, entry 4). The drawback to using palladium chloride is its low solubility. When one or more of the olefinic bonds in (**4**) are substituted ($R^1 = Me$, $R^2 = H$, or $R^1 = R^2 = Me$) the reaction is slower (Table 1, entries 9—13) but even for (**4b**; $R^1 = R^2 = Me$) cyclisation to (**5b**; $R^1 = R^2 = Me$) occurs smoothly (82%) in only 5 h in ethanol-free chloroform. Compound (**4a**; $R^1 = Me$, $R^2 = H$) cyclises regiospecifically to (**5a**; $R^1 = Me$, $R^2 = H$) and no (**5a**; $R^1 = H$, $R^2 = Me$) could be detected. However, cyclisation did not occur in the case of (**4a**; $R^1 = R^2 = Ph$), [**4a**; $R^1 = (CH_2)_3CH{=}CH_2$, $R^2 = H$] or [**4a**; $R^1 = R^2 = (CH_2)_3CH{=}CH_2$]. 3-Allyl-3-prop-2-ynylpentane-2,4-dione and 3,3-bis(2-methylallyl)pentane-2,4-dione also failed to cyclise. Hepta-1,6-dienes unsubstituted at the 4-position such as ethyl nona-3,8-dienoate and ethyl (2-ethoxycarbonyl)deca-4,9-dienoate also failed to react while 4-acetylhepta-1,6-diene with only one substituent at C-4 gave a mixture of seven major and three minor products which were not further studied. No heterocycles could be obtained from diallyl ether, *N,N*-diallylacetamide or allyl acrylate.

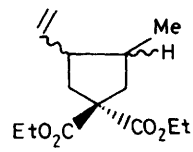
The substituted 1,7- and 1,8-dienes (**8**) and (**9**) were examined to see if they would cyclise to six- or seven-membered rings, but only five-membered carbocycles formed with palladium(II)



(**8**)



(**9**)



(**10**)

under type C conditions. The 1,8-diene (**9**) cyclised to (**5b**; $R^1 = R^2 = Me$) in 98% yield in 24 h (82% in 5 h). In marked contrast to the cyclisation of (**4a**; $R^1 = Me$, $R^2 = H$), (**8**) gave a 3:2 mixture of (**5b**; $R^1 = Me$, $R^2 = H$) and (**5b**; $R^1 = H$, $R^2 = Me$), together with three minor products. The mixture was not separated but all the products were shown to have a molecular ion at *m/z* 254 by gas chromatography/mass spectrometry (g.c./m.s.). The two major isomers were characterised by ^1H n.m.r. spectroscopy. Another 1,7-diene, tetraethyl octa-1,7-diene-4,4,5,5-tetracarboxylate failed to react at all under type C reaction conditions.

Reactions with Chlorotris(triphenylphosphine)rhodium.—The dienes (**4a—c, e**; $R^1 = R^2 = H$) when heated under reflux in chloroform with 1—2 mol % of chlorotris(triphenylphosphine)rhodium(I) gave the corresponding methylenecyclopentanes (**6a—c, e**; $R^1 = R^2 = H$) (Table 2). Sometimes it was necessary to pre-saturate the chloroform with dry hydrogen chloride. Reaction did not occur in ethanol-free chloroform in the absence of hydrogen chloride. Other rhodium complexes, $RhCl_3$, $[\{Rh(CO)_2Cl\}_2]$ and $[Rh(PPh_3)_2(CO)Cl]$ did not promote the cyclisation. The substituted barbituric acid derivative (**4f**; $R^1 = R^2 = H$) did not cyclise and the rhodium-catalysed cyclisation is less selective than the palladium(II)-catalysed reaction for substituted olefins. Thus, the diene (**4b**; $R^1 = R^2 = Me$) underwent rhodium(I)-catalysed cyclisation (94%) to a 79:9:18 mixture (n.m.r.) of *E*- and *Z*-(**6**; $R^1 = R^2 = Me$) and (**7b**; $R^1 = R^2 = Me$) in boiling ethanol over 24 h. The diene (**4b**; $R^1 = Me$, $R^2 = H$) gave a mixture (44%) of five isomeric products, *E*- and *Z*-(**6b**; $R^1 = Me$, $R^2 = H$), (**7b**; $R^1 = Me$, $R^2 = H$), (**5b**; $R^1 = Me$, $R^2 = H$) and (**5b**; $R^1 = H$, $R^2 = Me$) in the ratio 23:3:51:13:10 (by n.m.r.). In contrast dienes (**4a**; $R^1 = R^2 =$ Ph), [**4a**; $R^1 = (CH_2)_3CH{=}CH_2$, $R^2 = H$] and ethyl nona-3,8-dienoate failed to cyclise in the presence of chlorotris(triphenylphosphine)rhodium(I).

Attempts to make larger ring compounds using 1,7- and 1,8-

dienes were, as in the case of palladium, unsuccessful. Compound (**8**) gave a mixture of five isomeric products *E*- and *Z*-(**6b**; R^1 = Me, R^2 = H), (**6b**; R^1 = H, R^2 = Me), (**7b**; R^1 = Me, R^2 = H), and (**10**) in the approximate ratio 56:11:13:11:9, when cyclised in chloroform containing 1—2% ethanol. These products were not separated, indeed g.c./m.s. showed only three peaks (all with a parent ion at *m/z* 254). The presence of the other two products was established by ^{1}H n.m.r. spectroscopy. It was not possible to distinguish between *E*- and *Z*-(**6b**; R^1 = Me, R^2 = H) by ^{1}H n.m.r. spectroscopy; the *E*-configuration is assigned to the major isomer on steric grounds. Although the dienes (**4b**; R^1 = Me, R^2 = H) and (**8**) give rise to three common products, *E*- and *Z*-(**6b**; R^1 = Me, R^2 = H) and (**7b**; R^1 = Me, R^2 = H), the ratios are not the same and in addition each gives rise to two other isomeric cyclopentanes. These discrepancies arise from the difference in reaction conditions and solvents (see Experimental section) and it is considered that (**4b**; R^1 = Me, R^2 = H) is involved in both cyclisations. In particular, the cyclisation of (**4b**; R^1 = Me, R^2 = H) was conducted over 10 days (all the starting material was consumed after 10 h) to allow equilibration to occur.

Table 2. Cyclisation of (**4**) to (**6**) catalysed by $[RhCl(PPh_3)_3]$[a]

Starting material	Molar ratio of (**4**) to $[RhCl(PPh_3)_3]$	Reaction time (h)	Yield (%)[b]
(**4a**; R^1 = R^2 = H)	50:1	12	87
	50:1	12	85[c]
(**4b**; R^1 = R^2 = H)	60:1	8	90
	77:1	12	80[c]
(**4c**; R^1 = R^2 = H)	75:1	48	64
	75:1	72	0[c]
(**4e**; R^1 = R^2 = H)	52:1	72	60
	52:1	72	0[c]

[a] Dry HCl bubbled through stirred solution of hepta-1,6-diene and $[Rh(PPh_3)_3Cl]$ in chloroform for 5 min then boiled under reflux for the time indicated. [b] Isolated yields. [c] No HCl treatment.

Double-bond migration is a facile process with the rhodium(I) catalyst as shown by the clean isomerisation of the 1,8-diene (**9**) to (**4b**; R^1 = R^2 = Me) in chloroform containing 1—2% ethanol.

Interestingly, the isomer ratio of (**4b**; R^1 = R^2 = Me) prepared from commercial 1-bromobut-2-ene and by isomerisation of (**9**) differed significantly. The ratio of *trans, trans*-: *trans, cis*-:*cis,cis*-(**4b**; R^1 = R^2 = Me) was 70:28:2 in the material prepared from 1-bromobut-2-ene and 44:48:8 in the sample prepared by isomerisation of (**9**). Furthermore, (**9**) undergoes a rhodium(I)-catalysed cyclisation in boiling ethanol to an identical 79:9:18 mixture of *E*- and *Z*-(**6b**; R^1 = R^2 = Me) and (**7b**; R^1 = R^2 = Me) as is obtained from the cyclisation of (**4b**; R^1 = R^2 = Me).

When diethyl diallylmalonate (**4b**; R^1 = R^2 = H) was heated in boiling ethanol, which had been pre-saturated with dry hydrogen chloride, in the presence of 2 mol % chlorotris(triphenylphosphine)rhodium(I) for 12 h, cyclopentene (**7b**; R^1 = R^2 = H), isomeric with (**5b**; R^1 = R^2 = H) and (**6b**; R^1 = R^2 = H), could be isolated in 85% yield. Following the reaction by g.l.c. indicated that (**6b**; R^1 = R^2 = H) was formed first and then isomerised to (**7b**; R^1 = R^2 = H). This isomerisation is not merely acid catalysed since it does not occur in the absence of the rhodium compound. Compound (**5b**; R^1 = R^2 = H) however was unchanged on treatment with the rhodium compound in chloroform containing hydrogen chloride. Dienes (**4a** and **c**; R^1 = R^2 = H) could not be satisfactorily converted into (**7a** and **c**; R^1 = R^2 = H) since they tended to polymerise in ethanolic hydrogen chloride.

Cyclisation of (**4b**; R^1 = R^2 = H) using deuterium chloride and palladium acetate in chloroform gave (**5b**; R^1 = R^2 = H) containing no deuterium. Similarly, cyclisation of (**4b**; R^1 = R^2 = H) with deuterium chloride and chlorotris(triphenylphosphine)rhodium(I) in chloroform resulted in no deuterium incorporation in the product (**6b**; R^1 = R^2 = H). In contrast when (**4b**; R^1 = R^2 = H) was cyclised to (**7b**; R^1 = R^2 = H) using $[RhCl(PPh_3)_3]$ and deuterium chloride in ethanol, mass spectrometry and ^{1}H n.m.r. spectroscopy indicated that

Table 3. ^{1}H N.m.r. spectra (δ, $CDCl_3$) of the cyclopentenes (**5**)

	=CH	R^1CH_2	R^2CH_2	CH	Non-allylic CH_2[a]	R^1/R^2	X/Y Substituents
(**5a**; R^1 = R^2 = H)	5.59 (m)	1.75 (m)	1.05 (d)	2.75 (m)	1.88 (dd), 2.75 (m)		2.09, 2.12 (2 × s, 2 × Me)
(**5b**; R^1 = R^2 = H)	5.42 (m)	1.75 (t)	1.05 (d)	2.75 (m)	1.95, 2.75 (2 × m)		1.24, 1.25 (2 × t, 2 × Me), 4.15, 4.17 (2 × q, 2 × MeCH_2)
(**5c**; R^1 = R^2 = H)	5.78 (m)	1.73 (t)	1.10 (d)	2.87 (m)	2.13, 3.27 (2 × dd)		7.32 (6 H, m), 7.9 (4 H, m)
(**5d**; R^1 = R^2 = H)[b]	5.15 (m)	1.50, 1.65 (2 × br s)	0.95, 1.0 (2 × d)	2.52 (m)	1.75, 2.52 (2 × m)		1.2 (t, *Me*CH_2), 2.0, 2.02 (2 × s, MeCO), 3.95 (2 × q, MeCH_2)
(**5e**; R^1 = R^2 = H)	5.32 (m)	1.67 (dd)	1.50 (d)	2.07 (m)	1.6, 2.67 (2 × m)		0.88, 1.13 (2 × s, 2 × Me), 2.67 (4 H, m)
(**5f**; R^1 = R^2 = H)	5.19 (m)	1.60 (t)	1.20 (d)	2.58 (m)	2.20, 2.77 (2 × dd)		7.86 (2 H, br s)
(**5a**; R^1 = Me, R^2 = H)	5.34 (m)	1.82 (m)	1.03 (d)	2.70 (m)	1.82, 2.70 (2 × m)	1.10 (t)	2.10, 2.13 (2 × s, 2 × Me)
(**5b**; R^1 = Me, R^2 = H)	5.78 (m)	1.73, 1.88 (2 × m)	0.98 (m)	2.76 (m)	2.18, 3.03 (2 × dd)	0.98 (m)	0.98 (6 H, m), 4.05 (4 H, m)
(**5b**; R^1 = H, R^2 = Me)	5.78 (m)	1.53 (m)	1.12, 1.51 (2 × m)	2.58 (m)	2.26, 2.98 (2 × dd)	1.53 (m), 0.82 (t)	0.98 (6 H, m), 4.05 (4 H, m)
(**5a**; R^1 = R^2 = Me)	5.60 (m)	2.0 (m)	1.70 (m)	2.62 (m)	1.90 (dd), 2.62 (m)	0.90 (t), 1.10 (t)	2.12, 2.14 (2 × s, 2 × Me)
(**5b**; R^1 = R^2 = Me)[c]	5.75 (m)	1.76, 1.95 (2 × m)	1.11, 1.51 (2 × m)	2.65 (m)	2.24, 2.95 (2 × dd)	0.80 (t), 0.96 (m)	0.96 (6 H, m), 3.97 (4 H, m)

[a] AX Part of an ABX system. [b] 2:1 Mixture of stereoisomers. [c] Spectrum determined in C_6D_6.

Table 4. ^{1}H N.m.r. spectra (δ, C_6D_6) of methylenecyclopentanes (**6**)

	Olefinic H	Allylic CH_2	Non-allylic CH_2[a]	R^2CH_2	CH	R^1/R^2	X/Y Substituents
(**6a**; $R^1 = R^2 = H$)[b]	4.76, 4.90 (2 × m)	2.90 (br s)	1.56, 2.57 (2 × m)	1.08 (d)	2.57 (m)		2.08, 2.12 (2 × s)
(**6b**; $R^1 = R^2 = H$)[b]	4.75, 4.86 (2 × m, *J* 1.5, 2.5 Hz)	2.88, 3.0 (2 × d, *J* 18 Hz)	1.68 (dd), 2.55 (m)	1.04 (d)	2.52 (m)		1.19 (t), 4.13, 4.40 (2 × q)
(**6c**; $R^1 = R^2 = H$)[b]	4.86, 4.95 (2 × m, *J* 1.5, 2.5 Hz)	3.34, 3.46 (2 × d, *J* 14 Hz)	2.20, 2.88 (2 × dd)	1.18 (d)	2.68 (m)		7.42 (6 H, m) 7.9 (4 H, m)
(**6e**; $R^1 = R^2 = H$)[b]	4.82, 4.94 (2 × m, *J* 1, 2.5 Hz)	2.56, 2.58 (2 × d, *J* 6 Hz)	1.63 (d), 2.35 (dd)	1.10 (d)	2.6 (m)		0.98, 1.09 (2 × s, (2 × 3 H), 2.66, 2.92 (2 × s, 2 × 2 H)
E-(**6b**; R^1 = Me, R^2 = H)	5.17 (m)	3.14, 3.31 (2 × d, *J* 17 Hz)	1.99, 2.82 (2 × dd)	1.0 (m)	2.75 (m)	1.65 (m)	1.0 (6 H, m), 4.04 (4 H, q)
Z-(**6b**; R^1 = Me, R^2 = H)	5.28 (m)						
(**6b**; R^1 = H, R^2 = Me)	4.84, 4.95 (2 × m)			1.37, 1.73 (2 × m)		0.85 (t)	
E-(**6b**; $R^1 = R^2$ = Me)	5.25 (m)	3.10, 3.32 (2 × d, *J* 17 Hz)	1.98, 2.87 (2 × dd)	1.20, 1.67 (2 × m)	2.61 (m)	1.57 (m), 0.88 (t)	0.97 (6 H, m), 4.04 (4 H, m)
Z-(**6b**; $R^1 = R^2$ = Me)	5.35 (m)						

[a] AX Part of an ABX system. [b] Spectrum determined in $CDCl_3$.

deuterium was incorporated into the methyl groups attached to the olefinic bond, *ca.* 30% of the product having one deuterium, and 9% two deuterium atoms. Deuterium was similarly incorporated when (**5b**; $R^1 = R^2 = H$) was isomerised to (**7b**; $R^1 = R^2 = H$) under the same reaction conditions (59% $^2H_1$ 5% $^2H_2$).

Although all the isolated reaction products were examined by mass spectrometry, i.r. and elemental analysis, the principal evidence for their structures is based on their ^{1}H n.m.r. spectra. Details of the spectral assignments of compounds (**6**) and (**7**) including compounds which were not isolated are shown in Tables 3 and 4.

The cyclopentenes (**5**) have a chiral centre and so the adjacent ring methylene protons are diastereotopic (Table 3). These protons are deshielded by the carbonyl groups in X and Y, but in most cases the deshielding is unequal, and they give rise to signals *ca.* 1 p.p.m. apart. The difference in deshielding must arise from conformational factors. Similar effects can be observed (Table 4) in the methylenecyclopentanes (**6**). In the cyclopentenes (**5b**; R^1 = Me, R^2 = H, Me) the methylene protons adjacent to R^1 are also inequivalent. Models suggest this may be due to restricted rotation.

The mechanism(s) of these reactions is still largely speculative. Even the function of the carbonyl-containing substituents is not absolutely clear. That these are not required to exert a chelate effect is shown by the reactions of the dimedone and barbituric derivatives (**4e**; $R^1 = R^2 = H$) and (**4f**; $R^1 = R^2 = H$) where this cannot occur. However, co-ordination of one carbonyl group might stabilise a hydride or other intermediate. A range of rhodium complexes of diallyl ethers and related compounds including 4,4-diacetylhepta-1,6-diene were readily prepared from $[Rh(PPh_3)_3Cl]$ or $[Rh(C_2H_4)_2pd]$ (pd = pentane-2,4-dionato).[9] Dichloro(4,4-diacetylhepta-1,6-diene)platinum(II) was also prepared and its structure determined by a single crystal *X*-ray structure analysis (see Experimental section). A perspective drawing of the molecule is given in the Figure.

The analysis shows the expected π-complexation of the olefinic groups with the 1,6-diene in the 'chair' conformation. This allows one carbonyl oxygen atom to occupy an extended co-ordination site (Pt · · · O = 3.34 Å). The elongated octahedral co-ordination around Pt is completed by a Cl atom of the centrosymmetrically-related molecule as shown in (**11**);

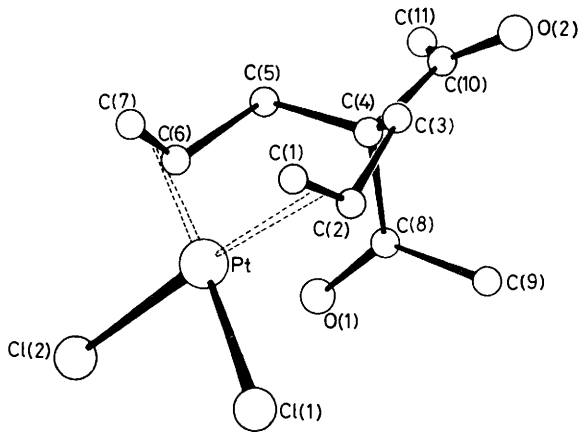
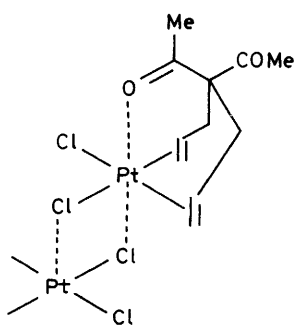


Figure.

(Pt · · · Cl(2′) = 3.71 Å. This type of interaction has been noted in some rhodium complexes of hepta-1,6-dienes where 'chair' ⇌ 'boat' interconversions of the type (**12**) ⇌ (**13**) were observed by variable-temperature ^{1}H n.m.r.[8,9]

Another possible function of geminal-substitution at C-4 in these 1,6-dienes is to facilitate diene binding and/or cyclisation by a Thorpe-Ingold effect.[13] Thus (**4**; $R^1 = R^2 = H$, X=Y=H) reacts with iodine by simple addition only whereas (**4**; R^1 =



(**11**)

Table 5. Final atomic fractional co-ordinates for dichloro(4,4-diacetylhepta-1,6-diene)platinum(II), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.401 9(1)	0.157 8(1)	0.053 0(2)
Cl(1)	0.532 3(8)	0.264 7(7)	−0.208 1(11)
Cl(2)	0.303 5(7)	−0.025 6(7)	−0.172 3(12)
O(1)	0.070 9(23)	0.200 0(19)	0.018 9(37)
O(2)	0.140 6(21)	0.450 7(18)	0.597 0(35)
C(1)	0.566 7(25)	0.310 3(30)	0.250 0(41)
C(2)	0.443 7(28)	0.347 3(26)	0.217 8(49)
C(3)	0.337 5(28)	0.367 2(26)	0.394 4(46)
C(4)	0.172 9(23)	0.285 6(20)	0.356 7(39)
C(5)	0.133 2(29)	0.142 7(25)	0.382 2(45)
C(6)	0.209 2(26)	0.062 8(22)	0.243 1(43)
C(7)	0.337 9(35)	0.041 2(25)	0.302 1(58)
C(8)	0.118 6(24)	0.295 7(22)	0.145 5(38)
C(9)	0.126 1(35)	0.423 2(25)	0.104 1(49)
C(10)	0.080 1(27)	0.343 9(22)	0.513 6(41)
C(11)	−0.079 7(29)	0.272 8(28)	0.543 2(56)

Table 6. Molecular dimensions

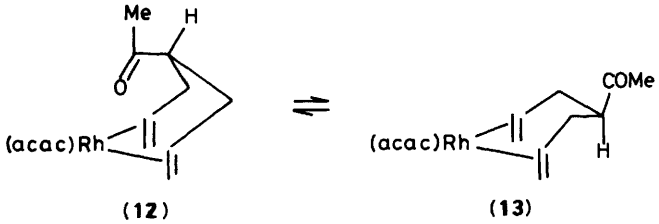
(a) Bond lengths (Å)

Pt–Cl(1)	2.322(7)	C(6)–C(7)	1.39(4)
Pt–Cl(2)	2.306(6)	C(4)–C(8)	1.55(4)
Pt–X(1)*	2.06(1)	C(8)–C(9)	1.45(4)
Pt–X(2)*	2.09(1)	C(8)–O(1)	1.24(3)
C(1)–C(2)	1.39(4)	C(4)–C(10)	1.57(3)
C(2)–C(3)	1.58(3)	C(10)–C(11)	1.47(3)
C(3)–C(4)	1.52(3)	C(10)–O(2)	1.20(3)
C(4)–C(5)	1.53(3)	Pt···O(1)	3.34(2)
C(5)–C(6)	1.54(3)	Pt···Cl(2′)	3.711(7)

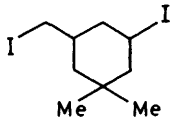
(b) Angles (°)

Cl(1)–Pt–Cl(2)	88.7(3)	C(5)–C(4)–C(10)	108(2)
Cl(1)–Pt-X(1)*	85.9(2)	C(8)–C(4)–C(10)	107(2)
Cl(2)–Pt–X(2)*	87.4(2)	C(4)–C(5)–C(6)	118(2)
X(1)*–Pt–X(2)*	98.0(1)	C(5)–C(6)–C(7)	122(2)
O(1)–Pt-Cl(2′)	162.1(4)	C(4)–C(8)–C(9)	117(2)
C(1)–C(2)–C(3)	122(2)	C(4)–C(8)–O(1)	122(2)
C(2)–C(3)–C(4)	114(2)	C(9)–C(8)–O(1)	122(2)
C(3)–C(4)–C(5)	115(2)	C(4)–C(10)–C(11)	120(2)
C(3)–C(4)–C(8)	112(2)	C(4)–C(10)–O(2)	118(2)
C(3)–C(4)–C(10)	107(2)	C(11)–C(10)–O(2)	121(2)
C(5)–C(4)–C(8)	109(2)		

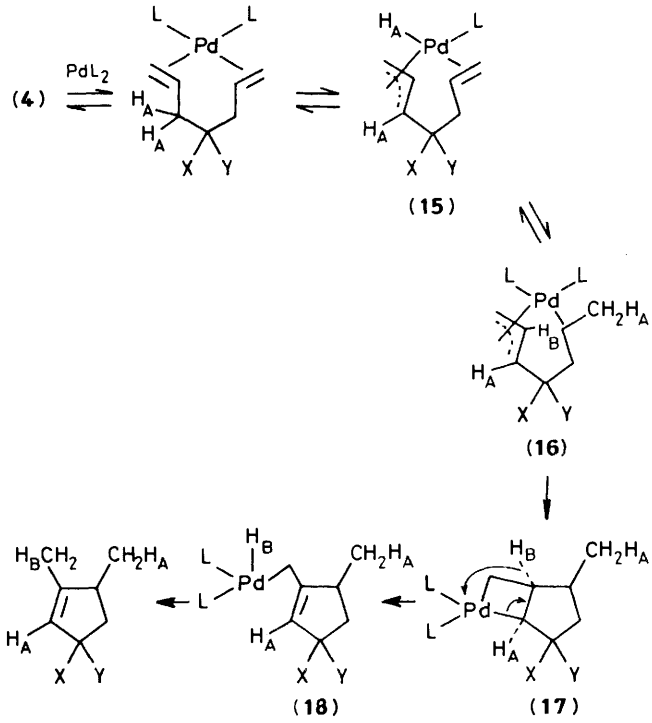
* X(1) and X(2) are the mid-points of the C(1)–C(2) and C(6)–C(7) bonds, respectively.



(12) (13)



(14)

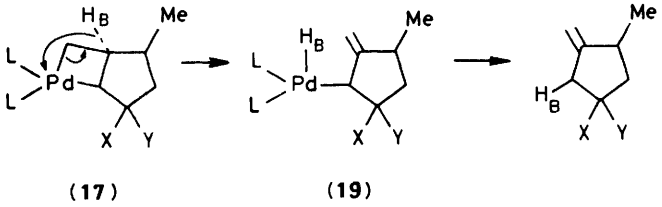


Scheme 1.

R^2 = H, X=Y=Me) cyclises to (**14**).[14] That geminal-disubstitution at C-4 cannot be the only factor in our system is demonstrated by the failure of (**4**; R^1 = R^2 = H, X=Y=CN or CH_2OH) to cyclise. Thus the co-ordinating ability of the carbonyl substituents at C-4 seems important.

The fact that the palladium and rhodium systems give different products and that these products, (**5**) and (**6**), cannot be interconverted under the reaction conditions suggests that different mechanisms are involved. The palladium acetate reaction has a requirement for chloride ions since neither acetic or toluene-*p*-sulphonic acids are suitable as substitutes. Not inconsistent with this is the fact that in at least one of the reactions, that of (**4b**; R^1 = R^2 = H), using palladium chloride in the absence of hydrogen chloride gives a very similar result to that obtained using palladium acetate with hydrogen chloride. To explain the lack of incorporation of deuterium from deuterium chloride into the product it must be assumed that any hydrido species involved must neither exchange with deuterium chloride nor be formed from hydrogen (deuterium) chloride. It is hard to envisage a mechanism which does not involve hydride intermediates and these must be formed from the organic substrate. A possible mechanism incorporating this feature is shown in Scheme 1.

π-Allylpalladium species are known normally to undergo attack at the terminal positions of the allyl moiety[15] rather than at the centre of such a π-species as in (**16**)→(**17**). However in the nickel-catalysed dimerisation of butadiene to 1-vinyl-2-methylenecyclopentane attack at the centre atom of a π-allyl is suggested.[16,17] Metallacyclobutanes like (**17**) have been proposed as intermediates in the dimerisation of simple olefins catalysed by niobium and tantalum complexes[18–20] and stable metallacyclobutane complexes are well known for platinum[21–23] and tungsten.[24,25] The intermediate (**17**) could rearrange to (**19**) which might then undergo reductive elimination to give methylenecyclopentane (Scheme 2), followed by isomerisation under the reaction conditions to give the minor product (**7**). An acetoxypalladiation–depalladiation

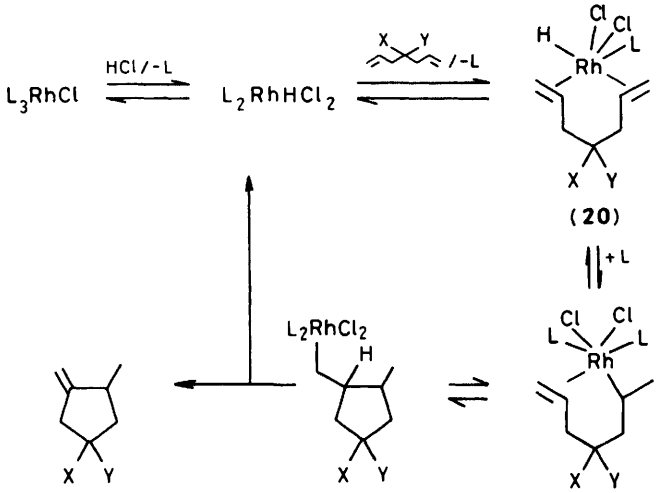


(17) (19)

Scheme 2.

mechanism seems unlikely in view of the fact that no acetoxylated products have been found.

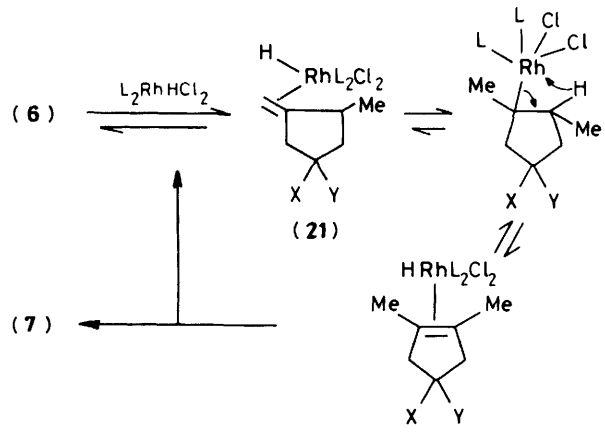
A mechanism similar to that shown in Schemes 1 and 2 can be written for the rhodium-catalysed reaction (in chloroform). However, it is known that $[Rh(PPh_3)_2HCl_2]$ is formed by reaction of hydrogen chloride with $[Rh(PPh_3)_3Cl]$ in chloroform[26] or by dissolving $[Rh(PPh_3)_3Cl]$ in ethanol–chloroform.[27] Moreover, some rhodium-catalysed isomerisations and dimerisations are known to proceed *via* a 1,2-metal hydride addition–elimination sequence.[28,29] Scheme 3 is thus consistent with known rhodium chemistry.



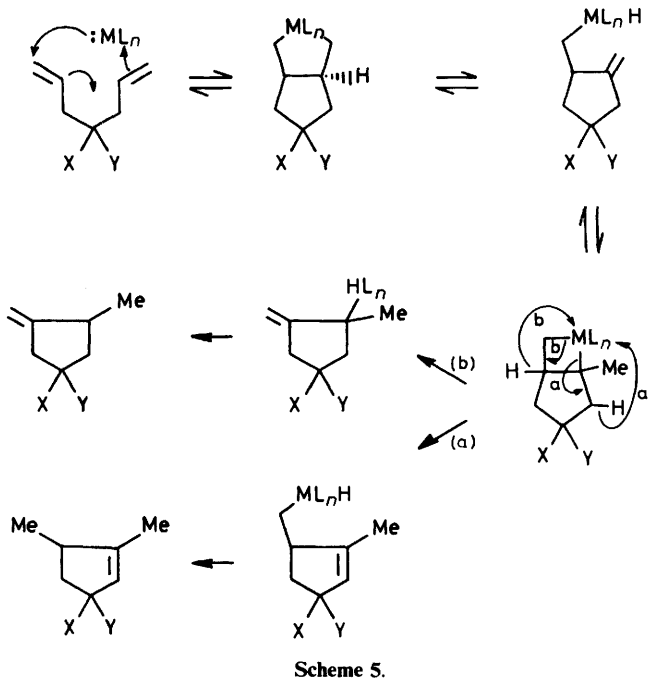
Scheme 3.

The rhodium-catalysed isomerisation of methylenecyclopentanes (**6**) to tetrasubstituted olefins (**7**) in ethanolic hydrogen chloride seems likely to occur by the sequence shown in Scheme 4. If these mechanisms (Schemes 2—4) are indeed operative, the deuterium chloride experiments imply that neither $[RhL_2HCl_2]$ nor (**20**) (Scheme 3) exchange hydrogen for deuterium in chloroform and that either $[RhL_2HCl_2]$ or (**21**) (Scheme 4) do exchange hydrogen for deuterium in ethanol. Since such exchange processes involve charged species this seems reasonable.

Another sequence which could explain the palladium and rhodium (in chloroform) reactions (Scheme 5) is based on the mechanism of dimerisation of mono-olefins using tantalum and niobium complexes which, it is believed, involves metallocyclopentane and metallocyclobutane intermediates.[18–20] There is other evidence attesting to the marked propensity for rhodium to form five-membered metallacycles,[30] and similar metallacycles are known for palladium.[31] The role of the hydrogen chloride in the rhodium(I)-catalysed process is presumably analogous to that of hydrogen chloride in the



Scheme 4.



Scheme 5.

$[\{Rh(CO)_2Cl\}_2]$-catalysed conversion of ethylene into butene.[32]

Experimental

N.m.r. spectra were recorded at 60 MHz (on Varian A60, Perkin-Elmer-Hitachi, and Jeol-PMX60 instruments), 90 MHz (on a Bruker WH90 instrument), 250 MHz (on a Bruker WH250 instrument), and 300 MHz (at the University of Manchester) using deuteriochloroform as solvent and tetramethylsilane as internal standard except where otherwise stated. Mass spectra were recorded on AE1 MS902 and MS30 instruments at 70 eV. Gas–liquid chromatography was performed on Perkin-Elmer F-11 and F-17, and Pye 104 machines. Gas chromatography/mass spectrometry (g.c./m.s.) was carried out using a Pye 104 and AE1 MS30 combination. M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected.

3-Allylpentane-2,4-dione,[33] (**4a**; $R^1 = R^2 = H$),[33] 3-(octa-2,7-dienyl)pentane-2,4-dione,[34] [**4a**; $R^1 = R^2 = (CH_2)_3CH{=}CH_2$],[34] (**4b**; $R^1 = R^2 = Me$),[35] diethyl octa-2,7-dienylmalonate,[34] (**4d**; $R^1 = R^2 = H$),[36,37] (**4f**; $R^1 = R^2 =$

Table 7. Substituted β-dicarbonyl compounds

	Yield (%)	Reaction time (days)	B.p./m.p. (°C)	Analysis [Found (Calc.)]		δ($CDCl_3$)
(**4a**; $R^1 = R^2$ = Me)	80	3	70—72/0.05 mmHg	75.15 (75.0)	9.75 (9.7)	1.63 (6 H, 2 × d), 2.08, 2.09 (6 H, 2 × s), 2.56 (4 H, d), 5.36 (4 H, m)
(**4a**; $R^1 = R^2$ = Ph)	60	3	52—54	83.35 (83.15)	7.4 (7.25)	2.16 (6 H, s), 2.83 (4 H, d), 5.35 (4 H, m), 7.3 (10 H, br s)
(**4a**; R^1 = Me, R^2 = H)[a]	54	3	65—66/0.2 mmHg	73.95 (74.25)	9.2 (9.3)	1.63 (3 H, m), 2.09, 2.10 (6 H, 2 × s), 2.63 (4 H, m), 5.36 (5 H, m)
[**4a**; $R^1 = CH_2{=}CH(CH_2)_3$, R^2 = H][b]	89	5	106—112/0.1 mmHg	77.05 (77.35)	9.7 (9.75)	1.4 (2 H, m), 2.0 (4 H, m), 2.03 (6 H, s), 2.60, 2.63 (4 H, 2 × d), 5.24 (8 H, m)
(**4b**; R^1 = Me, R^2 = H)	75		86—88/0.4 mmHg	66.3 (6.1)	8.7 (8.7)	1.24 (6 H, t), 1.44 (3 H, d), 1.96 (2 H, d), 2.64 (2 H, d), 4.16 (4 H, q)
(**4c**; $R^1 = R^2$ = H)	66	5	46—49	82.8 (82.85)	6.3 (6.6)	3.0 (4 H, d), 5.25 (6 H, m), 7.25, 7.8 (10 H, m)
(**4e**; $R^1 = R^2$ = H)	56	3	38—40			1.0 (6 H, s), 2.53 (4 H, d), 2.6 (4 H, s), 5.55 (6 H, m)
(**4**; $R^1 = R^2$ = H, X=Y=CN)	58	0.7	34			2.40 (4 H, d), 5.25 (6 H, m)
bis-3,3-β-methylallylpentane-2,4-dione[c]	65	5	84—86/14 mmHg			1.65 (3 H, br s), 2.15 (6 H, s), 2.78 (4 H, br s), 4.59, 4.82 (4 H, 2 × br s)
(**4a**; R^1 = allyl, R^2 = prop-2-ynyl)	89	4	99—103/12 mmHg			2.10 (1 H, t), 2.20 (6 H, s), 2.83 (2 H, d), 2.92 (2 H, d), 5.3 (3 H, m, ABX)
(**8**)	72		80—82/0.4 mmHg	66.5 (66.1)	9.0 (8.7)	1.26 (6 H, t), 1.98 (4 H, d), 2.66 (2 H, d), 4.19 (4 H, q), 5.0 (4 H, m), 5.68 (2 H, m)
(**9**)	34	0.7	92—94/0.01 mmHg	67.35 (67.15)	9.0 (9.0)	1.26 (6 H, t), 1.98 (8 H, d), 4.18 (4 H, q), 5.0 (4 H, m, 5.7 (4 H, m)
Tetraethyl octa-1,7-diene-4,4,5,5-tetracarboxylate	24	2	148—150/0.4 mmHg	82.8 (82.25)	6.3 (6.6)	3.0 (4 H, d), 5.25 (6 H, m), 7.25, 7.80 (10 H, m)

[a] From 3-allylpentane-2,4-dione. [b] From octa-2,7-dien-3-ylpentane-2,4-dione. [c] Made from β-methylallyl chloride.

H),[38] ethyl nona-3,8-dienoate,[39,40] *N,N*-diallylacetamide,[41] *N,N*-diallylbenzamide,[41] diethyl but-2-enylmalonate,[42] diethyl but-3-enylmalonate,[43] and tetraethyl ethane-1,1,2,2-tetracarboxylate[44] were made by literature methods.

Diene Syntheses.—Substituted β-diketones (**4a**) were made in the usual way[36] from the β-diketone and appropriate allylic bromide in acetone in the presence of anhydrous potassium carbonate. Unsymmetrically disubstituted β-diketones were made in two stages. 3-Allyl-3-prop-2-ynylpentane-2,4-dione and diallylmalononitrile were made analogously. The diesters (**4b**), (**8**), and (**9**) were synthesised from diethyl malonate and the appropriate bromide(s) in ethanol containing sodium ethoxide. Tetramethyl octa-1,7-diene-4,4,5,5-tetracarboxylate was made similarly from tetramethyl ethane-1,1,2,2-tetracarboxylate. Analytical and other data for the new dienes are given in Table 7.

Cyclisation of Diethyl Diallylmalonate (**4b**; $R^1 = R^2$ = H).—(a) *With* $Pd(OAc)_2$. Dry hydrogen chloride was bubbled through a solution of (**4b**; $R^1 = R^2$ = H) (4.8 g, 2 × 10^{-2} mol) and palladium acetate (0.224 g, 1 × 10^{-3} mol) in chloroform (30 ml) for *ca.* 5 min. The resulting brown solution was boiled under reflux for 6 h. The solvent was then removed under reduced pressure and the residue dissolved in light petroleum (b.p. 40—60 °C) and filtered through a short column of neutral alumina to remove the catalyst. The eluate was concentrated and the residue distilled to afford (**5b**; $R^1 = R^2$ = H) as a colourless oil (4.2 g, 87.5%), b.p. 102—108 °C/1 mmHg (Found: C, 64.8; H, 8.45. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%); δ_H (Table 3); $\nu_{max.}$(film) 2 980, 2 960, 1 750, 1 440, 1 345, 1 100, 1 060, 1 015, and 840 cm^{-1}; *m/z* 240 (M^+, 20%), 195 (4), 167 (90), 166 (100), 139 (29), 127 (30), 121 (25), 111 (15), 95 (25), 94 (23), 93 (80), 91 (18), 79 (23), and 77 (23). G.l.c. (5% SGR, 2 m; 15% Carbowax 20M, 2 m) and ^1H n.m.r. spectroscopy indicated that the product, prior to distillation, contained (**7b**; $R^1 = R^2$ = H) (8%).

(b) *With* $[Rh(PPh_3)_3Cl]$ *in chloroform.* Dry hydrogen chloride was bubbled through a stirred solution of (**4b**; $R^1 = R^2$ = H) (8.0 g, 0.033 mol) and $[(PPh_3)_3RhCl]$ (0.5 g, 5.4 × 10^{-4} mol) in chloroform (50 ml) for 5 min. The resulting mixture was boiled under reflux for 8 h and then worked up as described above to afford (**6b**; $R^1 = R^2$ = H) as a colourless oil (7.2 g, 90%), b.p. 106—107 °C/3 mmHg (Found: C, 64.95; H, 8.45. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%); δ_H (Table 4); δ_C 14.10 (2 × *Me*CH_2), 18.08 (*Me*CH), 37.43 (MeCH), 40.68, 42.30 (2 × ring CH_2), 58.36 (CH_2CCH_2), 61.42 (MeCH_2), 105.45 (C=CH_2), 153.57 (*C* = CH_2), and 171.89 and 172.02 (2 × CO); *m/z* 240 (M^+, 15%), 195 (21), 194 (11), 167 (22), 166 (97), 139 (13), 138 (11), 137 (13), 121 (18), 94 (14), 93 (100), 92 (17), 79 (16), and 77 (16).

(c) *With* $[Rh(PPh_3)_3Cl]$ *in ethanol.* Dry hydrogen chloride was bubbled through a solution of (**4b**; $R^1 = R^2$ = H) (2.4 g, 1 × 10^{-2} mol) and $[(PPh_3)_3RhCl]$ (0.1 g, 1.08 × 10^{-4} mol) in ethanol (20 ml) for 5 min. The solution was then boiled under reflux for 14 h. Work-up afforded (**7b**; $R^1 = R^2$ = H) (2 g, 85%) as a colourless oil, b.p. 100—102 °C/2 mmHg (Found: C, 65.25; H, 8.6. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%); δ 1.24 (t, 6 H, 2 × *Me*CH_2), 1.59 (6 H, br s, 2 × Me), 2.92 (4 H, br d, ring CH_2), and 4.18 (4 H, q, 2 × Me*CH*$_2$); $\nu_{max.}$(film) 2 980, 1 730, 1 455, 1 250, 1 115, 1 090, 1 060, 925, and 850 cm^{-1}; *m/z* 240 (M^+, 20%), 195 (25), 167 (32), 166 (80), 94 (15), and 93 (100). G.l.c. monitoring (15% Carbowax 20M, 2 m, 140 °C) of the reaction indicated that (**6b**; $R^1 = R^2$ = H) was formed first and then isomerised to (**7b**; $R^1 = R^2$ = H).

The following compounds, (**5a**—**f**) and (**6a**, **c**, **e**), were prepared in analogous fashion.

Compound*	B.p. or m.p. (°C)	Microanalysis (%) Found (Calc.) C	H	m/z (M^+)
(**5a**; $R^1 = R^2 = H$)	43—45 at 0.05 mmHg	73.05 (73.3)	8.95 (8.95)	180
(**5c**; $R^1 = R^2 = H$)	114—115	83.0 (82.85)	6.5 (6.6)	304
(**5d**; $R^1 = R^2 = H$)	104—105 at 10 mmHg	68.6 (68.55)	8.5 (8.65)	210
(**5e**; $R^1 = R^2 = H$)	101—103	75.65 (76.35)	8.95 (9.1)	220
(**5f**; $R^1 = R^2 = H$)	264—267	57.5 (57.5)†	6.0 (5.75)	208
(**5a**; R^1 = Me, R^2 = H)	110—120 at 10 mmHg	74.1 (74.2)	9.4 (9.35)	194
(**5a**; $R^1 = R^2$ = Me)	88—90 at 8 mmHg	75.1 (74.95)	9.8 (9.7)	208
(**5b**; $R^1 = R^2$ = Me)	92—95 at 0.2 mmHg	67.05 (67.15)	9.0 (9.0)	268
(**6a**; $R^1 = R^2 = H$)	116—120 at 18 mmHg	73.1 (73.3)	8.9 (8.95)	180
(**6c**; $R^1 = R^2 = H$)	64—66	82.95 (82.85)	6.85 (6.6)	304
(**6e**; $R^1 = R^2 = H$)	98—100			200

* See Tables 1 and 2 for yields and conditions † Found: N, 13.45%. Required N, 13.45%.

Cyclisation of Diethyl Allyl(but-2-enyl)malonate (**4b**; R^1 = Me, R^2 = H).—A suspension of $[Rh(PPh_3)_3Cl]$ (0.73 g, 8.0×10^{-4} mol) in diethyl allyl(but-2-enyl)malonate (10.12 g, 0.04 mol) and absolute ethanol (50 ml), was purged with nitrogen for 10 min and dry hydrogen chloride was then bubbled through for 5 min. The mixture was then boiled under reflux for 10 h when g.l.c. (SGR, 5%, 2 m, 105 °C) showed the absence of starting material and the appearance of two product peaks (in a 3:2 ratio). Earlier g.l.c. samples showed the proportions of these products were changing with time so boiling was continued to equilibrate the mixture. After 10 days the ratio was constant at 3:7. Passage through a short column of neutral alumina using light petroleum (b.p. 40—60 °C) afforded a clear, colourless oil (4.44 g, 44%), b.p. 70—74 °C/0.01 mmHg composed of five isomeric cyclopentenes (Found: C, 65.85; H, 8.7. $C_{14}H_{22}O_4$ requires C, 66.1; H, 8.7%). Capillary g.l.c. analysis (Carbowax 20M, 100M, 180 °C) demonstrated the presence of four products whilst the 250 MHz n.m.r. spectrum of the mixture showed five products to be present: *E*- and *Z*-(**6b**; R^1 = Me, R^2 = H), (**7b**; R^1 = Me, R^2 = H), (**5b**; R^1 = Me, R^2 = H), and (**5b**; R^1 = H, R^2 = Me) in the ratio 23:3:51:13:10. Compounds (**5b**; R^1 = Me, R^2 = H) and (**7b**; R^1 = Me, R^2 = H) were co-eluted on g.l.c.

Diethyl 1-ethyl-2-methylcyclopent-1-ene-4,4-dicarboxylate (**7b**; R^1 = Me, R^2 = H): R_t 26.8 min; $\delta(C_6D_6)$ 0.93 3 H, t, *J* 7 Hz, CH_3CH_2), 1.00 (6 H, m, 2 × CH_3CH_2), 1.59 (3 H, s, Me), 1.97 (2 H, q, *J* 7 Hz, CH_3CH_2), 3.22 (2 H, s, CH_2), 3.27 (2 H, s, CH_2), and 4.04 (4 H, m, 2 × CH_3CH_2).

Diethyl *E*-ethylidene-2-methylcyclopentane-4,4-dicarboxylate (**6b**; R^1 = Me, R^2 = H): R_t 28.8 min; δ (C_6D_6) 1.00 (3 H, m, *Me*CH), 1.65 (3 H, m, *Me*CH), 2.67 (1 H, m, MeC*H*), 2.81 (1 H, ABX, J_{AB} 7 Hz, J_{AX} 15 Hz), 3.14 (1 H, d, *J* 17 Hz, CH_2), and 5.16 (1 H, m, MeC*H*=C); *m/z* 254 (M^+, 4%), 180 (35), 151 (12), 108 (11), 107 (92), 106 (17), 93 (17), 91 (27), 79 (16), 77 (15), 41 (18), 39 (15), 29 (100), and 27 (34).

Diethyl 1-(*Z*-ethylidene)-2-methylcyclopentane-4,4-dicarboxylate (**6b**; R^1 = Me, R^2 = H): R_t 28 min; $\delta(C_6D_6)$ 5.28 (1 H, m, MeC*H*=C), other signals obscured; *m/z* 254 (M^+, 5%) 180 (35), 151 (11), 107 (85), 106 (15), 93 (17), 91 (26), 79 (16), 77 (15), 43 (10), 41 (17), 39 (12), 29 (100), and 27 (34).

Diethyl 1-ethyl-2-methylcyclopent-5-ene-4,4-dicarboxylate (**5**; R^1 = Me, R^2 = H): R_t 26.8 min; $\delta(C_6D_6)$ 2.18 (1 H, ABX, J_{AB} 13 Hz, J_{AX} 6 Hz, diastereotopic H of CH_2), other signals obscured.

Diethyl 1-ethyl-2-methylcyclopent-2-ene-4,4-dicarboxylate (**5**; R^1 = H, R^2 = Me): R_t 29.15 min; $\delta(C_6D_6)$ 2.26 (1 H, ABX, J_{AB} 13 Hz, J_{AX} 6 Hz, diastereotopic H of CH_2) and 5.74 (1 H, m, C=CH), other signals obscured; *m/z* 254 (M^+, 4%), 181 (37), 180 (21), 125 (12), 108 (14), 107 (100), 106 (17), 79 (25), 77 (25), 67 (11), 44 (22), 43 (37), 38 (11), 29 (69), and 27 (35).

Cyclisation of Diethyl Allyl(but-3-enyl)malonate (**8**).—A solution of diethyl allyl(but-3-enyl)malonate (9.66 g, 3.8×10^{-2} mol) and $[Rh(PPh_3)_3Cl]$ (0.69 g, 7.60×10^{-4} mol) in chloroform (50 ml) was degassed by bubbling oxygen-free nitrogen through it for 10 min, followed by dry hydrogen chloride for 5 min. The resulting clear red solution was boiled under reflux for 20 h. The solvent was then evaporated and the residue washed through a short (3 in × 1 in) column of neutral alumina with light petroleum (b.p. 40—60 °C) as eluant. Removal of the light petroleum left a colourless oil which was distilled to give a clear, colourless oil (6.0 g, 62%), b.p. 82—85 °C/0.03 mmHg; this proved to be a mixture of five isomeric cyclopentenes (Found: C, 65.8; H, 8.45. $C_{14}H_{22}O_4$ requires C, 66.1; H, 8.7%). The 250 MHz n.m.r. spectrum of the mixture showed it to consist of *E*- and *Z*-(**6b**; R^1 = Me, R^2 = H), (**6b**; R^1 = H, R^2 = Me), (**7b**; R^1 = Me, R^2 = H), and (**10**) in the approximate ratio 56:11:13:11:9.

Diethyl 1-(*E*-ethylidene)-2-methylcyclopentane-4,4-dicarboxylate (**6b**; R^1 = Me, R^2 = H); $\delta(C_6D_6)$ 1.00 (9 H, m, 2 × *Me*CH_2 and *Me*CH), 1.65 (3 H, m, Me), 1.99 (1 H, ABX, J_{AB} 7 Hz, J_{AX} 20 Hz, CH_2), 2.82 (1 H, ABX, J_{AB} 7 Hz, J_{AX} 15 Hz, CH_2), 2.75 (1 H, m, MeC*H*), 3.14 (1 H, d, *J* 17 Hz, CH_2C=C), 3.31 (1 H, d, *J* 17 Hz, CH_2C=C), 4.04 (4 H, q, *J* 7 Hz, 2 × MeCH_2), and 5.17 (1 H, m, CH=C); *m/z* 254 (M^+, 3%), 180 (29), 151 (10), 107 (81), 106 (15), 93 (16), 91 (26), 79 (16), 77 (15), 41 (18), 39 (15), 29 (100), and 27 (35).

Diethyl 2-ethyl(methylene)cyclopentane-4,4-dicarboxylate (**6b**; R^1 = H, R^2 = Me): $\delta(C_6D_6)$ 0.85 (3 H, t, *J* 7 Hz, *Me*CH_2), 1.37 (1 H, m, MeCH_2), 1.73 (1 H, m, MeCH_2), 4.84 (1 H, m, CH=C), and 4.95 (1 H, m, CH=C).

Diethyl 1-methyl-2-vinylcyclopentane-4,4-dicarboxylate (**10**): $\delta(C_6D_6)$ 5.48 (2 H, m, CH_2=C) and 5.69 (1 H, m, CH_2=C*H*), other signals were obscured.

Diethyl 1-ethyl-2-methylcyclopent-1-ene-4,4-dicarboxylate (**7b**; R^1 = Me, R^2 = H): $\delta(C_6D_6)$ and *m/z* (%) as noted above.

Diethyl 1-(*Z*-ethylidene)-2-methylcyclopentane-4,4-dicarboxylate (**6b**; R^1 = Me, R^2 = H): $\delta(C_6D_6)$ and *m/z* (%) as noted above.

Cyclisation of Diethyl Dibut-2-enylmalonate (**4b**; $R^1 = R^2$ = Me).—$[Rh(PPh_3)_3Cl]$ (0.34 g, 3.72×10^{-4} mol) was suspended in a solution of diethyl dibut-2-enylmalonate (2 g, 7.46×10^{-3} mol) in absolute ethanol (100 ml). The mixture was

boiled under reflux for 24 h and, on work-up, gave a clear, colourless oil (1.89 g, 94%), b.p. 100—102 °C/0.3 mmHg (Found: C, 67.0; H, 9.1. $C_{15}H_{24}O_4$ requires C, 67.15; H, 9.0%); the 250 MHz n.m.r. spectrum of the product showed it to comprise a 79 : 9 : 18 mixture of *E*- and *Z*-(**6b**; $R^1 = R^2 = Me$) and (**7b**; $R^1 = R^2 = Me$).

Diethyl 1-ethyl-2-(*E*-ethylidene)cyclopentane-4,4-dicarboxylate (**6b**; $R^1 = R^2 = Me$): R_t (Carbowax 20M, 100 m, 180 °C) 34.85 min; δ(C_6D_6) 0.88 (3 H, t, *J* 7 Hz, $MeCH_2$), 0.97 (6 H, m, 2 × $MeCH_2$), 1.20 (1 H, m, $MeCH_2$), 1.57 (3 H, m, MeC=C), 1.67 (1 H, m, diastereotopic H of CH_2), 1.98 (1 H, ABX, J_{AB} 12 Hz, J_{AX} 10 Hz, diastereotopic H of $CHCH_2$), 2.61 (1 H, m, CH_2CHCH_2), 2.87 (1 H, ABX, J_{AB} 12 Hz, J_{AX} 7 Hz diastereotopic H of $CHCH_2$), 3.10 and 3.32 (2 × d, 2 × 1 H, *J* 17 Hz, diastereotopic H of CH_2C=C), 4.04 (4 H, m, 2 × $MeCH_2$), and 5.25 (1 H, m, C*H*=C); *m/z* 268 (M^+, 5%), 194 (26), 166 (13), 165 (14), 121 (65), 120 (12), 93 (37), 92 (11), 91 (22), 79 (16), 77 (19), 41 (17), 39 (11), 29 (100), and 27 (40).

Diethyl 1,2-diethylcyclopent-1-ene-4,4-dicarboxylate (**7b**; $R^1 = R^2 = Me$), R_t (Carbowax 20M, 100 m, 180 °C) 30 min; δ(C_6D_6) 3.28 (4 H, s, 2 × CH_2C=C), other signals obscured; *m/z* 268 (M^+, 7%), 194 (30), 165 (17), 121 (62), 120 (28), 93 (39), 91 (23), 79 (18), 77 (18), 41 (13), 29 (100), and 27 (38).

Diethyl 2-ethyl-1-(Z-ethylidene)cyclopentane-4,4-dicarboxylate (**6b**; $R^1 = R^2 = Me$): δ(C_6D_6) 5.35 (1 H, m, C*H*=C), other signals obscured.

Cyclisation of Diethyl Dibut-3-enylmalonate (**9**).—Dry hydrogen chloride was gently bubbled through a solution of [$Rh(PPh_3)_3Cl$] (0.17 g, 1.86 × 10^{-4} mol) and diethy dibut-3-enylmalonate (1.0 g, 3.73 × 10^{-3} mol) in ethanol (100 ml). The mixture was boiled under reflux for 24 h and then worked up. The product (0.95 g, 95%), b.p. 96—98 °C/0.4 mmHg was a clear colourless oil the n.m.r. spectrum of which showed it to consist of a similar mixture of isomers in the same ratio as obtained in the preceding experiment.

Catalytic Isomerisation of Diethyl Dibut-3-enylmalonate to Diethyl Dibut-2-enylmalonate (**4b**; $R^1 = R^2 = Me$).—Dry hydrogen chloride was gently bubbled through a solution of [$Rh(PPh_3)_3Cl$] (0.17 g, 1.86 × 10^{-4} mol) and diethyl dibut-3-enylmalonate (1.0 g, 3.73 × 10^{-3} mol) in degassed chloroform (100 ml) for 4 min. After boiling under reflux for 23 h, the mixture was worked up to give diethyl dibut-2-enylmalonate (0.96 g, 96%) as a clear, colourless oil, b.p. 92—95 °C/0.2 mmHg (Found: C, 67.05; H, 9.3. Calc. for $C_{15}H_{24}O_4$: C, 67.15; H, 9.0%); δ 1.24 (6 H, t, *J* 7 Hz, 2 × $MeCH_2$), 1.62 (6 H, m, 2 × MeCH=C), 2.55 (d, *J* 7 Hz, C=CHCH_2-*trans*), 2.63 (d, *J* 7 Hz, C=CHCH_2-*cis*), 4.16 (4 H, q, *J* 7 Hz, 2 × $MeCH_2$), 5.27 (1 H, m, vinyl-H), and 5.54 (1 H, m, vinyl-H); $\nu_{max.}$ (film) 2 965, 2 920, 1 725, 1 440, 1 360, 1 270, 1 200, 1 125, 1 040, 965, and 855 cm^{-1}; *m/z* 268 (M^+, 9%), 223 (18), 214 (13), 213 (77), 194 (14), 177 (15), 168 (11), 167 (100), 122 (20), 121 (53), 95 (23), 93 (18), 55 (34), 29 (22), and 28 (12).

Catalytic Isomerisation of Methylenecyclopentane (**6b**; $R^1 = R^2 = H$).—(a) Hydrogen chloride was bubbled through a solution of (**6b**; $R^1 = R^2 = H$) (0.5 g, 2.0 × 10^{-3} mol) and [$RhCl(PPh_3)_3$] (0.025 g, 2.7 × 10^{-5} mol) in chloroform (15 ml) for *ca.* 7 min. The mixture was heated under reflux for 18 h to give quantitative isomerisation to (**7b**; $R^1 = R^2 = H$). The spectral characteristics of the product were identical with those of a sample prepared directly from (**4b**; $R^1 = R^2 = H$) in ethanol as described above.

(b) The reaction was carried out as above but using ethanol (10 ml) as solvent. Isomerisation was complete in 3 h.

(c) The reaction was carried out as in (a) above but using deuterium chloride. The product formed, (**7b**; $R^1 = R^2 = H$), contained deuterium as detailed in the discussion.

(d) The reaction was carried out as in (a) above but using palladium acetate (0.025 g, 1 × 10^{-4} mol) as catalyst. Isomerisation to (**7b**; $R^1 = R^2 = H$) was complete in 8 h.

(e) Compound (**5b**; $R^1 = R^2 = H$) (0.5 g, 2.08 × 10^{-3} mol) was unchanged after being heated under reflux for 24 h with [$RhCl(PPh_3)_3$] (0.05 g, 5.25 × 10^{-5} mol) in chloroform (5 ml) after pre-treatment with hydrogen chloride.

Reaction of (**4a**; $R^1 = R^2 = H$) *with Potassium Tetrachloroplatinate*(II).—A two-phase mixture of (**4a**; $R^1 = R^2 = H$) (0.5 g, 2.78 × 10^{-3} mol) and an aqueous solution of K_2PtCl_4 (1.0 g, 1.24 × 10^{-3} mol) in water (5 ml) was stirred at room temperature. After 24 h a yellow precipitate began to form. After 3 days the precipitate was filtered off, washed well with water, and crystallised from chloroform as colourless needles (0.40 g, 72%), m.p. 178—182 °C (decomp.) (Found: C, 29.5; H, 3.5; Cl, 15.4. $C_{11}H_{16}Cl_2O_2Pt$ requires C, 29.6; H, 3.6; Cl, 15.9%); δ 1.87 (2 H, q, ABX, *J* 5 and 8.5 Hz,), 2.19 and 2.38 (6 H, 2 × s), 2.86 (2 H, q, ABX, *J* 4 and 8.5 Hz), 3.16 (2 H, m, $J_{H,H}$ 8.7 Hz, $J_{Pt,H}$ 27 Hz,), 4.32 (2 H, m, $J_{H,H}$ 4.5 Hz, $J_{Pt,H}$ 39.5 Hz), and 5.0 (2 H, m); $\nu_{max.}$ (CsI disc) 2 920, 2 850, 1 700, 1 610, 1 430, 1 360, 1 195, 1 180, 1 140, 1 040, 1 000, 920, 850, and 800 cm^{-1}; *m/z* 448, 446, 445, 440 (M^+, 1%), 180 (5), 171 (5), 138 (32), 123 (40), 97 (52), and 43 (100).

Crystal Data.—$C_{11}H_{16}Cl_2O_2Pt$, *M* = 446.2, Triclinic, *a* = 9.46(2), *b* = 11.08(2), *c* = 6.72(1) Å, α = 96.9(2), β = 88.5(2), γ = 110.1(2)°, *U* = 656.7 $Å^3$, D_c = 2.26 g cm^{-3}, D_m = 2.24 g cm^{-3}, *Z* = 2, *F*(000) = 420, space group $P\bar{1}$, Cu-K_α radiation, λ = 1.5418 Å, μ*R* = 0.9.

Structure Determination.—Crystals were clear, well-formed, elongated, pale yellow prisms. The lattice was characterised initially by oscillation and Weissenberg photographs. Diffraction intensities were measured on an Enraf-Nonius CAD3 automatic diffractometer. 2357 Independent reflections were scanned, of which 1801 with $I > 3\sigma(I)$ were used in the subsequent analysis after correction for Lorentz and polarisation, but no absorption, effects. The structure was solved by routine Patterson (Pt and Cl atoms) and difference Fourier methods. Least-squares refinement with allowance for anisotropic vibration for all (non-hydrogen) atoms produced convergence at a final $R = 0.101$. The weighting scheme used in the final stages of refinement was $\omega = (10 + |F_o| + 0.0002|F_o|^3)^{-1}$. Atomic scattering factors were taken from ref. 45 with inclusion of the real part ($\Delta f'$) of anomalous dispersion for Pt. Final atomic co-ordinates are given in Table 5 and selected bond lengths and angles in Table 6. A full listing of the crystallographic data is available as Supplementary Publication No. 23950 (21 pp.).

Acknowledgements

We thank the Queen's University and the Department of Education for Northern Ireland for support.

References

1 W. Brenner, P. Heimbach, H. Hey, E. W. Muller, and G. Wilke, *Liebigs Ann. Chem.*, 1969, **727**, 161; H. Breil, P. Heimbach, M. Kroner, H. Muller, and G. Wilke, *Makromol. Chem.*, 1963, **69**, 18; E. J. Corey and E. K. W. Wat, *J. Am. Chem. Soc.*, 1967, **89**, 2757; E. J. Corey, M. F. Semmelhack and L. S. Hegedus, *ibid.*, 1968, **90**, 2416, 2417; B. M. Trost and T. R. Verhoeven, *ibid.*, 1979, **101**, 1595.

2 A. Cowell and J. K. Stille, *Tetrahedron Lett.*, 1979, 133.

3 M. Mori, Y. Hashimoto and Y. Bau, *Tetrahedron Lett.*, 1980, 631.

4 B. M. Trost, *Pure Appl. Chem.*, 1981, **53**, 2357; B. M. Trost and T. A. Runge, *J. Am. Chem. Soc.*, 1981, **103**, 7559; J. Tsuji, *Pure Appl. Chem.*, 1981, **53**, 2371; 1982, **54**, 197.

5 R. Jira and W. Freiesleben in 'Organometallic Reactions,' ed. E. I. Becker and M. Tsutsui, Wiley Interscience, New York, 1972, vol. 3, p. 1.
6 R. F. Heck, 'Organotransition Metal Chemistry,' Academic Press, London, 1974.
7 A. Bright, J. F. Malone, J. K. Nicholson, J. Powell, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1971, 712.
8 B. Kongkathip, Ph.D. Thesis 1977, Queen's University, Belfast.
9 R. Grigg, B. Kongkathip, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1978, 333.
10 E. Schmitz, U. Hench, and D. Habisch, *J. Prakt. Chem.*, 1976, **318**, 471, also ref. 4.
11 R. Grigg, T. R. B. Mitchell, and A. Ramasubbu, *J. Chem. Soc., Chem. Commun.*, 1979, 669.
12 R. Grigg, T. R. B. Mitchell, and A. Ramasubbu, *J. Chem. Soc., Chem. Commun.*, 1980, 27.
13 N. L. Allinger and V. Zalkow, *J. Org. Chem.*, 1960, **25**, 701; B. Capon and S. P. McManus, 'Neighbouring Group Participation,' Plenum Press, 1976, vol. I; C. Galli, G. Giovannelli, G. Illuminati, and L. Mandolini, *J. Org. Chem.*, 1979, **44**, 1259.
14 H. G. Gunther, V. Jager, and P. S. Skell, *Tetrahedron Lett.*, 1977, 2539.
15 P. M. Maitlis, 'Organic Chemistry of Palladium,' Academic Press, London, vols. I and II, 1971.
16 J. Kiji, K. Masui, and J. Furukawa, *Tetrahedron Lett.*, 1971, **44**, 1956.
17 J. Kiji, K. Yammamoto, S. Mitani, S. Yoshikawa, and J. Furukawa, *Bull. Soc. Chem. Jpn.*, 1973, **46**, 1791.
18 S. J. McClain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, 1977, **99**, 3519.
19 J. Fellerman, G. A. Rupprecht, and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 5099 and references therein.
20 S. J. McClain, J. Sancho, and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 5451, and references therein.
21 D. M. Adams, J. Chatt, R. Guy, and N. Sheppard, *J. Chem. Soc.*, 1961, 738.
22 S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and F. Pilbrow, *J. Chem. Soc. A*, 1969, 1227.
23 P. W. Hall, R. Puddephatt, and C. F. H. Tipper, *J. Organometal. Chem.*, 1975, **84**, 407.
24 M. Ephritikhine, M. L. H. Green, and R. MacKenzie, *J. Chem. Soc., Chem. Commun.*, 1976, 619.
25 M. Ephritikhine and M. L. M. Green, *J. Chem. Soc., Chem. Commun.*, 1976, 926.
26 M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1966, 129.
27 G. G. Strathdee and R. M. Given, *J. Catal.*, 1973, **30**, 30.
28 R. Cramer, *J. Am. Chem. Soc.*, 1966, **88**, 2272.
29 R. Cramer and V. Lindsay, *J. Am. Chem. Soc.*, 1966, **88**, 3534.
30 E. Muller, *Synthesis*, 1974, 761; R. Grigg, R. Scott, and P. Stevenson, *Tetrahedron Lett.*, 1982, 2691 and unpublished observations.
31 H. Suzuki, K. Itoh, Y. Ishii, K. Simon, and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 8494; D. L. Thorn and R. Hoffmann, *Nouv. J. Chim.*, 1979, **3**, 39.
32 R. Cramer, *J. Am. Chem. Soc.*, 1965, **87**, 4717.
33 R. K. Bramley, R. Grigg, G. Guilford, and P. Milner, *Tetrahedron*, 1973, **29**, 4159.
34 G. Hata, K. Takahashi, and A. Miyake, *Chem. Ind. (London)*, 1969, 1836.
35 J. V. Braun and W. Schirmacher, *Chem. Ber.*, 1923, **56B**, 538.
36 A. W. Johnson, E. Markam, and R. Price, *Org. Synth.*, Coll. Vol. V, 1973, p. 785.
37 C. Wolff, *Annalen*, 1880, **201**, 45.
38 T. B. Johnson and A. J. Hill, *Am. Chem. J.*, 1911, **46**, 537.
39 W. E. Billups, W. E. Walker, and T. C. Shields, *J. Chem. Soc., Chem. Commun.*, 1971, 1067.
40 J. Tsuji, M. Hara, and Y. Mori, *Tetrahedron*, 1972, **28**, 3721.
41 N. O. Brace, *J. Org. Chem.*, 1971, **36**, 3187.
42 T. Cuvigny and N. Normant, *Bull. Soc. Chim. Fr.*, 1961, 2423.
43 R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1934, 1995.
44 W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, 1956, **78**, 2287.
45 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. III, 1962.

Received 14*th November* 1983; *Paper* 3/2022