Reactions and Properties of Some Trimethyleneplatinum(IV) Complexes. Part 11.[1] Platinacyclobutanes derived from Methylcyclopropane

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It is shown that platinacyclobutanes derived from methylcyclopropane exist as a mixture of isomers with partial structures $\overline{PtCH_2CHMeCH_2}$ and $\overline{PtCH_2CH_2CHMe}$, and that these isomers interconvert easily. In some cases decomposition of these platinacyclobutanes gives ylide complexes $[PtCl_2\{CH(L)CH_2CH_2Me\}L]$, *e.g.* L = 2-methylpyridine, while in other cases but-1-ene complexes $[PtCl_2(CH_2{=}CHCH_2Me)L]$, *e.g.* L = CD_3CN, are formed. In both cases the products are formed selectively from the least stable isomer of the platinacyclobutane. At higher temperatures or on photolysis, platinacyclobutane complexes such as $[PtCl_2(C_3H_5Me)$(1,10-phenanthroline)] decompose to give but-1-ene, 2-methylpropene, propene, and ethylene and the relative yields depend on the experimental conditions. Possible mechanisms are discussed.

THERE has been considerable interest in the chemistry of platinacyclobutanes recently, particularly since such complexes can act as models for metallacyclobutanes thought to be intermediates in many catalytic reactions.[2-6]

The most general synthetic route to platinacyclobutanes involves reaction of Zeise's dimer, $[\{PtCl(\mu\text{-}Cl)(C_2H_4)\}_2]$, with cyclopropane derivatives, C_3H_5R, to displace ethylene from platinum and give the oligomeric $[PtCl_2(C_3H_5R)]$.[7] The platinacyclobutane ring may have the structure $\overline{PtCH_2CHRCH_2}$, (1), or $\overline{PtCHRCH_2CH_2}$, (2). When R = phenyl, it has been shown that the initial cyclopropane ring-opening occurs primarily at the most substituted bond to give the partial structure (2), but isomerisation may then occur to give an equilibrium mixture of (2) with the thermodynamically more stable isomer (1).[8] The mechanism has been studied and the reaction shown to be general for arylcyclopropanes. Platinum(II) appears to act as an electrophile in these ring-opening reactions,[7,9] and many other electrophilic reagents [*e.g.* halogens, hydrogen halides, mercury(II)] also react with arylcyclopropanes and with alkylcyclopropanes at the most substituted bond. The electrophilic ring-opening reactions often occur through ionic intermediates such as $Hg^{II}CH_2CH_2CHR^+$ and, when the most substituted C–C bond of the cyclopropane is attacked, the carbonium ion is stabilised by the alkyl or aryl substituent R.[10] The transition state formed in ring-opening by platinum(II) is thought to be much less polar and this effect should not be so important in influencing the selectivity.[6,9] In all cases studied, platinacyclobutanes derived from alkylcyclopropanes have been found to have partial structure (1) [*e.g.* R = Et, n-C_3H_7, n-C_6H_{13}, CH_2Ph].[7,11] This could indicate that ring-opening of the cyclopropane C_3H_5R occurs at the least substituted bond to give (1) directly, but it is also possible that the initial reaction gives (2) which then rearranges rapidly and quantitatively to (1). Since, when R = aryl, the isomer (1) appears to be more stable than (2) at least partly due to greater steric hindrance in (2),[8] it seemed likely that isomer (2) might be most readily detected when R = alkyl for small alkyl groups and we were thus led to investigate platinacyclobutanes derived from methylcyclopropane.

In this paper it will be shown that, when R = Me, both partial structures (1) and (2) can be detected and evidence will be presented that these isomers interconvert readily. The isomerisation is important in understanding the general chemistry of the platinacyclobutanes, which may decompose to give ylide complexes, alkene complexes, or free methylcyclopropane and alkenes under different conditions. A preliminary account of some of this work has been published.[12]

RESULTS AND DISCUSSION

Synthesis of Platinacyclobutanes.—It has been reported that methylcyclopropane fails to react with Zeise's dimer in diethyl ether,[11] but we find that reaction occurs in the usual way [equation (1)] if the reaction is carried out in freshly distilled tetrahydrofuran with precautions to prevent escape of the volatile methylcyclopropane from the reaction flask.

$$\tfrac{1}{2}[\{PtCl_2(C_2H_4)\}_2] + Me\overline{CHCH_2CH_2} \longrightarrow \underset{(3)}{\tfrac{1}{n}[\{PtCl_2(C_3H_5Me)\}_n]} + C_2H_4 \quad (1)$$

As with similar derivatives, the product is a chloride-bridged oligomer which is very sparingly soluble in non-donor solvents and so is difficult to characterise structurally.

The analogous bromo-derivative was prepared by displacement of cyclopropane from $[\{\overline{PtBr_2(CH_2CH_2CH_2)}\}_n]$ by methylcyclopropane [equation (2)].

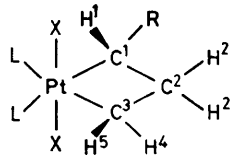
$$\tfrac{1}{n}[\{\overline{PtBr_2(CH_2CH_2CH_2)}\}_n] + Me\overline{CHCH_2CH_2} \longrightarrow \underset{(4)}{\tfrac{1}{n}[\{PtBr_2(C_3H_5Me)\}_n]} + \overline{CH_2CH_2CH_2} \quad (2)$$

The complexes were characterised by conversion to more soluble monomeric complexes with nitrogen-donor ligands [equation (3)] [(5a), X = Cl, L = C_5H_5N; (5b), X = Cl, L = 4-MeC_5H_4N; (5c), X = Cl, L = 3-MeC_5H_4N; (5d), X = Cl, L = ½(1,10-phenanthroline); (5e), X = Cl, L = ½(2,2′-bipyridyl); (5f), X = Br, L = C_5H_5N; (5g), X = Br, L = ½(1,10-phenanthroline)].

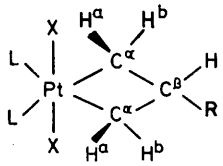
$$\frac{1}{n}[\{PtX_2(C_3H_5Me)\}_n] + 2L \longrightarrow [PtX_2(C_3H_5Me)L_2] \quad (3)$$
(5)

For the purposes of comparison, a similar complex $[PtCl_2(C_3H_5Bu)(C_5H_5N)_2]$, derived from butylcyclopropane, was prepared. We find that complexes (5) cannot be isolated with ligands 2-methylpyridine or methyl cyanide since decomposition occurs readily (see below) but the complexes can be identified in solution by their ^1H n.m.r. spectra.

Characterisation and Equilibrium Studies.—The above complexes (5) exist in solution as a mixture of isomers



(6)



(7)

(6) and (7) (R = Me, X = Cl or Br) as determined by studies of the ^1H and ^{13}C n.m.r. spectra, and the complex $[PtCl_2(C_3H_5Bu)(C_5H_5N)_2]$ probably exists as a similar mixture. Some ^1H n.m.r. data are given in Table 1, and ^{13}C n.m.r. data are given in Table 2. Since it has generally been claimed that alkylcyclopropanes give only isomer (7) [7,11] we discuss here the evidence for minor amounts of isomer (6). It has been shown elsewhere that for platinacyclobutanes having a methyl substituent on the α carbon $^3J(PtCH_3) = 20$—40 Hz, but when on the β carbon $^4J(PtCH_3) < 10$ Hz.[6,11] Figure 1(*a*) shows the resonances due to methyl groups in the ^1H n.m.r. spectrum of complex (5a). The major resonance is a doublet due to isomer (7) with $^4J(PtCH_3)$ 5 Hz, while the minor resonance with $^3J(PtCH_3)$ 22 Hz is assigned to isomer (6). This pattern is common to most of the platinacyclobutanes derived from methylcyclopropane, and Figure 1(*b*) shows the analogous part of the spectrum for complex (5f). Here the methyl resonance due to isomer (7) has anomalously high intensity at the centre of the doublet, where ^{195}Pt satellites of the main peaks overlap. This phenomenon has been observed to a lesser extent in some other derivatives and is not understood. The presence of isomer (6), R = Me, is clearly shown by the characteristic methyl resonance, but would be much more difficult to detect in complexes from other alkylcyclopropanes by ^1H n.m.r. spectroscopy. The use of ^{13}C n.m.r. spectroscopy to detect isomer (6) was therefore attempted. Figure 2(*a*) shows the ^{13}C-{^1H} n.m.r. spectrum for complex (5a), in the region of the carbon atoms directly bonded to platinum. The chief resonance with ^{195}Pt satellites is due to carbon atoms C^α of isomer (7) and the minor peaks are then due to carbons C^1 and C^3 of isomer (6). Due to the low relative concentration of isomer (6) the ^{195}Pt satellites could not be assigned with confidence, but the presence of CH and CH_2 groups for C^1 and C^3 was confirmed in the off-resonance decoupled spectrum which showed a doublet

TABLE 1

^1H N.m.r. data for complexes (6) and (7) [a]

Complex			Isomer (6)			Isomer (7)						
X	R	L	δ(R)	^3J(HH)	^3J(PtH)	δ(R)	^3J(HH)	^4J(PtH)	δ(H^a)	^2J(PtH)	δ(H^b)	^2J(PtH)	δ(H^c)
Cl	Me	C_5H_5N	0.84 (d)	8	22	1.30 (d)	6.5	5	3.02 (m) [b]	81	2.67 (m) [c]	79	3.08 (m)
Cl	Me	3-MeC_5H_4N	0.60 (d) [d]	6	22	1.15 (d) [d]	6	6	2.87 (m)	78	1.83 (m)	76	2.83 (m)
Cl	Me	4-MeC_5H_4N	0.68 (d) [e]	6	22	1.00 (d) [e]	7	7	2.69 (m)	79	2.06 (m)	83	2.72 (m)
Cl	Me	½phen	*f*			1.07 (d)	6	4	2.72 (m)	81	2.44 (m)	79	2.74 (m)
Cl	Me	CD_3CN	0.70 (d)	6	36	0.93 (d)	7.5	4	2.70 (m)	*f*	2.35 (m)	*f*	*f*
Cl	Me	C_4D_8O	0.46 (d)	7	45	0.85 (d)	7.5	8	2.78 (m) [b]	108	2.36 (m) [c]	109	2.82 (m)
Cl	Me	NH_3	*f*			0.95 (d) [g]	7	*f*					
Cl	Bu	C_5H_5N	*f*			*h*			2.73 (m)	82	2.42 (m)	80	2.70 (m)
Cl	CH_2Ph	C_5H_5N	*f*			*i*			3.15 (m)			84	
Br	Me	C_5H_5N	0.60 (d)	6.5	22	0.92 (d)	6	7.5	2.92 (m) [j]	87	2.64 [k]	81	2.7 (m)
Br	Me	CD_3CN	0.95 (d) [l]	6	*f*	0.78 (d)	6	6.5	*f*		*f*		*f*

[a] d = Doublet, m = multiplet; δ values in p.p.m., *J* in Hz. [b] $^2J(H^aH^b)$ 2 Hz, $^3J(H^aH^c)$ 8.5 Hz. [c] $^3J(H^bH^c)$ 8.5 Hz. [d] δ(3Mepy) 2.38 p.p.m. [e] δ(4Mepy) 2.37 p.p.m. [f] Not observed. [g] δ(NH_3) 2.3 p.p.m. [h] δ($MeCH_2CH_2CH_3$) 0.9 (t) p.p.m., δ$(CH_2)_3$ 1.3 (m) p.p.m. [i] δ(CH_2Ph) 3.22 (d) p.p.m., *J*(HH) 9 Hz. [j] $^3J(H^aH^c)$ 8.5 Hz, $^2J(H^aH^b)$ 4 Hz. [k] $^3J(H^bH^c)$ 6 Hz. [l] Tentative assignment.

TABLE 2

^{13}C N.m.r. data for complexes (6) and (7) [a]

Complex			Isomer (6)				Isomer (7)					
X	R	L	δ(R)	δ(C^1)	δ(C^2)	δ(C^3)	δ(R)	^3J(PtC)	δ(C$^\alpha$)	^1J(PtC$^\alpha$)	δ(C$^\beta$)	^2J(PtC$^\beta$)
Cl	Me	C_5H_5N	29.1	5.6	45.2	−8.0	29.1	54	1.0	344	42.6	98
Cl	Me	C_4D_8O	21.8	5.5	40.6	−12.8	21.8	74	−5.1	398	37.6	109
Cl	Bu	C_5H_5N	43.7 [b]	11.8 [b]	*c*	−7.9 [b]	37.5 [d]	49	−5.2	344	43.4	95

[a] δ Values in p.p.m., *J* in Hz. [b] Tentative assignment. [c] Not observed. [d] δ(C^1) for the $C^4H_3C^3H_2C^2H_2C^1H_2$ group; δ(C^2) 28.0 p.p.m., δ(C^3) 22.5 p.p.m., δ(C^4) 14.1 p.p.m.

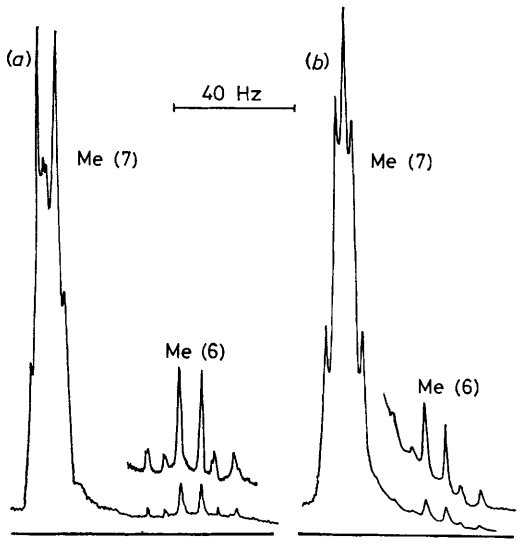


FIGURE 1 ^{1}H N.m.r. spectra (100 MHz) of complexes (*a*) (5a) and (*b*) (5f), showing only the resonances due to the methyl groups of isomers (6) and (7) in each case

and triplet respectively. The corresponding part of the ^{13}C-{^{1}H} n.m.r. spectrum for $[PtCl_2(C_3H_5Bu)(C_5H_5N)_2]$ is shown in Figure 2(*b*). Again small resonances assigned as due to carbon atoms C^1 and C^3 of the minor isomer (6), R = Bu, are seen. Certainly no peaks due to adventitious impurities are expected in this high-field part of the spectrum, and the remainder of the spectrum was very clean. Thus, although in this case isomer (6) could not be detected in the ^{1}H n.m.r. spectrum, it is almost certainly present in low abundance. It is reasonable to expect that isomer (6) was also present in low abundance

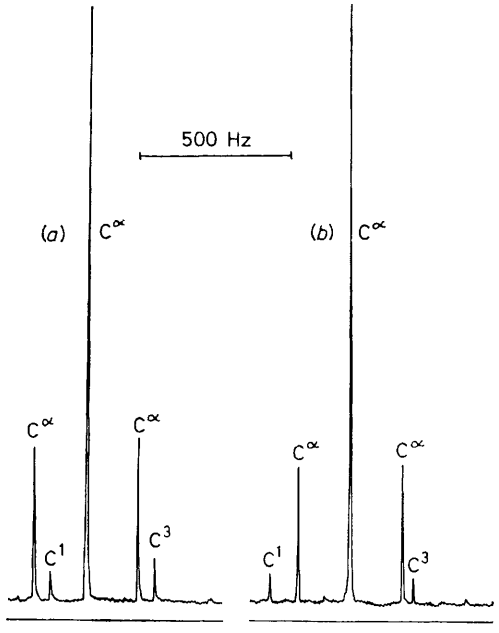


FIGURE 2 ^{13}C N.m.r. spectra (25.2 MHz) of complexes (*a*) (5a) and (*b*) $[PtCl_2(C_3H_5Bu)(C_5H_5N)_2]$, showing only the resonances due to the carbon atoms directly bonded to platinum of isomers (6) and (7) in each case

in platinacyclobutanes derived from other alkylcyclopropanes, but as it could not be detected by ^{1}H n.m.r. spectroscopy, it was assumed to be absent.

By integration of the ^{1}H n.m.r. spectra (100 MHz) it was possible to estimate relative abundances of isomers (6) and (7), R = Me, in the complexes (5). It was found that the ratio (7) : (6) varied with the nature of the ligand and, in the case of (5a), with the temperature, even when the complexes were prepared from the same sample of oligomer $[\{PtCl_2(C_3H_5Me)\}_n]$ with no purification step. These results can only be understood if there is an equilibrium between isomers (6) and (7), similar to that discovered for the complex $[PtCl_2(C_3H_5Ph)(C_5H_5N)_2]$.[8] In addition, the isomerisation must occur rapidly to explain the data given in Table 3.

TABLE 3

Equilibrium constants, K, for isomerisation of platinacyclobutanes $[PtCl_2(C_3H_5Me)L_2]$ between isomers (6) $\rightleftharpoons$ (7)

θ_c/°C	L = C_5H_5N [a]	L = C_4H_8O [b]	L = CD_3CN [c]
50	11.6 ± 0.2		*d*
37	13.2 ± 0.6	10.5 ± 0.6	8.0 ± 0.5
25	15.6 ± 0.5	10.5 ± 0.3	7.8 ± 0.5
15	18.5 ± 0.7		7.9 ± 0.6
10	18.8 ± 0.8	10.4 ± 0.5	7.5 ± 0.4
0	19.4 ± 0.7	9.2 ± 0.5	*e*
−10	19.3 ± 1.0	*e*	*e*

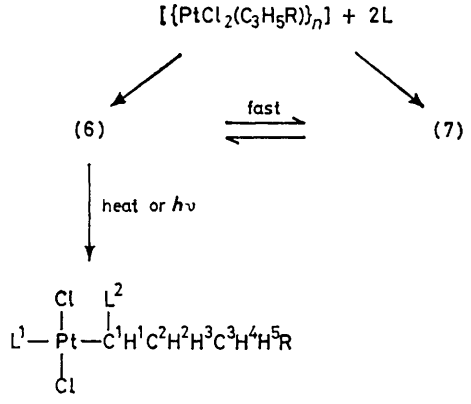
[a] Solvent $CDCl_3$. [b] Solvent C_4D_8O, $\Delta H^\ominus = 0$, $\Delta G_{298}^\ominus = -6$ kJ mol^{-1}, $\Delta S^\ominus = +20$ J K^{-1} mol^{-1}. [c] Solvent CD_3CN, $\Delta H^\ominus = 0$, $\Delta G_{298}^\ominus = -5$ kJ mol^{-1}, $\Delta S^\ominus = +17$ J K^{-1} mol^{-1}. [d] Decomposed. [e] Peaks broadened. The error bars represent the range for at least three measurements. Previous values measured at 60 MHz were inaccurate, probably due to some overlap of resonances at this frequency.

For complex (5a), a graph of ln$K$ *vs.* T^{-1} gives a straight line in the temperature range 15—50 °C and for the equilibrium (6) $\rightleftharpoons$ (7) gives $\Delta G_{298}^\ominus$ − 6.8 kJ mol^{-1}, $\Delta H^\ominus$ − 12 kJ mol^{-1}, $\Delta S_{298}^\ominus$ − 18 J K^{-1} mol^{-1}. At lower temperatures, poorer reproducibility of apparent equilibrium constants was obtained and it seems likely that the approach to equilibrium is slow and hence that integration of spectra does not give true equilibrium constants in the region −10 to 10 °C.

For the complex $[\{PtCl_2(C_3H_5Me)\}_n]$ dissolved in [$^2H_8$]tetrahydrofuran or [$^2H_3$]acetonitrile no significant temperature dependence was observed but equilibration must be possible since the ratios of (6) : (7) are significantly different. The magnitude of the equilibrium constants appears to reflect the bulk of the ligands since isomer (7), with the alkyl substituent further from the ligands, is favoured for L = C_5H_5N > C_4D_8O > CD_3CN. However, the solvents are different in each case and solvation effects could also influence the magnitude of K. The complex (5f) gives a value of K for the reaction of (6) $\rightleftharpoons$ (7) in $CDCl_3$ solution at 30 °C of 25 ± 8, and again it is likely that the greater bulk of the bromo-ligands over chloro-ligands leads to the larger value of K for (5f) over (5a). Complex (5d) with 1,10-phenanthroline (phen) as ligand did not contain any isomer (6) detectable by ^{1}H n.m.r. spectroscopy. We suggest that the major

isomer (7) crystallised preferentially and that, as expected for the chelate complex,[8] isomerisation (6) ⇌ (7) does not occur readily in this case.

Since it appears that an equilibrium mixture of isomers (6) and (7) is generally formed, it is clearly not possible to deduce the initial position of insertion into the cyclopropane ring. It has previously been assumed that the formation of isomer (7) indicates insertion into the least substituted C–C bond of the alkylcyclopropane, but our results show that insertion into the most substituted bond followed by rapid skeletal rearrangement to give an equilibrium mixture of (6) and (7) cannot be excluded.



(8a), L = C_5H_5N, R = Me
(8b), L = 2-MeC_5H_4N, R = Me
(8c), L = C_5H_5N, R = Bu
(8d), L = 2-MeC_5H_4N, R = Bu

SCHEME 1 The formation of ylide complexes from platinacyclobutanes

Decomposition of Platinacyclobutanes to Ylide Complexes.—An attempt to prepare a complex (5) with X = Cl and L = 2-methylpyridine, 2Me-py, by reaction (3) gave instead a deep yellow complex, identified as the ylide derivative *trans*-[$PtCl_2${CH(2Me-py)$CH_2CH_2CH_3$}-(2Me-py)]. The corresponding pyridine complex was subsequently prepared by the very slow thermal decomposition of complex (5a) at room temperature or, preferably, by photolysis of (5a), and analogous complexes derived from butylcyclopropane were also prepared. The complexes are considered to be formed according to Scheme 1. It can be seen that the ylides (8) are formed as only one isomer having an unbranched carbon chain and this is necessarily formed from the minor platinacyclobutane isomer (6). Further, the reaction occurs selectively by a hydrogen shift with apparent transfer of the H^4 or H^5 atom of isomer (6) from C^3 to C^1, followed by attack of ligand at C^3. Labelling studies on related complexes suggest that this is indeed what occurs, and a mechanism involving ligand loss from (6) followed by α elimination with transfer of H^4 or H^5 first to platinum and then to C^1 has been proposed.[13] The ylide is then formed by attack of L on the proposed carbene intermediate, [$PtCl_2(CHCH_2CH_2R)L$]. It is not clear why the reaction is so selective, but the facile isomerisation of (7) ⇌ (6) is clearly a key step in allowing the final products to be formed from the less stable platinacyclobutane isomer (6).

The rapid decomposition of the platinacyclobutanes (6) and (7) when L = 2-methylpyridine is clearly a result of steric effects due to the *ortho*-methyl group since similar platinacyclobutanes with L = 3- or 4-methylpyridine are thermally stable. Clearly, steric hindrance should promote the initial dissociation of ligand L and it is also possible that steric effects promote the α-elimination reaction. There is good evidence that steric effects promote α-elimination in alkyltantalum complexes.[14]

The structures of the ylide complexes were deduced from the ^1H n.m.r. spectra (Table 4) and, in one case, confirmed from the ^{13}C n.m.r. spectrum. A prominent feature in the ^1H n.m.r. spectra is the characteristic ylide hydrogen resonance [H^1, structure (8)] which appears as a triplet with satellites due to coupling with ^{195}Pt.[15] The methylene protons H^2, H^3 are non-equivalent and give rise to a complex multiplet in the ^1H n.m.r. spectrum, and the resonance due to H^3, H^4 is similarly complex. In the ^{13}C n.m.r. spectrum of (8b), the ylide carbon appears as a doublet in the off-resonance decoupled spectrum due to coupling with a single hydrogen [δ(Pt-*C*H) 37.8 p.p.m., J(PtC) 802 Hz]. The chemical shift and coupling constant $^1J(^{195}Pt^{13}C)$ are both consistent with the presence of a Pt^{II}–C σ bond in the complex and show that this carbon has no carbene character.[16] The remainder of the ^{13}C n.m.r. data also supports the assigned structure for (8b) [δ(C^2) 20.7 (t) p.p.m.; δ(C^3) 40.0 (t) p.p.m., $^3J(PtC^3)$ 27 Hz; (R = Me) 14.0 (qrt) p.p.m.; δ(2*Me*-py, L^1) 25.2 (qrt) p.p.m.; δ(2*Me*-py, L^2) 21.8 (qrt) p.p.m.; multiplicity due to ^1J(CH) coupling is given in parentheses].

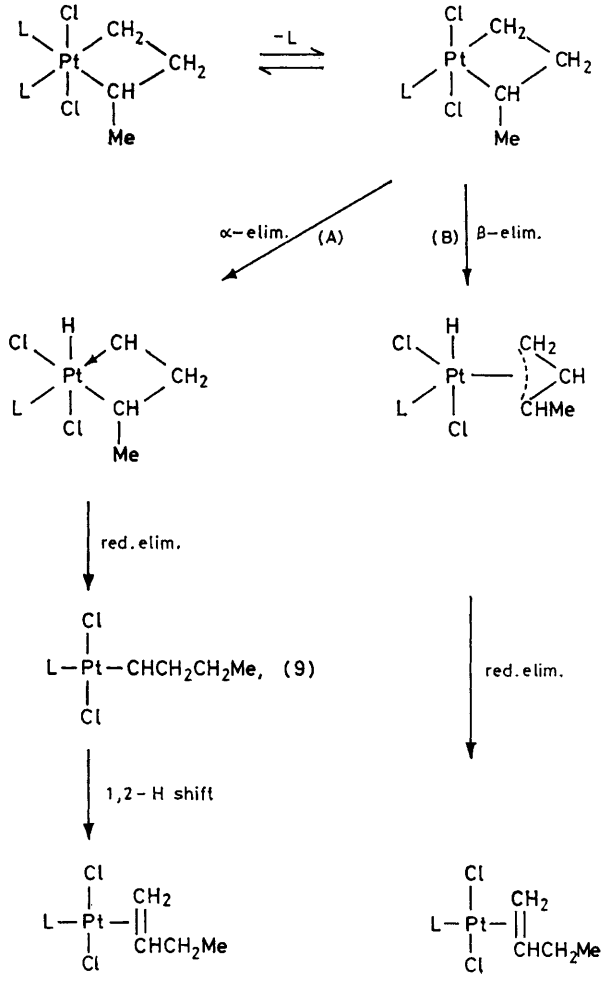
TABLE 4

^1H N.m.r. data for the ylide complexes (8a)—(8d) [a]

Complex	δ(H^1)/ p.p.m.	^2J(PtH^1)/ Hz	^3J($H^1H^{2,3}$)/ Hz	δ(H^2,H^3)/ p.p.m.	δ(H^4,H^5)/ p.p.m.	δ(R)/ p.p.m.
(8a)	5.84 (t)	112	7	2.42 (m)	1.67 (m)	0.96 (t) [b]
(8b) [c]	5.61 (t)	112	7	2.40 (m)	1.78 (m)	0.97 (t) [d]
(8c)	6.20 (t)	112	7	2.1 (m)	*e*	*f*
(8d) [g]	5.98 (t)	114	7	2.1 (m)	*e*	*f*

[a] s = Singlet, t = triplet, m = multiplet. [b] R = Me, J(HH) 7 Hz. [c] δ(2Mepy) 3.03 (s) p.p.m. (L^1), J(PtH) 5 Hz, 3.10 (s) p.p.m. (L^2). [d] R = Me, J(HH) 6 Hz. [e] Obscured. [f] R = Bu, δ(Me) 1.26 (t) p.p.m., δ(CH_2)$_3$ 1.72 (m) p.p.m. [g] δ(2*Me*py) 3.44 (s) p.p.m. (L^1), J(PtH) 4 Hz, 3.54 (s) p.p.m. (L^2).

Decomposition of Platinacyclobutanes to Alkene Complexes.—As discussed above, solutions of $[\{PtCl_2(C_3H_5Me)_n\}]$ in CD_3CN contain the complex $[PtCl_2(C_3H_5Me)(NCCD_3)_2]$ as a mixture of the isomers (6) and (7). These solutions decompose slowly at room temperature but within a few minutes at 50 °C to give *trans*-$[PtCl_2(CH_2{=}CHCH_2CH_3)(NCCD_3)]$, which can be isolated from the solution. The course of the reaction can readily be followed using ^1H n.m.r. or u.v. spectroscopy, and followed good first-order kinetics with $k_{obs.}$(25 °C) 2.62×10^{-4} s^{-1}. Decomposition of $[\{PtBr_2(C_3H_5Me)\}_n]$ in CD_3CN was fast and gave *trans*-$[PtBr_2(CH_2{=}CHCH_2CH_3)(NCCD_3)]$ within a few minutes at room temperature. Similar complexes were prepared using benzonitrile in place of $[^2H_3]$acetonitrile.



SCHEME 2 Possible mechanisms of formation of alkene complexes

It is noteworthy that the above reactions are highly selective, giving only the but-1-ene complex which is again necessarily formed from the minor platinacyclobutane isomer (6). The reactions could occur by either of the mechanisms shown in Scheme 2. The obvious mechanism is (B) involving an initial β-elimination step for which there is good precedent, for example in the formation of an alkene complex from $[PtCl_2(CH_2CMe_2CHMe)(C_5H_5N)_2]$.[17] However, the alternative mechanism (A) would give a carbene intermediate (9) and this would not be trapped as an ylide complex by the weak base L = acetonitrile or benzonitrile but would presumably undergo a 1,2-hydrogen shift to give the alkene complex. There is good precedent for this mechanism in the formation of alkene complex from $[PtCl_2(CH_2CMe_2CH_2)(2,6\text{-}Me_2C_5H_3N)_2]$,[13] and the initial intermediates would then be the same as those suggested in the formation of pyridine ylide complexes. Without detailed labelling studies it is not possible to distinguish between these mechanisms.

The but-1-ene complexes were characterised by elemental analysis and by the ^1H n.m.r. spectra. In some cases, the complexes were prepared independently from $[\{PtCl_2(CH_2{=}CHCH_2CH_3)\}_2]$ [*e.g.* equation (4)] and shown to be identical (n.m.r., m.p., mixed m.p.).

$$[Pt_2Cl_4(CH_2{=}CH_2)_2] \xrightarrow[-C_2H_4]{\text{but-1-ene}} [Pt_2Cl_4(CH_2{=}CHCH_2CH_3)_2] \xrightarrow{CD_3CN} \textit{trans}\text{-}[PtCl_2(CH_2{=}CHCH_2CH_3)(NCCD_3)] \quad (4)$$

In addition, treatment of the complexes with triphenylphosphine liberated pure but-1-ene (with no 2-methylpropene) which was identified by gas chromatography–mass spectrometry (g.c.–m.s.) by comparison with an authentic sample.

Thermal and Photochemical Decomposition to give Free Alkenes.—Thermal decomposition of the complexes (5a), (8a), or *trans*-$[PtCl_2(CH_2{=}CHCH_2CH_3)(C_5H_5N)]$ in chlorobenzene solution at 100 °C gave in each case only but-1-ene as the volatile product, and this observation is fully consistent with the mechanisms found under milder conditions and discussed above. Johnson and Hefty [18] have reported that flash pyrolysis of $[PtCl_2(C_3H_5Me)(thf)_2]$ in tetrahydrofuran (thf) solution at 130 °C gives 81% but-1-ene and 19% *cis*-but-2-ene, both of which must be formed from the minor platinacyclobutane isomer (6).

Thermal and photochemical decomposition of complexes with bidentate ligands have been studied in greater detail and results are given in Tables 5 and 6. We have shown elsewhere that decomposition of $[PtCl_2(CH_2CH_2CH_2)(N{-}N)]$, where N–N is 2,2′-bipyridyl (bipy) or phen, gives cyclopropane, propene, and ethylene as major products and that the relative yields are very strongly dependent on reaction conditions.[19–21] The platinum-containing product is always $[PtCl_2(N{-}N)]$, and the reactions are not complicated by intermediate formation of ylide complexes. In this case, it can confidently be predicted that the skeletal isomerisation (6) ⇌ (7) will be much slower with chelate complexes such as (5d) than with complexes having unidentate

TABLE 5

Products from the photolysis of complexes $[PtX_2(C_3H_5Me)(N{-}N)]$ [a]

Complex				Volatile products [c] (mol% of total)				
X	N–N [b]	Additive [b]	Solvent	C_2H_4	C_3H_6	C_3H_5Me	1-C_4H_8	iso-C_4H_8
Cl	phen		CH_3CN		9	59	12	20
Cl	phen	20 PPh_3	CH_3CN		6	68	16	10
Br	phen		CH_3CN	1	9	85	4	1
Cl	phen		dmso		5	61	9	25
Cl	bipy		dmso		9	53	12	26
Cl	phen	20 phen	dmso	5	4	86	3	2
Cl	bipy	20 bipy	dmso		5	80	7	8
Cl	phen	20 PPh_3	dmso		5	59	16	20
Cl	phen	20[$NHEt_3$]Cl	dmso		5	56	4	35
Cl	phen		1,2-$C_6H_4Cl_2$		14	36	30	20
Cl	phen	20 phen	1,2-$C_6H_4Cl_2$	2	17	58	7	16

[a] At 25 °C, photolysis time typically 2 h, concentration of platinum complex 6 × 10^{-3} mol dm^{-3}. [b] Number gives mols additive per mol complex. [c] C_3H_6 = propene, C_3H_5Me = methylcyclopropane, 1-C_4H_8 = but-1-ene, iso-C_4H_8 = 2-methylpropene. Traces (<1%) of *cis*-but-2-ene were observed in some cases.

TABLE 6

Products from thermolysis of complexes $[PtX_2(C_3H_5Me)(N{-}N)]$

					Volatile products (mol% of total) *					
X	N–N	Additive	θ_c/°C	t/h	C_2H_4	C_3H_6	C_3H_5Me	1-C_4H_8	iso-C_4H_8	Other
(*a*) Solvent *o*-$C_6H_4Cl_2$										
Cl	phen		20	28		5	30	10	55	
Cl	phen		100	2		10	55	20	15	
Cl	phen		150	1		1	17	80		CH_4
Cl	bipy		17	44	3	22	8	63	4	
Cl	bipy		100	2		5	65	25	5	
(*b*) Solvent CH_3CN										
Cl	phen		17	95		10	46	19	25	
Cl	phen	20 PPh_3	20	29	17	18	29	10	26	
Cl	phen	20 dppm	24	23	32	6	57	3	2	
Br	phen		20	170		5	64	31		
Br	phen	20 PPh_3	18	96	19	24	51	5	1	
Br	phen	20 dppm	20	20	16.5	7.5	73.5	1.5	1	
(*c*) Solvent dmso										
Cl	phen		20	18	1	5	17	72	5	
Cl	bipy		20	18		7.5	42.5	50		
Cl	phen	20 PPh_3	19	18	25	27.5	16.5	31		CH_3Cl
Cl	phen	20 PPh_3 + [$NHEt_3$]Cl	19	18	4.5	7.5	36	52		
Cl	phen	20 PPh_3	100	2			>99			
Cl	phen	20 dppm	25	18	14	5	65	4	12	CH_3Cl
Br	phen		20	170		5	64.5	23	7.5	
Br	phen		100	4			>95			
Br	phen	20 PPh_3	20	24	9.5	22.5	18	50		
				170	10	40.5	42.5	7		
Br	phen	10 dppm	20	24	2.5	6	40	8	6	
				170	5	6	70.6		10.5	

* *cis*-But-2-ene also detected, usually in a trace amount but sometimes up to 2%. dppm = Bis(diphenylphosphino)methane.

ligands such as (5a), since the ligand dissociation which precedes isomerisation will be very slow.[8]

Looking first at the photochemical decomposition reactions, the following trends are significant.

1. The relative yield of methylcyclopropane to alkenes is considerably higher than the corresponding cyclopropane to alkene ratio found for photolysis of $[PtCl_2(CH_2CH_2CH_2)(phen)]$.[20] The relative yield of methylcyclopropane to butenes was further increased if free bidentate ligand was present. These results may indicate that methylcyclopropane is formed directly from the photoexcited molecules but that formation of butenes is preceded by dissociation of the bidentate ligand.

2. The relative yields of volatile products are not greatly affected by the solvent polarity or by addition of tertiary phosphine or halide. Thus halide ionisation at an intermediate stage is considered unlikely in this case, although evidence has been presented for such a process in related systems.[20,21] The bromo-derivatives consistently gave higher yields of methylcyclopropane than did the chloro-derivatives on thermolysis or photolysis.

3. Both but-1-ene [presumably formed from isomer (6)] and 2-methylpropene [presumably formed from isomer (7)] are formed in significant quantities. The most reasonable explanation for this is that the rate of formation of butenes from the proposed intermediate $[PtCl_2(C_3H_5Me)]$ is competitive with the rate of skeletal isomerisation (6) ⇌ (7), and hence the high selectivity towards formation of but-1-ene observed in complexes with unidentate ligands is not observed.

4. Significant yields of products of C–C bond fission were observed, especially in the solvent 1,2-dichlorobenzene. Such fission in the isomer $\overline{PtCH_2CHMeCH_2}$ can give only propene but the isomer $\overline{PtCH_2CH_2CHMe}$ could give propene and ethylene. Propene was formed preferentially in almost every case. The yield of ethylene from the analogous reaction of $[\overline{PtCl_2(CH_2CH_2CH_2)}(phen)]$ was greatly increased in the presence of triphenylphosphine [21] but no such effect was observed in this case. Ephritikhine and Green [22] have shown that propene is the major product of photolysis of either of the complexes $[\overline{W(CH_2CH_2CHMe)}(\eta\text{-}C_5H_5)_2]$ or $[\overline{W(CH_2CHMeCH_2)}(\eta\text{-}C_5H_5)_2]$. It is therefore not possible to deduce whether the propene from complex (5d) is formed from isomer (6) or (7) or from either of these.

In general, the products of thermolysis of the platinacyclobutanes were similar to those of photolysis (Table 6), but the following differences or additional features may be noted.

1. The yield of but-1-ene compared to 2-methylpropene increased remarkably as the temperature increased for decomposition of (5d) in 1,2-dichlorobenzene. In the very slow decomposition at room temperature 2-methylpropene was the major volatile product but at 150 °C none of this was formed and the major product was but-1-ene.

2. In the polar solvents acetonitrile and dimethyl sulphoxide (dmso), addition of tertiary phosphine ligands did increase the relative yields of ethylene and propene with respect to C_4 hydrocarbons. In this sense, the thermal and photochemical reactions differ.

It is clear that the skeletal isomerisation (6) $\rightleftharpoons$ (7) must be invoked to explain many of the results shown in Tables 5 and 6, and the products are then probably formed by mechanisms which have been discussed in detail above and elsewhere.[19-21]

EXPERIMENTAL

General techniques have been described elsewhere.[8,9,19-21] Hydrogen-1 and ^{13}C n.m.r. spectra were recorded using a Varian XL100 spectrometer. The solvent for n.m.r. spectra was $CDCl_3$ except when L = CD_3CN or C_4D_8O when the solvent was CD_3CN or C_4D_8O respectively.

Methylcyclopropane was prepared by reaction of 1,3-dibromobutane with zinc powder in refluxing ethanol (85%), and was purified by passage through activated carbon and then acidified aqueous potassium permanganate solution. It was shown to be pure (free of butenes) by g.c. analysis, and was stored in a tube fitted with a Teflon stopcock. Samples were taken as required using conventional vacuum-line transfer techniques.

Synthesis of Platinacyclobutanes.—Dichloro(methylpropane-1,3-diyl)platinum(IV). Methylcyclopropane (2 cm³) was condensed into a flask containing $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$ (0.5 g) in freshly purified tetrahydrofuran (7 cm³) cooled in liquid nitrogen. The cold flask was fitted with a condenser cooled by acetone–solid CO_2 to prevent escape of methylcyclopropane, and the mixture was then warmed in a water bath at 45 °C for 9 h. The solvent was evaporated to give a grey-brown solid product, which was washed with diethyl ether and dried under vacuum (Found: C, 14.6; H, 2.5. Calc. for $C_4H_8Cl_2Pt$: C, 14.9; H, 2.5%).

Dibromo(methylpropane-1,3-diyl)platinum(IV). This was prepared similarly but $[\{\overline{PtBr_2(CH_2CH_2CH_2)}\}_4]$ was used as reagent and the reaction was carried out in a thick-walled Pyrex tube fitted with a Teflon stopcock to avoid loss of volatile methylcyclopropane (see also ref. 1).

Dichloro(methylpropane-1,3-diyl)bis(pyridine)platinum(IV). The above product (0.10 g) was suspended in CH_2Cl_2 (3 cm³) cooled to 0 °C and pyridine (3 drops) was added until the solution clarified. The volume of solvent was reduced in a stream of nitrogen, pentane (5 cm³) was added, and the mixture left in the refrigerator overnight. The pale yellow crystals of product were separated, washed with pentane, and dried under vacuum. Yield 0.14 g, m.p. 112 °C (decomp.) (Found: C, 34.9; H, 3.6; N, 5.7. Calc. for $C_{14}H_{18}Cl_2N_2Pt$: C, 35.0; H, 3.8; N, 5.8%).

Similarly, were prepared $[PtCl_2(C_3H_5Me)(4\text{-}MeC_5H_4N)_2]$, m.p. 157 °C (decomp.) (Found: C, 37.6; H, 4.2; N, 5.5. Calc. for $C_{16}H_{22}Cl_2N_2Pt$: C, 37.8; H, 4.3; N, 5.5%); $[PtCl_2(C_3H_5Me)(3\text{-}MeC_5H_4N)_2]$, m.p. 120 °C (decomp.) (Found: C, 37.4; H, 4.2; N, 5.4. Calc. for $C_{16}H_{22}Cl_2N_2Pt$: C, 37.8; H, 4.3; N, 5.5%); $[PtCl_2(C_3H_5Me)(phen)]$, m.p. 302 °C (decomp.) (Found: C, 38.1; H, 3.2; N, 5.7. Calc. for $C_{16}H_{16}Cl_2N_2Pt$: C, 38.2; H, 3.2; N, 5.5%).

(Butylpropane-1,3-diyl)dichloroplatinum(IV). This was prepared by reaction of n-butylcyclopropane (1.2 g) with $[\{PtCl(\mu\text{-}Cl)(C_2H_4)\}_2]$ (0.5 g) in tetrahydrofuran (5 cm³) at 38 °C for 10 h. The solvent was evaporated to give the yellow product, which was washed with pentane and dried under vacuum.

(2-Butylpropane-1,3-diyl)dichlorobis(pyridine)platinum(IV). The above product (0.10 g) was suspended in CH_2Cl_2 (3 cm³) and pyridine (4 drops) added until the solution clarified. The solvent was pumped off to give a yellow oil, which then gave yellow crystals from $CHCl_3$–pentane, m.p. 132 °C (decomp.) (Found: C, 38.8; H, 4.3; N, 5.5. Calc. for $C_{17}H_{24}Cl_2N_2Pt$: C, 39.1; H, 4.6; N, 5.4%).

Synthesis of Ylide Complexes.—trans-$[PtCl_2\{CH(C_5H_5N)CH_2CH_2CH_3\}(C_5H_5N)]$. A solution of the complex $[\overline{PtCl_2(CH_2CHMeCH_2)}(C_5H_5N)_2]$ (0.04 g) in $CDCl_3$ (0.5 cm³) in a Pyrex n.m.r. tube was irradiated with light from a fluorescent tube. After 10 d the n.m.r. spectrum indicated that reaction was complete. The solution was evaporated to give the yellow *product*, which was recrystallised from $CHCl_3$–pentane, m.p. 80 °C (Found: C, 35.0; H, 3.8; N, 5.8. Calc. for $C_{14}H_{18}Cl_2N_2Pt$: C, 35.1; H, 3.8; N, 5.9%).

trans-$[PtCl_2\{CH(2\text{-}MeC_5H_4N)CH_2CH_2CH_3\}(2\text{-}MeC_5H_4N)]$. A suspension of $[\{\overline{PtCl_2(CH_2CHMeCH_2)}\}_4]$ (0.04 g) in CH_2Cl_2 (2 cm³) was treated with 2-methylpyridine (3 drops) until a clear yellow solution was obtained. Pentane (10 cm³) was added and the mixture was allowed to stand in the refrigerator overnight. The yellow crystalline *product* was filtered off, washed with pentane, and dried under vacuum, m.p. 40 °C (Found: C, 37.4; H, 4.1; N, 5.3. Calc. for $C_{16}H_{22}Cl_2N_2Pt$: C, 37.8; H, 4.3; N, 4.7%). Similarly, was prepared *trans*-$[PtCl_2\{CH(2\text{-}MeC_5H_4N)(CH_2)_5Me\}(2\text{-}MeC_5H_4N)]$ from $[\{\overline{PtCl_2(CH_2CHBuCH_2)}\}_4]$, m.p. 48 °C (Found: C, 41.1; H, 6.0; N, 5.0. Calc. for $C_{19}H_{28}Cl_2N_2Pt$: C, 41.4; H, 5.1; N, 5.0%).

Synthesis of Alkene Complexes.—*trans*-[$PtCl_2(CH_2$=$CHCH_2CH_3)(NCCD_3)$]. (*i*) A solution of the complex [{$PtCl_2(CH_2CHMeCH_2)$}$_4$] (0.05 g) in CD_3CN (0.6 cm^3) was allowed to stand at room temperature. After 5 h the n.m.r. spectrum indicated that reaction was complete, and the solvent was evaporated to yield the *product*, m.p. 70 °C. The ^1H n.m.r. spectrum was identical with that of an authentic specimen prepared in (*ii*) below.

(*ii*) A solution of [{$PtCl(\mu$-$Cl)(C_2H_4)$}$_2$] (0.10 g) and but-1-ene (1 cm^3) in dry tetrahydrofuran (5 cm^3) was warmed at 45 °C for 7 h. The solvent was evaporated and CD_3CN (0.5 cm^3) was added to the residue. The *product* was precipitated by addition of n-pentane. Yield 0.08 g, m.p. 69—70 °C (Found: C, 20.1; H, 3.6; N, 3.9. Calc. for $C_6H_8Cl_2D_3NPt$: C, 19.6; H + D, 3.8; N, 3.8%).

Similarly, were prepared *trans*-[$PtCl_2(CH_2$=$CHCH_2CH_3)$-(C_5H_5N)], m.p. 78—80 °C, and *trans*-[$PtCl_2(CH_2$=$CHCH_2$-$CH_3)(NCPh)$], m.p. 90 °C (decomp.).

trans-[$PtCl_2(CH_2$=$CHCH_2CH_3)(NCPh)$]. To a suspension of [{$PtCl_2(CH_2CHMeCH_2)$}$_4$] (0.04 g) in $CHCl_3$ (1 cm^3) was added benzonitrile (5 drops). A clear yellow solution was obtained. The *product* was precipitated by addition of pentane (10 cm^3), filtered off, and dried under vacuum, m.p. 90 °C (decomp.) (Found: C, 28.8; H, 2.1; N, 3.2. Calc. for $C_{11}H_{13}Cl_2NPt$: C, 31.0; H, 3.0; N, 3.3%).

One of us, R. J. P., thanks NSERC (Canada) for financial support, and D. C. L. P. and M. C. R. thank the S. R. C. (Great Britain) for support. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support. We thank Johnson Matthey Ltd. for the generous loan of platinum.

[0/1815 *Received*, 24*th November*, 1980]

REFERENCES

[1] Part 10, G. E. Riley, C. F. H. Tipper, and R. J. Puddephatt, *J. Organomet. Chem.*, in the press.
[2] For a review, see R. J. Puddephatt, *Coord. Chem. Rev.*, 1980, **33**, 149.
[3] K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 1978, 604.
[4] C. O'Donohue, J. K. A. Clarke, and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1*, 1980, 345.
[5] G. W. Parshall, T. Herskovitz, F. N. Tebbe, A. D. English, and J. V. Zeile, 'Fundamental Research in Homogeneous Catalysis,' ed. M. Tsutsui, Plenum, New York, 1979, vol. 3.
[6] R. J. Al-Essa, R. J. Puddephatt, P. J. Thompson, and C. F. H. Tipper, *J. Am. Chem. Soc.*, 1980, **102**, 7546.
[7] F. J. McQuillen and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 1972, 2123; G. W. Littlecott, F. J. McQuillin, and K. G. Powell, *Inorg. Synth.*, 1976, **16**, 113.
[8] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Am. Chem. Soc.*, 1979, **101**, 364.
[9] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organomet. Chem.*, 1978, **150**, 295.
[10] R. J. Ouellette, R. D. Robins, and A. Smith, *J. Am. Chem. Soc.*, 1968, **90**, 1619.
[11] B. M. Cushman, S. E. Earnest, and D. B. Brown, *J. Organomet. Chem.*, 1978, **159**, 431.
[12] R. J. Al-Essa, R. J. Puddephatt, C. F. H. Tipper, and P. J. Thompson, *J. Organomet. Chem.*, 1978, **157**, C40.
[13] R. J. Al-Essa and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1980, 45.
[14] R. R. Schrock and J. D. Fellman, *J. Am. Chem. Soc.*, 1978, **100**, 3359.
[15] R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organomet. Chem.*, 1971, **33**, 247; M. Keeton, R. Mason, and D. R. Russell, *ibid.*, 1971, **33**, 259.
[16] B. E. Mann, *Adv. Organomet. Chem.*, 1974, **12**, 135.
[17] B. M. Cushman and D. B. Brown, *J. Organomet. Chem.*, 1978, **152**, C42; T. H. Johnson and S.-S. Cheng, *J. Am. Chem. Soc.*, 1979, **101**, 5277.
[18] T. H. Johnson and E. C. Hefty, *J. Org. Chem.*, 1979, **44**, 4896.
[19] F. Iwanciw, M. A. Quyser, R. J. Puddephatt, and C. F. H. Tipper, *J. Organomet. Chem.*, 1976, **113**, 91.
[20] D. C. L. Perkins, R. J. Puddephatt, and C. F. H. Tipper, *J. Organomet. Chem.*, 1980, **186**, 419.
[21] D. C. L. Perkins, R. J. Puddephatt, M. C. Rendle, and C. F. H. Tipper, *J. Organomet. Chem.*, 1980, **195**, 105.
[22] M. Ephritikhine and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1976, 926.