Reactivity and Mechanism in the Reactions of Platinacyclobutanes To Give Alkene or Ylide Complexes: Evidence for α-Elimination

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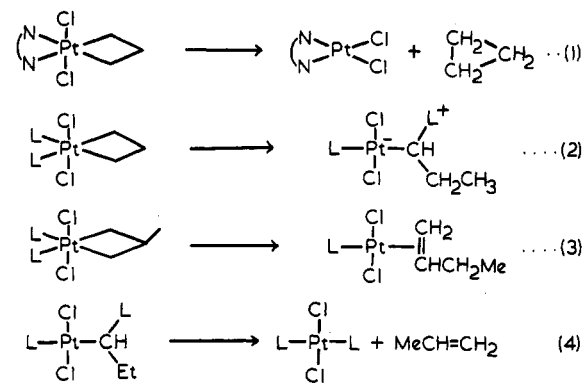
Platinacyclobutanes of formula $\{PtCl_2(CHR^1CR^2R^3CH_2)\}_n$ are decomposed on treatment with bulky pyridine derivatives, L; the rates follow the pyridine derivative sequence 2,6-dimethylpyridine > 2-methylpyridine > pyridine. The products of such reactions are the ylide complexes *trans*-$[PtCl_2\{CH(L)CHR^1CHR^2R^3\}L]$, when R^1 is H, L is 2-methylpyridine, and R^2 and R^3 are H and Ph, H and 4-MeC_6H_4, or Me and Me, or the alkene complexes *trans*-$[PtCl_2\{CH_2{=}C(R^1)CHR^2R^3\}L]$, when R^1 is Me, R^2 and R^3 are Me and Me or H and Me, and L is 2-methylpyridine. The ligands 2,6-dimethylpyridine or CD_3CN always gave the alkene complexes. The reactions typically involve skeletal isomerization of the platinacyclobutane $PtCHR^1CR^2R^3CH_2 \rightleftharpoons PtCR^2R^3CHR^1CH_2$ at a rate much faster than the decomposition to alkene or ylide complexes. Labeling studies have shown that the ylide complexes are formed by a 1,3-H shift, for example, $PtCl_2(CH_2CD_2CHPh)L_2 \rightarrow PtCl_2CH(L)CD_2CH_2Ph$, and it is suggested that the reaction involves (i) loss of a ligand L, (ii) α-elimination from the CH_2 group, (iii) reductive elimination to give the carbene derivative, $PtCl_2(=CHCD_2CH_2Ph)L$, and (iv) trapping of the carbene by free L to give the ylide derivative. An alternative mechanism involving initial β-elimination is disproved. Labeling studies show that the same initial step is followed in the formation of alkene complexes, and the intermediacy of the same carbene species is proposed, e.g., $PtCl_2(CD_2CHMeCHMe)L_2 \rightarrow PtCl_2(=CDCHMeCHDMe)L \rightarrow PtCl_2(CHD{=}CMeCHDMe)L$. In some cases, low-temperature NMR studies have shown that ylide complexes are formed and then react further to give alkene complexes. The selectivity for formation of ylide or alkene complexes results from steric hindrance to formation of ylides with the very bulky base 2,6-dimethylpyridine or, when the β-carbon is secondary, with all pyridine bases. The ligand CD_3CN is not a strong enough base to give an ylide derivative and so it always gives alkene complexes. The reactions are relevant to several catalytic reactions involving metallacyclobutane intermediates.

Introduction

Metallacyclobutane complexes may be involved as intermediates in such diverse catalytic processes as alkene metathesis and polymerization, cracking and isomerization of alkanes, and rearrangements of strained-ring compounds.[1-5] It is therefore of considerable importance to understand the factors that govern the formation, stability, and reactions of metallacyclobutanes. Platinacyclobutanes were the first such compounds to be prepared, and their chemistry has been studied in-depth.[1,6] The platinum(IV) derivatives may decompose by reductive elimination of cyclopropane (eq 1, NN = 2,2′-bipyridine), by rearrangement to ylide complexes (eq 2, L = pyridine), or, with ligand dissociation, to alkene complexes (eq 3, L = CD_3CN).[1-16] Both the ylide and alkene complexes can then give free alkenes (eq 4, L = pyridine).[12]



This paper is concerned with the factors that influence whether platinacyclobutanes will give ylide or alkene complexes on decomposition and with the detailed mechanism of the reactions. Preliminary accounts of parts of this work have been published,[15-17] and there is much relevant work by others which is summarized below.

The reaction to form an ylide complex (eq 2) was studied by Gillard and Pilbrow.[11] They showed that the reaction was retarded by added pyridine, and the observed rate law indicated that a five-coordinate intermediate $PtCl_2$-

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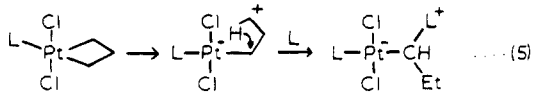
Table I. Products Formed from Platinacyclobutanes[a]

platinacyclobutane	ligand, L	product
$PtCl_2(CH_2CHMeCH_2)$[b]	C_5H_5N	$PtCl_2(CH_2CHMeCH_2)L_2$[b,c]
$PtCl_2(CHMeCH_2CH_2)$[b]		$PtCl_2(CHMeCH_2CH_2)L_2$[b,c]
	2-MeC_5H_4N	*trans*-$[PtCl_2\{CH(L)CH_2CH_2Me\}L]$
	MeCN	*trans*-$[PtCl_2(CH_2{=}CHCH_2Me)L]$
$PtCl_2(CH_2CHBuCH_2)$[b]	2-MeC_5H_4N	*trans*-$[PtCl_2\{CH(L)CH_2CH_2Bu\}L]$
$PtCl_2(CH_2CMe_2CH_2)$	C_5H_5N	$PtCl_2(CH_2CMe_2CH_2)L_2$
	2-MeC_5H_4N	*trans*-$[PtCl_2\{CH(L)CH_2CHMe_2\}L]$
	2,6-$Me_2C_5H_3N$	*trans*-$[PtCl_2\{CH_2{=}CHCHMe_2\}L]$
	MeCN	*trans*-$[PtCl_2\{CH_2{=}CHCHMe_2\}L]$
$PtCl_2(CHPhCH_2CH_2)$	2-MeC_5H_4N	*trans*-$[PtCl_2\{CH(L)CH_2CH_2Ph\}L]$
$PtCl_2\{CH(4\text{-}MeC_6H_4)CH_2CH_2\}$	2-MeC_5H_4N	*trans*-$[PtCl_2\{CH(L)CH_2CH_2C_6H_4Me\}L]$
$PtCl_2(CHMeCHMeCH_2)$	2-MeC_5H_4N	*trans*-$[PtCl_2(CH_2{=}CMeEt)L]$
	MeCN	*trans*-$[PtCl_2(CH_2{=}CMeEt)L]$
$PtCl_2(CHMeCMe_2CH_2)$	C_5H_5N	*trans*-$[PtCl_2(CH_2{=}CMe\text{-}i\text{-}Pr)L]$[d]
	2-MeC_5H_4N	*trans*-$[PtCl_2(CH_2{=}CMe\text{-}i\text{-}Pr)L]$

[a] Isolated products only. Other intermediates could often be detected at low temperatures or on thermolysis or photolysis (see text). [b] Isomeric mixture; ref 12. [c] Photolysis of this mixture gave *trans*-$[PtCl_2\{CH(L)CH_2CH_2Me\}L]$, and then, in the presence of oxygen, $[PtCl_2L_2]$ and PrCHO. [d] Reference 10.

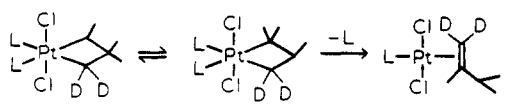
$(CH_2CH_2CH_2)$py was formed. This was suggested to rearrange according to eq 5 (L = pyridine.



(5)

The nature of the hydride shift (eq 5) is inconsistent with data obtained later,[1] but the work was important in demonstrating that pyridine dissociation was involved and that the five-coordinate intermediate rearranged in a unimolecular step (eq 5). The ylide complex decomposed to some extent to give propene and *trans*-$[PtCl_2(py)_2]$ under the reaction conditions of 50–80 °C and in benzene solvent (eq 4).

Decomposition of platinacyclobutanes to alkene complexes was later shown to occur (eq 3, L = CD_3CN; eq 6, L = pyridine) and often involved skeletal rearrangement of the platinacyclobutane.[9,10,12-18]



(6)

The labeling study of eq 6 appeared to demonstrate a β-elimination mechanism for the reaction,[13,14] and it was suggested that the formation of ylide complexes also involved intial β-elimination.[14] However, our own preliminary studies had indicated an α-elimination mechanism for ylide formation,[15] and so, in order to resolve this mechanistic problem, a detailed study was carried out on reactions of platinacyclobutanes to give ylide and alkene complexes.

Results and Discussion

Soluble platinacyclobutanes $PtCl_2(CH_2CH_2CH_2)L_2$ are usually prepared by reaction of the chloride-bridged oligomeric species $\{PtCl_2(CH_2CH_2CH_2)\}_n$ with a nitrogen-donor ligand, L, such as pyridine.[1,19,20] A simple discovery, which made mechanistic studies much easier, was that bulkier ligands such as 2-methylpyridine and 2,6-dimethylpyridine or the weak ligand acetonitrile did not give stable platinacyclobutanes but that decomposition to ylide or alkene complexes occurred at room temperature or below. Some complexes which could be isolated in pure form from such reactions are shown in Table I. The yields were high although, in some cases, the complex $PtCl_2L_2$ and free alkene or cyclopropane were also formed.[10,11]

Two interesting results were obtained from these preliminary studies. Firstly, the products observed depended on the nature of the ligand used. Thus, 2-methylpyridine gave ylide complexes in most cases but the bulkier 2,6-dimethylpyridine or the weaker base acetonitrile always gave alkene complexes. There was also some dependence on the platinacyclobutane used. For example, reaction of 2-methylpyridine, L, with $PtCl_2(CH_2CMe_2CH_2)$ gave the ylide *trans*-$[PtCl_2(CHLCH_2CHMe_2)L]$ but with $PtCl_2(CH_2CHMeCHMe)$ it gave the alkene complex $PtCl_2(CH_2{=}CMeEt)L$. Secondly, the carbon skeleton in the products often differed from that in the platinacyclobutane precursors. This was most dramatically seen in reactions of $PtCl_2(CH_2CMe_2CH_2)$, which has the neopentane skeleton, to give ylide or alkene complexes, *trans*-$[PtCl_2(CHLCH_2CHMe_2)L]$ or *trans*-$[PtCl_2(CH_2{=}CHCHMe_2)L]$, respectively, each of which has the isopentane carbon skeleton. This skeletal isomerization resembles that in platinum-catalyzed isomerization of neopentane to isopentane and related reactions which are important in the re-forming of hydrocarbons.[1,3,21]

The products were characterized by ^1H NMR spectrometry and in some cases by ^{13}C NMR spectrometry. Details are given in the Experimental Section and, because spectra of similar compounds have been discussed,[11-18] they will not be described individually. In the ^1H NMR spectra of the ylide complexes *trans*-$[PtCl_2(C^1H^1LC^2H_2C^3HRR^1)L]$, the resonance for H^1 appeared as a triplet in the region δ 5.6–6.2 ppm, with $^3J(HH) \sim 7$ Hz and with satellites due to coupling to ^{195}Pt with $^2J(PtH) = 108–118$ Hz. Since carbon atom C^1 is chiral, the C^2H_2 protons gave two resonances and, when R and R^1 are Me, two methyl resonances were observed. The alkene complexes were characterized initially by ^1H and ^{13}C NMR spectrometry and confirmation was obtained by independent synthesis. Thus reaction of Zeise's dimer $Pt_2Cl_4(C_2H_4)_2$ with the required alkene, $CH_2{=}CRR^1$, followed by addition of the ligand L gave the products *trans*-$[PtCl_2(CH_2{=}CRR^1)L]$ in high yields. In addition, treatment of the alkene complexes with triphenylphosphine

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gave the free alkene, which could be characterized readily by NMR.

The platinacyclobutanes $PtCl_2(CH_2CMe_2CH_2)py_2$ and $PtCl_2(CH_2CHPhCH_2)py_2$ were stable at room temperature but the ylide complexes *trans*-$[PtCl_2(CH(py)CH_2CHMe_2)py]$ and $PtCl_2(CH(py)CH_2CH_2Ph)py$ could be prepared from them by photolysis or thermolysis. For the photochemical synthesis it was important to exclude air since extended photolysis of the ylide products in the presence of oxygen gave $PtCl_2(py)_2$ and Me_2CHCH_2CHO or $PhCH_2CH_2CHO$.

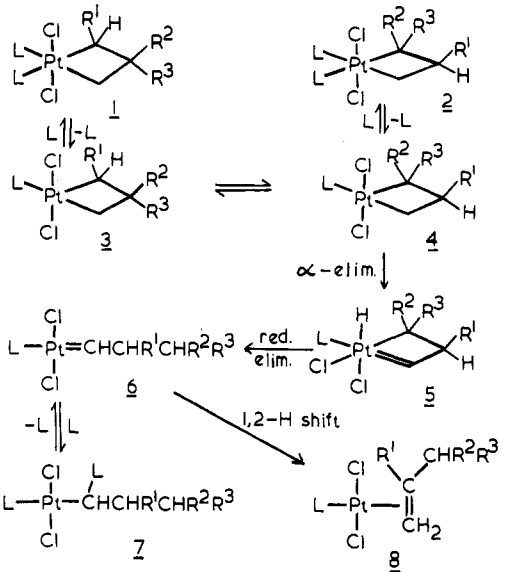
Low-Temperature NMR Studies. Reaction of the platinacyclobutane $\{PtCl_2(CHPhCH_2CH_2)\}_n$ with 2-Me(py), L, at −50 °C gave $PtCl_2(CHPhCH_2CH_2)L_2$. This isomerized quantitatively to $PtCl_2(CH_2CHPhCH_2)L_2$ below 0 °C. The similar isomerization with L representing py occurs much more slowly and leads to an equilibrium mixture of the skeletal isomers.[22] Decomposition to the ylide complex *trans*-$[PtCl_2(CHLCH_2CH_2Ph)L]$ (L = 2-methylpyridine) occurred at ~10 °C, whereas the corresponding transformation with L representing pyridine occurred at ~60 °C. It is therefore clear that both the skeletal isomerization of the platinacyclobutane and the decomposition to the ylide complex are greatly accelerated by the bulkier ligand. Since the skeletal isomerization is shown to be the faster reaction, it is not surprising that the ylide is formed from the less stable, more sterically hindered, isomer.

In a similar way, reaction of $\{PtCl_2(CH_2CMe_2CH_2)\}_n$ with 2-methylpyridine, L, gave $PtCl_2(CH_2CMe_2CH_2)L_2$ at −50 °C and this decomposed at ~10 °C to give the ylide *trans*-$[PtCl_2(CHLCH_2CHMe_2)L]$. This must be formed from the less stable platinacyclobutane $PtCl_2(CH_2CH_2CMe_2)L_2$ although this complex was not present in sufficient abundance to be detected by NMR. With 2,6-dimethylpyridine, L, the complex $PtCl_2(CH_2CMe_2CH_2)L_2$ was observed at −50 °C and, when the mixture was warmed to −30 °C, characteristic signals due to the ylide complex *trans*-$[PtCl_2(CHLCH_2CHMe_2)L]$ were observed. At −20 °C, the signals due to the ylide complex had largely decayed and those due to the alkene complex had grown, and at 0 °C no ylide complex remained.

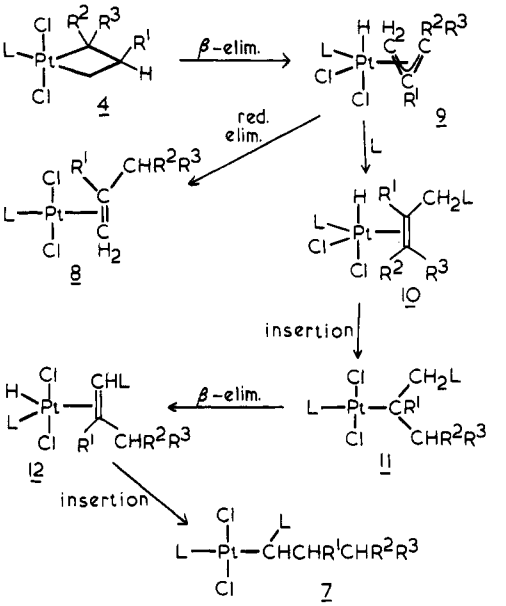
No ylide intermediates were detected in reactions with the ligand CD_3CN and none were detected in reactions of the platinacyclobutanes $\{PtCl_2(CH_2CHMeCHMe)\}_n$ and $\{PtCl_2(CH_2CMe_2CHMe)\}_n$ with pyridine or 2-methylpyridine. The complexes $PtCl_2(CH_2CHMeCHMe)L_2$ and $PtCl_2(CH_2CMe_2CHMe)L_2$ appeared to give the product alkene complexes (Table I) directly.

Possible Mechanisms of Reaction. On the basis of the selectivity of reaction (Table I) and the observation of intermediates in the low-temperature NMR experiments, the mechanism of Scheme I was hypothesized.[15] Both the skeletal isomerization 1 ⇌ 2 and the decomposition to the ylide 7 are thought to involve a five-coordinate platinacyclobutane 4.[1] The ylide 7 is formed after α-elimination/reductive elimination which gives the carbene complex 6. Complex 6 can then be trapped as the ylide, 7, or it may rearrange to the alkene complex 8. It is suggested that the ylide 7 can decompose by re-forming 6, which can then give 8, thus accounting for the observation of intermediate ylide complexes in some cases (e.g., when R^1 = H, R^2 = R^3 = Me, L = 2,6-dimethylpyridine). There were precedents for α-elimination only in tantalum and tungsten compounds, though recent evidence for α-elimination in iridium compounds has been obtained.[23-25]

Scheme I. The α-Elimination Mechanism



Scheme II. The β-Elimination Mechanism



The mechanism of Scheme I was challenged by Cushman and Brown, who proposed the mechanism of Scheme II.[14] In this mechanism, intermediate 4 (Scheme I) decomposes by β-elimination to give the η-allyl–hydride intermediate 9 and then the alkene complex 8 by reductive elimination. There are good precedents for this overall process in early transition metallacycles,[26-28] though the

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Table II. First-Order Rate Constants for the Conversion of $PtCl_2(CH_2CMe_2CH_2)L_2$ to *trans*-$[PtCl_2(CHLCH_2CHMe_2)_6]$ (L = pyridine) in 1,2-$C_6H_4Cl_2$

added ligand	[L]/M	T/°C	$k/10^{-4}$ s^{-1}
		35	2.7
		40	4.4
		43	8.5
		50	23.3
py	1×10^{-4}	43	6.3
py	2×10^{-4}	43	3.8
py	3×10^{-4}	43	2.6
py	4×10^{-4}	43	2.0
py	5×10^{-4}	43	1.5
py	6×10^{-4}	43	1.4
2-Me(py)	5×10^{-4}	43	4.2
2-Me(py)	1×10^{-3}	43	4.5
2-Me(py)	2×10^{-2}	43	6.2
2,6-Me_2(py)	5×10^{-4}	43	4.7
2,6-Me_2(py)	5×10^{-3}	43	4.6

direct observation of the metallacyclobutane to allyl–hydride complex has not yet been observed. In addition, platinum(IV) alkyls may decompose by β-elimination.[29] It was suggested that ligand attack on the η-allyl group of **9** could give **10** and then, by a series of insertion/β-elimination steps, the ylide complex **7**.

Other mechanisms could not be eliminated and it was also considered possible that Scheme I could apply to ylide formation and Scheme II to alkene complex formation. It has been suggested that ylides can rearrange back to platinacyclobutanes under some conditions,[30] and β-elimination could then give alkene complexes. Labeling studies were clearly needed to resolve the mechanistic problem.

Mechanism of Ylide Formation. A brief study of the kinetics of isomerization of the platinacyclobutane $PtCl_2(CH_2CMe_2CH_2)L_2$ to the ylide complex *trans*-$[PtCl_2(CHLCH_2CHMe_2)L]$ (L = pyridine) in the solvent 1,2-dichlorobenzene was caried out. Results are given in Table II. The reaction occurs cleanly under these conditions, and the results are very similar to those found earlier for the reaction of eq 2.[11] The reaction followed good first-order kinetics and was retarded in the presence of free pyridine. The apparent activation energy was 120 ∓ 5 kJ mol^{-1}. Gillard's proposal that pyridine dissociation from the platinacyclobutane precedes ylide formation is confirmed in this case. The bulky ligands 2-methylpyridine and 2,6-dimethylpyridine were much less effective in retarding the isomerization, and higher concentrations of 2-methylpyridine led to a slight acceleration in rate. All of these data are consistent with the mechanism of Scheme I, involving pyridine dissociation as a preliminary step.

The platinacyclobutane derivatives $PtCl_2(CH_2CHPhCD_2)$ [as a mixture with its skeletal isomers $PtCl_2(CH_2CD_2CHPh)$ and $PtCl_2(CD_2CH_2CHPh)$] and $PtCl_2(CH_2CMe_2CD_2)$ were prepared from the corresponding cyclopropane-d_2 derivatives. As shown in Scheme III, the α-elimination and β-elimination mechanisms of Schemes I and II predict that different labeled ylides should be formed. Note that two ylide products are expected from each reaction since the platinacyclobutane precursors, **13** and **14** (corresponding to **4** in Scheme I), are equally probable.

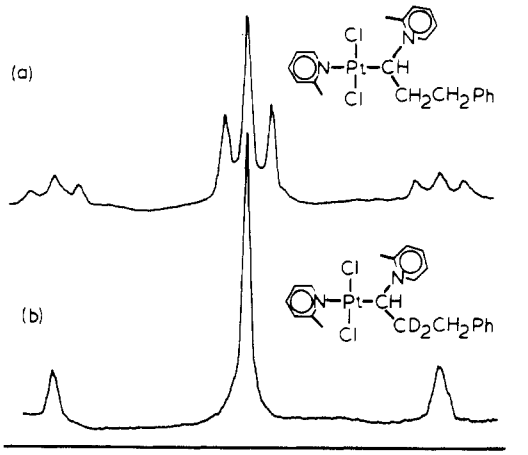
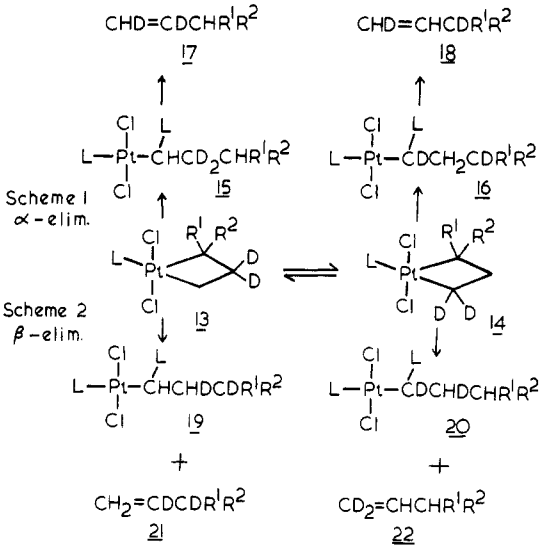


Figure 1. ^{1}H NMR spectra (100 MHz) of ylide complexes showing only the PtC*H* resonance of (a) *trans*-$[PtCl_2(CHLCH_2CH_2Ph)L]$ and (b) *trans*-$[PtCl_2(CHLCD_2CH_2Ph)L]$ (L = 2-methylpyridine) [δ 5.60, ^2J(PtH) = 112 Hz].

Scheme III

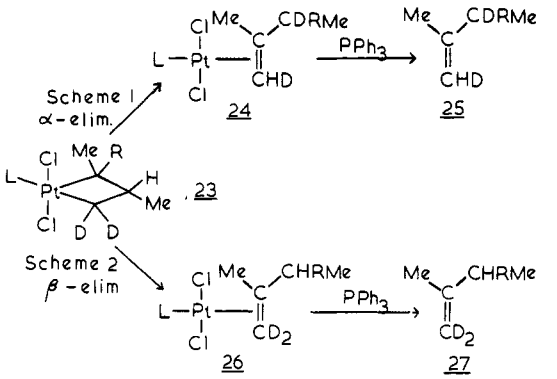


The ^{1}H NMR spectrum of the ylide where L = 2-methylpyridine, R^1 = H, and R^2 = Ph, showed that **15** was present but not **19**. The usual triplet resonance for the ylide CH proton (δ 5.6, ^3J(HH) = 7, ^2J(PtH) = 112 Hz) of *trans*-$[PtCl_2(CHLCH_2CH_2Ph)L]$ had collapsed to a singlet, showing that the ylide CH group was adjacent to CD_2 and not CHD (Figure 1). The species **16** and **20** would not, of course, give an ylide C*H* resonance. The β-elimination mechanism of Scheme II is therefore disproved in this case.

A more detailed study was carried out with the ylide where $R^1 = R^2$ = Me (Scheme III). Again treatment with 2-methylpyridine gave **15** as determined by the singlet resonance for the ylide C*H* proton [δ 5.78, ^1J(PtH) = 114 Hz]. In addition the $^{13}C\{^1H\}$ NMR spectrum gave a singlet due to carbon C^2 (δ 24.9, ^2J(PtC) = 27 Hz) as expected for structure **16**. Both **19** and **20** should give a 1:1:1 triplet due to C^2 due to ^1J(CD) coupling in the CHD groups and so are clearly not formed. The expected quintet due to **15** was not observed but is expected to be very weak since there will be no nuclear Overhauser effect. The result again strongly supports the α-elimination mechanism. The ^{2}H NMR spectrum of the mixture of **15** and **16** gave resonances at δ 5.8 (due to the ylide CD group of **16**) and a broad peak at δ ~2 (due to the unresolved C^2D_2 signals of **15** and the C^3D signal of **16**). Integration of this spec-

(28) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 541.
(29) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1613.
(30) Puddephatt, R. J.; Rendle, M. C.; Tipper, C. F. H. *J. Organomet. Chem.* **1984**, *269*, 305.

Scheme IV



trum gave the ratio of **15**:**16** ~ 1.6 (±0.1):1, indicating a significant isotope effect on product formation.

The unstable ylide complex formed from 2,6-dimethylpyridine and $PtCl_2(CH_2CMe_2CD_2)$ was shown to contain **15** by the singlet ylide C*H* resonance (δ 6.0, ^2J(PtH) = 108 Hz), and so the α-elimination mechanism was again preferred for this unstable ylide.

Mechanism of Alkene Complex Formation. For this study, two additional platinacyclobutanes were prepared from the cyclopropanes *trans*-1,2-dimethylcyclopropane-*3,3-d*$_2$ and 1,1,2-trimethylcyclopropane-*3,3-d*$_2$. The predicted products according to the α- and β-elimination mechanisms of Schemes I and II, respectively, are shown in Scheme IV. The alkene complexes were studied by ^{1}H, ^{2}H, and ^{13}C NMR spectrometry and then the alkene was liberated by treatment of the complex with triphenylphosphine and studied by the same NMR methods. The distinction between the products **24** and **25** or **26** and **27** (Scheme IV) was more straightforward than for the ylide complexes (Scheme III) since single products are predicted and found.

Reaction of $PtCl_2(CD_2CHMeCHMe)$ with 2-methylpyridine was found to give **24** rather than **26** (R = H, L = 2-methylpyridine. In the ^{1}H NMR spectrum a resonance was observed at δ 4.89 ppm, ^2J(PtH) = 62 Hz, integrating as a single hydrogen, due to the =C*H*D proton; structure **26** would contain no such resonance. The methyl protons of the C*H*$_3$CHD group of **24** (R = H, L = 2-methylpyridine) occurred as a 1:1 doublet due to ^3J(HH) coupling, whereas **26** would give a triplet resonance as is observed for the nonlabeled derivative (Figure 2). A further point of interest is that the CH_2 protons of the CH_3CH_2 group are diastereotopic and in the unlabeled compound appear as multiplets at δ 2.35 ppm, ^3J(HH) = 7 Hz, and at δ = 2.63 ppm, ^3J(HH) = 7 Hz. In the d_2-labeled derivative, the resonance at δ 2.35 ppm integrated as one proton and the resonance at δ 2.63 ppm was not observed. This indicates that deuterium adds selectively and proves that the alkene is formed and remains within the coordination sphere of the platinum. In the free alkene **25** (R = H) these CH_3CH_2 protons are equivalent.

Further identification was made on the free alkene **25** (R = H) liberated by reaction of **24** with triphenylphosphine. In the ^{1}H NMR spectrum the C*H*$_3$CHD protons occurred as a 1:1 doublet of 1:1:1 triplets with ^3J(HH) = 7.5 Hz and ^3J(HD) = 1.1 Hz (Figure 2). The alkene **27** (R = H) would give a 1:2:1 triplet resonance for the C*H*$_3$CH$_2$ protons. The resonances due to the –C*H*D and CH$_3$C*H*D protons each integrated as one proton. Confirmation of structure **25** (R = H) was obtained from the ^{2}H NMR spectrum, which contained equal intensity peaks at δ 1.9 and 4.6 ppm due to the CH$_3$CH*D* and =CH*D*

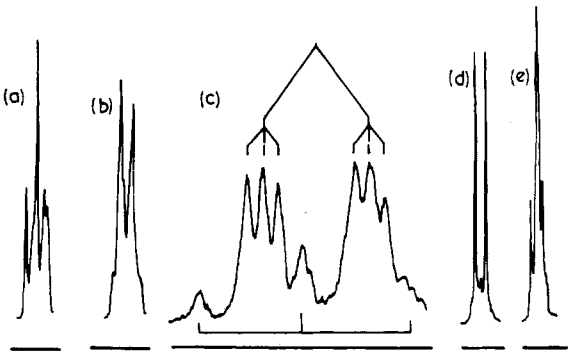


Figure 2. ^{1}H NMR spectra (100 MHz) showing the following: (a) the *Me*CH$_2$ resonance of *trans*-[PtCl$_2$(CH$_2$=CMeEt)L] [δ 1.38, ^3J(HH) = 7 Hz]; (b) the *Me*CHD resonance of *trans*-[PtCl$_2$-{CHD=CMe(CHDMe)}L] [δ 1.36, ^3J(HH) = 7 Hz] (L = 2-methylpyridine); (c) the *Me*CHD resonance of CHD=CMe-(CHDMe), expanded to show the couplings ^3J(HD) [δ = 0.92, ^3J(HH) = 7, ^3J(HD) = 1.1 Hz], a low intensity triplet due to CH_3CH_2 group impurity is shown below; (d) the *Me*$_2$CH resonance of CH$_2$=CMe(CHMe$_2$) [δ 1.03, ^3J(HH) = 7 Hz]; (e) the *Me*$_2$CD resonance of CHD=CMe(CDMe$_2$) [δ 1.01, ^3J(HD) = 1.1 Hz], the low intensity doublet being at least partly due to an impurity of CHD=CMe(CHMe$_2$).

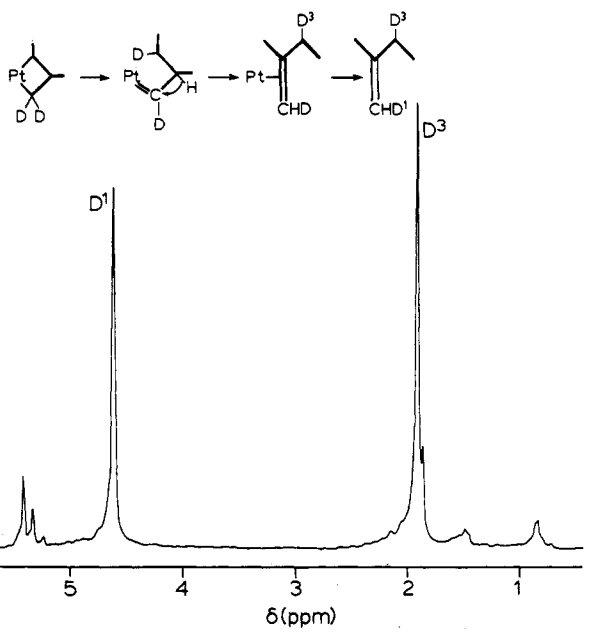


Figure 3. ^{2}H{^{1}H} NMR spectrum (15.4 MHz) of CHD^1=CMe-(CHD^{3}Me).

groups, respectively (Figure 3). No deuterium incorporation into the methyl groups was observed. Finally, the ^{13}C{^{1}H} NMR spectrum showed 1:1:1 triplets due to ^1J(CD) coupling for the =C*H*D and CH$_3$C*H*D carbon atoms of **25** (R = H).[17] These data are clearly inconsistent with structure **27**.

Because this system clearly indicated that the alkene was formed by an initial α-elimination, the system based on the cyclopropane $CD_2CHMeCMe_2$, which had been suggested to give a β-elimination product (eq 6)[13] was reinvestigated. Our sample of the cyclopropane contained ~10% impurity of CHDCHMeCMe$_2$ and this made interpretation of the spectra of products a little more difficult than in the previous case. The reaction of $PtCl_2(CD_2CMe_2CHMe)$ with pyridine gave **24** (R = Me) and this was treated with triphenylphosphine to liberate **25** (R = Me). Since our results do not agree with an earlier report,[13] we give details of the NMR spectra of the alkene

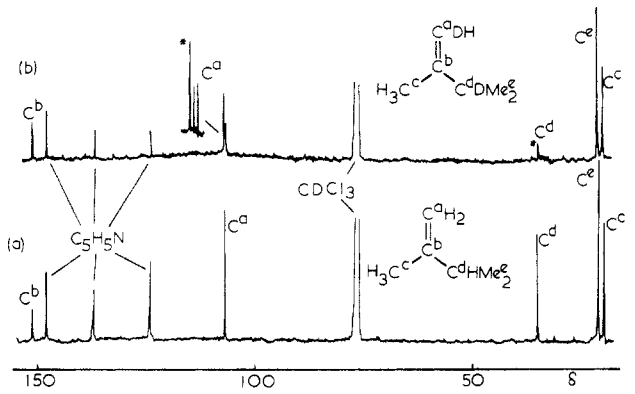
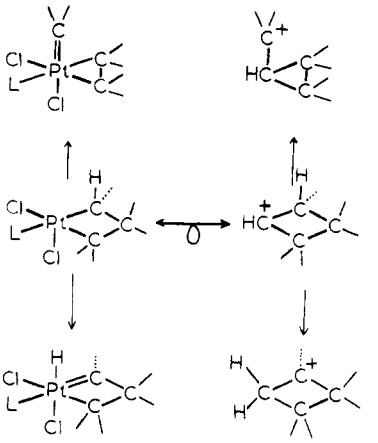


Figure 4. $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz) of (a) CH_2=CMe($CHMe_2$) and (b) CDH=CMe($CDMe_2$). The peaks labeled with an asterisk are due to impurities of CH_2=CMe($CDMe_2$) and CHD=CMe($CHMe_2$).

25. In the ^1H NMR spectrum, the *Me*$_2$CD resonance appeared as a 1:1:1 triplet with ^3J(HD) = 1 Hz but there was an additional doublet due to *Me*$_2$CH groups (Figure 2). The Me$_2$C*H* resonance was barely resolved. The =C*H*D resonance at δ 4.7 ppm integrated as one proton. In the $^2H\{^1H\}$ NMR spectrum, approximately equal intensity peaks were observed for the =C*H*D and Me$_2$C*D* resonances at δ 4.7 and δ 2.2 ppm, respectively.[16] These data are not consistent with structure **27** (R = Me), for which only Me$_2$CH groups are expected and so should give a doublet for the *Me*$_2$CH protons and a strong signal due to Me$_2$C*H* protons in the ^1H NMR spectrum, and no Me$_2$C*D* signals should be observed in the ^2H NMR. These data were confirmed by the ^{13}C NMR spectrum (Figure 4). The Me$_2$CH resonance was only one-tenth of the intensity in the nonlabeled alkene, and the =CHD resonance was a 1:1:1 triplet due to ^1J(CD) coupling with a low-intensity singlet due to =CH_2 superimposed. Both the ^2H and ^{13}C NMR showed that there was little deuterium incorporation into the methyl groups.[16] These spectra are entirely as expected for **25** (R = Me), with low quantities of CH_2=CMe($CDMe_2$) and CHD=CMe($CHMe_2$) arising from the impurity in the starting cyclopropane derivative and CH_2=CMe($CHMeCD_2H$) arising from β-elimination from an exocyclic methyl group.[13,16] Previously, ^1H and ^{13}C NMR spectra indicating that the reaction gave **27** were reported.[13] We have prepared the alkene in the manner reported[13] and also by using 2-methylpyridine as ligand, but our spectra clearly indicate that alkene **25** (R = Me) is always formed. The reason for the discrepancy is not clear and could result from subtle differences in reaction conditions. However, since we have repeated the reaction several times with the same result, we are confident that the product **25** is formed under most conditions and results from an initial α-elimination (Scheme I).

Finally, we have examined the alkenes formed by decomposition of the mixture of ylide complexes **15** and **16** (R^1 = R^2 = Me, L = 2-methylpyridine or 2,6-dimethylpyridine). The problem is to distinguish between the alkenes **17** and **18** and **21** and **22** (R^1 = R^2 = Me) (Scheme III). The $^{13}C\{^1H\}$ NMR spectrum contained a 1:1:1 triplet for the *C*HD carbon as expected for **17** and **18** but not for **21** or **22**. The ^1H and ^2H NMR spectra did not distinguish clearly between the possible products in this case. However, after identification by ^{13}C NMR, integration of the *Me*$_2$CH vs. *Me*$_2$CD resonances in the ^1H NMR, or the CHD=C*D* vs. *C*DMe$_2$ resonances in the ^2H NMR, gave independent measures of the abundances of **17**:**18** (R^1 = R^2 = Me) of 1.65(±0.1):1. This is in good agreement with the relative abundances of the ylide precursors **15**:**16** of 1.6(±0.1):1, determined earlier. Hence both the ^2H label distribution in the product alkenes and the relative yields of **17** and **18** are fully consistent with formation of the alkenes **17** and **18** directly from the ylides **15** and **16**, respectively (R^1 = R^2 = Me).

Scheme V



Discussion

The isotopic labeling studies described above show that decomposition of these platinacyclobutanes to ylide or alkene complexes cannot occur by the β-elimination mechanism of Scheme II,[14] but the results are consistent in all cases with the α-elimination mechanism of Scheme I. We were unable to reproduce the labeling experiment of eq 6,[13] which was the basis for the general β-elimination mechanism of Scheme II.[14] This result was a surprise since there are good precedents for β-elimination in other metallacyclobutanes and since most alkylplatinum complexes do decompose by β-elimination.[31] It is known that β-elimination is difficult in metallacyclopentanes, including platinum(IV) derivatives, because conformational problems hinder the transition to the hydride–alkene intermediate.[32,33] A similar problem may account for the lack of β-elimination in these platina(IV)cyclobutanes, though in this case a hydrido(η-allyl) derivative should be formed (Scheme II). β-Elimination from exocyclic methyl groups is not observed to a major extent either, probably for the same reason.[34]

Wilker and Hoffmann have suggested[35] that the skeletal isomerization of platinacyclobutanes **3** ⇌ **4**, Scheme I, occurs by way of an isomer of structure **28** which is isolobal with the cyclobutyl cation $C_4H_7^+$, **29**, which also undergoes exchange of methylene groups (Scheme V). Intermediate **30**, which is isolobal with the cyclopropylmethyl cation **31**, was proposed. In a similar way, there is an obvious analogy between the proposed α-elimination of Scheme I (but involving **4** → **28** → **5**) and the 1,2-hydride shifts which are

(31) Note however that most studies have dealt with alkylplatinum(II) complexes. Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528, and references therein.

(32) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481.

(33) Brown, M. P.; Hollings, A.; Houston, K. J.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 786. Cheetham, A. K.; Puddephatt, R. J.; Zalkin, A.; Templeton, D. H.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2997. Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1980**, *191*, 481.

(34) Evidence for this process, and its reverse insertion, has been obtained in metallacycles of rhenium. Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *4*, 129.

(35) Wilker, C. N.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 5285.

commonly observed in cycloalkyl cations (Scheme V).[36]

It should be noted that there is no direct evidence for the hydride intermediate **5**, though there are good precedents for α-hydride eliminations in other alkylmetal complexes.[23-25] The labeling studies prove only that an overall 1,3-hydride shift is involved in transforming **4** → **6**. A one-step mechanism not involving **5** is not precluded by the data. Another possible mechanism, which has the virtue of explaining the selectivity of the reactions readily, involves formation of the most stable carbonium ion $[Cl_2LPtCH_2CHR^1CR^2R^3]^+$ from **4** followed by a direct 1,3-hydride shift. However, a 1,2-hydride shift leading directly to the alkene complex appears much more likely to occur form such a cation, and so we suggest that the intermediate **5** is most probable. The detailed mechanism of the reaction **6** → **8** (Scheme I) is again not known. A direct 1,2-hydride shift is the simplest mechanism, but a β-elimination to give a vinyl(hydrido) intermediate followed by reductive elimination would give the same product **8**.

According to Scheme I, the selectivity of product formation depends on the α-elimination reductive elimination steps. The products appear always to be formed from the more hindered isomer **4** rather than from **3**, and this is rationalized since the overall reaction **4** → **6** reduces steric hindrance and will be favored by increased steric hindrance in **4**. There is a still more sterically hindered platinacyclobutane $LCl_2\overline{PtCHR^1CH_2CR^2R^3}$ that might be expected to undergo α-elimination even more readily but that does not play a major part in the reactions when R^1 = Me and R^2 = H and R^3 = Me or $R^2 = R^3$ = Me.[37] The reasons for this are not obvious. According to Scheme I, α-elimination always occurs from a CH_2 group and the hydride is always transferred to the most substituted carbon atom of the platinacyclobutane. The products given in Table I will then result. As mentioned above, the selectivity is more easily accounted for by a carbonium ion mechanism. For example, the carbonium ions $[LCl_2PtCH_2CHMeCMe_2]^+$ or $[LCl_2PtCH_2CHMeCHMe]^+$ are expected to be more stable (the least substituted carbon adjacent to platinum and most substituted carbon as the carbonium ion center) and a 1,3-hydride shift would then lead to the observed products via **6** (Scheme I).

Finally, the formation of ylide or alkene complexes follows naturally from Scheme I, based on the intermediate **6**. The small, basic ligands pyridine and 2-methylpyridine react with **6** to give stable ylide derivatives **7** so long as R^1 = H. If R^1 = Me, steric hindrance prevents ylide formation and so the reaction **6** → **8** occurs and gives the alkene complex. The bulky ligand 2,6-dimethylpyridine gives the ylides **7** (R^1 = H) at low temperature but they decompose easily to the alkene complexes **8** at higher temperatures. Steric hindrance presumably leads to easy dissociation of the bulky ligand from **7** to regenerate **6** and hence form **8** (Scheme I) in this case.[23] Alkene complexes are always formed when L = CD_3CN because the ligand is not a strong enough base to trap the carbene derivative **6** as the ylide **7**; again the isomerization of **6** → **8** occurs in the absence of this trapping.

The observed isotope effect of $k_H/k_D = 1.6 \pm 0.1$ for the reaction of **13** → **15** or **14** → **16** ($R^1 = R^2$ = Me, Scheme III) is probably a true kinetic isotope effect since the equilibration **13** → **14** is evidently fast compared to the rate of α-elimination. However, it is not possible to determine if the α-elimination step (**4** → **5**, Scheme I) or the reductive elimination step (**5** → **6**) is rate determining.[38] The selectivity observed is more consistent with the latter since the reductive elimination leads to lower steric congestion.

This work has shown that platina(IV)cyclobutanes undergo α- rather than β-elimination. There is good evidence for intermediacy of the carbene derivative **6** of Scheme I in this reaction. If this process were general and if the carbene **6** could react with an alkene to give a higher metallacyclobutane, it could give a novel mechanism for polymerization of alkenes.[15,39] Such carbene intermediates may also be involved in the transition metal catalyzed rearrangements of cyclopropane derivatives.[5]

Experimental Section

General methods have been described previously.[7,12,22] NMR spectra were recorded with Varian XL100 or XL200 NMR spectrometers in $CDCl_3$ (or $CHCl_3$) solution unless otherwise stated. The platinacyclobutane complexes were prepared by known methods.[12,14,22]

$PhCHCD_2CH_2$. This was prepared by reduction of $PhCHCBr_2CH_2$ with Bu_3SnD[40,41] and the purity was established by ^1H NMR in $CDCl_3$: δ 1.2 [m, 2 H, CH_2], 2.25 [m, 1 H, CH].

$Me_2CCD_2CH_2$. To a stirred suspension of finely divided sodium (8 g) in dry diglyme (50 mL) was added dropwise a mixture of $Me_2CCBr_2CH_2$ (20 g),[40] C_2H_5OD (10 g), and D_2O (2 mL). The reaction was exothermic and the temperature was maintained below 70 °C. The *product* distilled from the flask was collected in a trap, cooled to −78 °C, and purified by distillation; yield 2.7 g. NMR in $CDCl_3$: δ 0.93 [s, 6 H, *Me*]; 0.1 [s, 2 H, CH_2].

trans-[CHMeCHMeCD$_2$] (2.3 g) was similarly prepared from *trans*-[CHMeCHMeCBr$_2$] (20.5 g). NMR in $CDCl_3$: δ 1.0 [d, 6 H, *Me*]; 0.19 [m, 2 H, MeC*H*].

Me_2CCD_2CHMe. This was prepared by the literature method,[13] but our samples always contained some $Me_2CCHDCHMe$, as shown by ^1H and ^{13}C NMR. The CHD group gave a 1:1:1 triplet in the ^{13}C NMR at δ 21.1. Our best sample contained ~10% $Me_2CCHDCHMe$ impurity.

Synthesis of Ylide Complexes. To a suspension of $PtCl_2(CH_2CMe_2CH_2)$ (0.04 g) in CH_2Cl_2 (2 mL) was added 2-methylpyridine (0.05 g), until all the solid dissolved and a yellow solution was formed. The product *trans*-[$PtCl_2$[CH(2-Me(py))CH_2CHMe](2-Me(py))] was obtained by precipitation with pentane (10 mL) and then was washed with pentane and recrystallized from CH_2Cl_2/pentane: yield 64%; mp 117 °C. Anal. Calcd for $C_{17}H_{24}Cl_2N_2Pt$: C, 39.1; H, 3.8; N, 5.3. Found: C, 38.7; H, 4.6; N, 5.3. NMR: ^1H, δ 5.80 [t, ^3J(HH) = 7.5, ^2J(PtH) = 114 Hz, PtC*H*], 1.70 and 2.40 [m, CH^aH^b], 2.02 [m, C*H*Me$_2$], 0.98 and 1.02 [d, ^3J(HH) = 6.5 Hz, *Me*$_2$CH], 3.06 and 3.17 [s, *Me*(py)]. ^{13}C, δ 35.3 [CH, ^1J(PtC) = 795 Hz, PtCH], 24.9 [CH_2, ^2J(PtC) = 27 Hz, CH_2], 46.5 [CH, *C*HMe$_2$]; 22.6 [CH_3, *Me*$_2$CH].

The following were similarly prepared: *trans*-[$PtCl_2$[CH(2-Me(py))CH_2CH_2Ph](2-Me(py))]; mp 54 °C. Anal. Calcd for $C_{21}H_{21}Cl_2N_2Pt$: C, 44.2; H, 4.2; N, 4.9. Found: C, 44.0; H, 4.0; N, 4.6. ^1H NMR: δ 5.60 [t, ^3J(HH) = 7, ^2J(PtH) = 112 Hz, PtC*H*], 1.9 [m, CH_2CH_2], 2.94 and 3.03 [s, Me(py)]. *trans*-[$PtCl_2$[CH-

(36) Olah, G. A.; Schleyer, P. v. R. *Carbonium Ions*; Wiley: New York, 1972.

(37) A minor product, identified as *trans*-2-pentene, is formed along with the major product 2-methyl-1-butene in the decomposition of $PtCl_2$(*trans*-CH_2CHMeCHMe) and presumably is formed from the isomeric $PtCl_2$(CHMeCH$_2$CHMe).

(38) If the reductive elimination is rate determining, interpretation of the observed isotope effect is complicated because an equilibrium isotope effect on the α-elimination step is expected.

(39) However, our attempts to trap the carbene **6** with alkenes have been unsuccessful. Since β-elimination is observed in other metallacyclobutanes, the generality of the α-elimination process with other metals remains to be determined.

(40) Seyferth, D.; Yamazaki, H.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703.

(41) Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, *53*, 4660.

(2-Me(py))CH_2CH_2(4-MeC_6H_4)}(2-Me(py))]; mp 76 °C. Anal. Calcd for $C_{22}H_{24}Cl_2N_2Pt$: C, 45.2; H, 4.5; N, 4.8. Found: C, 44.6; H, 4.2; N, 4.5. ^1H NMR: δ 5.59 [t, ^3J(HH) = 7, ^2J(PtH) = 116 Hz, PtC*H*], ~1.9 [m, CH_2CH_2], 2.23 [s, *Me*C_6H_4], 2.94 and 3.00 [s, *Me*(py)].

A solution of $PtCl_2(CH_2CMe_2CH_2)py_2$ (0.04 g) in $CDCl_3$ (0.5 mL) was photolyzed for 2 days with light from a fluorescent lamp. The color became yellow and ^1H NMR showed that reaction was complete. The product, *trans*-[$PtCl_2${CH(py)CH_2CHMe$_2$}py], was purified as above; mp 47 °C. Anal. Calcd for $C_{15}H_{20}Cl_2N_2Pt$: C, 36.4; H, 4.0; N, 5.7. Found: C, 36.6; H, 4.1; N, 5.5. NMR: ^1H, δ 5.84 [t, ^2J(HH) = 7, ^3J(PtH) = 110 Hz, PtCH], 1.62 and 2.36 [m, CH^aH^b], 1.96 [m, C*H*Me_2], 0.97 and 1.00 [d, ^3J(HH) = 6.5 Hz, *Me*$_2$CH]. ^{13}C, δ 41.8 [CH, ^1J(PtC) = 785 Hz, PtC*H*], 25.5 [CH_2, ^2J(PtC) = 43 Hz, CH_2]; 45.7 [CH, ^3J(PtC) = 35 Hz, C*H*Me_2], 22.85 and 22.36 [CH_3, *Me*$_2$CH]. The above reaction was completely inhibited in the presence of 1 drop of free pyridine.

Synthesis of Alkene Complexes from Platinacyclobutanes. To a suspension of $PtCl_2$(*trans*-CH_2CHMeCHMe) (0.04 g) in $CDCl_3$ (0.5 mL) was added 2-methylpyridine (~0.05 mL) until a clear solution was obtained. The product, *trans*-[$PtCl_2$-(CH_2=CMeEt)(2-Me(py))], was precipitated by addition of pentane and recrystallized from CH_2Cl_2/pentane: yield 0.031 g, mp 70 °C. Anal. Calcd for $C_{11}H_{17}Cl_2NPt$: C, 30.75; H, 4.0; N, 3.3. Found: C, 30.7; H, 3.8; N, 3.15. NMR: ^1H, δ 4.8 [s, ^2J(PtH) = 62 Hz, =C*H*$_2$], 1.96 [s, ^3J(PtH) = 11 Hz, C*H*$_3$C], 2.35 and 2.63 [*m*, ^3J(HH) = 7 Hz, C*H*$^aH^b$], 1.38 [t, ^3J(HH) = 7 Hz, C*H*$_3$CH$_2$]. ^{13}C, 68.2 [CH_2, ^1J(PtC) = 155 Hz, =*C*H$_2$], 132.6 [C, ^1J(PtC) = 135 Hz, CH_2=*C*], 25.8 [CH_3, ^2J(PtC) = 25 Hz, *C*H$_3$C], 34.0 [CH_2, ^2J(PtC) = 23 Hz, *C*H$_2$CH$_3$], 12.35 [CH_3, ^3J(PtC) = 30 Hz, *C*H$_3$CH$_2$], 25.42 [CH_3, ^3J(PtC) = 18 Hz, *Me*(py)].

Similarly, from $PtCl_2(CH_2CMe_2CH_2)$ and 2,6-Me_2(py), *trans*-[$PtCl_2$(CH_2=CHCHMe$_2$)(2,6-Me_2(py))] was prepared: yield 35%; mp 58 °C. Anal. Calcd for $C_{12}H_{19}Cl_2NPt$: C, 32.5; H, 4.3; N, 3.2. Found: C, 32.0; H, 4.1; N, 2.9. ^1H NMR: δ 4.8 [m, =C*H*$^aH^b$], 5.3 [*m*, CH_2=C*H*], 2.2 [m, C*H*Me_2], 1.17 and 1.54 [d, ^3J(HH) = 7 Hz, *Me*$_2$CH]. From $PtCl_2${CH_2CH(4-MeC_6H_4)CH_2} and 2.6-Me_2(py) was prepared *trans*-[$PtCl_2$(CH_2=CHCH_2-4-MeC_6H_4)(2,6-Me_2(py))]: yield 45%; mp 78 °C dec. Anal. Calcd for $C_{26}H_{25}Cl_2NPt$: C, 40.4; H, 4.0; N, 2.8. Found: C, 39.4; H, 4.3; N, 2.6.

To a suspension of $PtCl_2$(*trans*-CH_2CHMeCHMe) (0.04 g) in $CDCl_3$ (1 mL) was added CD_3CN (0.3 mL) until a clear solution was obtained. After 30 min at room temperature, the solvent was evaporated and the product, *trans*-[$PtCl_2$(CH_2=CMeEt)(CD_3CN)], was recrystallized from $CHCl_3$/pentane; yield 0.24 g. Anal. Calcd for $C_7H_{10}Cl_2D_3NPt$: C, 22.1; H + D, 4.2; N, 3.6. Found: C, 22.4; H + D, 4.4; N, 3.6. ^1H NMR: 4.53 [s, ^2J(PtH) = 69 Hz, =CH_2], 1.73 [s, *Me*C], 2.15 [m, CH_2CH$_3$], 1.23 [t, ^3J(HH) = 7 Hz, CH_3CH$_2$].

Similarly was prepared, from $PtCl_2(CH_2CMe_2CH_2)$ and CD_3-CN, *trans*-[$PtCl_2$(CH_2=CHCHMe$_2$)(CD_3CN)]: yield 39%; mp 95 °C dec. Anal. Calcd for $C_7H_{10}Cl_2D_3NPt$: C, 22.1; H + D, 4.2; N, 3.6. Found: C, 22.3; H + D, 4.3; N, 3.6. ^1H NMR: δ 4.3 [*m*, =CH$^aH^b$], 4.8 [m, CH_2=C*H*], 2.31 [m, C*H*Me_2], 1.01 and 1.33 [d, ^3J(HH) = 7 Hz, *Me*$_2$CH].

A solution of $PtCl_2(CH_2CHMeCHMe)py_2$ (0.04 g) in $CDCl_3$ (0.5 mL) in an NMR tube was allowed to stand in sunlight for 10 days. The product was largely *trans*-[$PtCl_2$(CH_2=CMeEt)py] as identified by ^1H NMR, but it could not be separated from impurity of *trans*-[$PtCl_2(py)_2$]. ^1H NMR: δ 4.69 [s, ^2J(PtH) = 65 Hz, CH_2], 1.70 [s, ^3J(PtH) = 39 Hz, CH_3C], 1.25 [t, ^3J(HH) = 7 Hz, CH_3CH$_2$], CH$_3$CH^aH^b resonances were not resolved.

Synthesis of Alkene Complexes from Zeise's Dimer. A solution of $Pt_2Cl_4(C_2H_4)_2$ (0.1 g) in $CHCl_3$ (6 mL) at −15 °C was treated with CH_2=CHCHMe$_2$ (0.5 mL). The solution was allowed to warm to room temperature and the solvent was evaporated to give orange crystals, identified as Pt_2Cl_4(CH_2=CHCHMe$_2$)$_2$, mp 115 °C dec. ^1H NMR: δ 4.6 [m, =C*H*$_2$], 5.3 [m, CH_2=C*H*], 1.25 and 1.72 [d, ^3J(HH) = 7 Hz, CH*Me*$_2$], C*H*Me_2 signal not resolved. The above compound was dissolved in CH_2Cl_2 (1 mL) and 2-Me(py) (2 drops) added. The product *trans*-[$PtCl_2$-(CH_2=CHCHMe$_2$)(2-Me(py))] was precipitated by addition of pentane, washed thoroughly with pentane, and recrystalized from CH_2Cl_2/pentane. Anal. Calcd for $C_{11}H_{17}Cl_2NPt$: C, 30.75; H, 4.0; N, 3.3. Found: C, 30.6; H, 3.7; N, 3.4. ^1H NMR: δ 4.8 [m, =CH_2], 5.4 [m, CH_2=C*H*], 1.85 [m, C*H*Me_2], 1.28 and 1.68 [d, ^3J(HH) = 7 Hz, *Me*$_2$CH], 3.3 [s, Me(py)].

Similarly were prepared *trans*-[$PtCl_2$(CH_2=CHCHMe$_2$)(2,6-Me_2(py))] and *trans*-[$PtCl_2$(CH_2=CHCHMe$_2$)(CD_3CN)], identified by their ^1H NMR spectra (see above).

Treatment of Labeled Derivatives. To a solution of Pt_2-$Cl_4(C_2H_4)_2$ (0.20 g) in tetrahydrofuran (4 mL) was added *trans*-CD_2CHMeCHMe (0.3 mL). The solution was stirred for 16 h at 40 °C, and the solvent was evaporated to give an oil. Trituration with $CHCl_3$ gave an off-white solid of $PtCl_2(CD_2CHMeCHMe)$. This was treated with pyridine to give $PtCl_2$-(CD_2CHMeCHMe)py_2, yield 0.10 g, identified by its ^1H NMR spectrum (δ 0.51 [d, ^3J(HH) = 6.5, ^3J(PtH) = 24 Hz, PtC*Me*], 0.90 [d, ^3J(HH) = 5.0, ^4J(PtH) = 7 Hz, PtCC*Me*], 2.95 [*m*, PtC*H* and PtCC*H*]; no resonance at δ 2.30, where the CH_2 resonance is expected). No H, D scrambling was observed at this stage.

To a suspension of $PtCl_2(CD_2CHMeCHMe)$ (0.10 g) in $CHCl_3$ (2 mL) was added 2-Me(py) (0.06 mL). After 2 h, the yellow solution was passed through a short column of Florisil, eluting with $CHCl_3$. The yellow band was collected and the product *trans*-[$PtCl_2$(CHD=CMeCHDMe)(2-Me(py))] was obtained by evaporation of the solvent; yield 0.10 g. NMR: ^1H, δ 1.36 [d, ^3J(HH) = 7 Hz, CHD*Me*], 1.96 [s, ^3J(PtH) = 40 Hz, *Me*C], 2.35 [m, ^3J(HH) = 7 Hz, C*H*DMe], 4.76 [s, ^2J(PtH) = 62 Hz, =CHD]. ^{13}C{^1H}, δ 12.5 [s, ^3J(PtC) = 30 Hz, *C*H$_3$CHD], 25.8 [s, ^2J(PtC) = 25 Hz, *C*H$_3$C], 33.8 [t, ^1J(CD) = 20.1, ^2J(PtC) = 34 Hz, CH$_3$*C*HD], 68.0 [t, ^1J(CD) = 24.1, ^1J(PtC) = 155 Hz, =*C*HD], 132.7 [s, ^{1}J(PtC) = 140 Hz, CHD=*C*].

The above complex (0.10 g) in $CDCl_3$ (1.0 mL) was treated with PPh_3 (0.3 g). The volatiles were transferred on the vacuum line to an NMR tube cooled in liquid nitrogen, and the tube was flame-sealed. The alkene was identified as CHD=CMeCHDMe by NMR (^1H, δ 0.92 [1:1 d of 1:1:1 t, ^3J(HH) = 7, ^3J(HD) = 1.1 Hz, CDHC*H*$_3$], 1.65 [s, =C*Me*], 1.93 [q, ^3J(HH) = 7 Hz, C*H*DCH$_3$], 4.6 [s, =C*H*D]. ^2H{^1H}, 1.9 [*CD*HMe], 4.6 [=*CD*H]. ^{13}C{^1H}, 12.0 [s, *C*H$_3$CHD], 22.1 [s, *C*H$_3$C], 30.1 [t, ^1J(CD) = 19 Hz, CH$_3$*C*HD], 107.8 [t, ^1J(CD) = 23.7 Hz, =CHD], 147.7 [s, CHD=*C*]). The ^2H{^1H} NMR spectrum was obtained from a sample prepared in CH_2Cl_2 solution by the above method.

The same method was used to obtain the alkene CHD=CMeCDMe$_2$, with H impurities, from $PtCl_2$(CHD=CMeCDMe$_2$)(py). NMR (in $CDCl_3$ or $CHCl_3$): ^1H, 1.01 [1:1:1 t, ^3J(HD) = 1.0 Hz, CD*Me*$_2$], 1.70 [d, ^4J(HH) = 1.3 Hz, =C*Me*], 4.65 [m, =CHD]. ^2H{^1H}, δ 2.23 [s, *CD*Me$_2$], 4.7 [s, =C*HD*]. ^{13}C{^1H}, δ 20.0 [s, *C*H$_3$C], 21.3 [s, *Me*$_2$CD], 34.8 [CDMe$_2$], 107.2 [1:1:1 t, ^1J(CD) = 24 Hz, =*C*HD], 151.7 [s, CHD=*C*].

Kinetic Studies. A solution of $PtCl_2(CH_2CMe_2CH_2)py_2$ (10^{-3} M) in 1,2-$C_6H_4Cl_2$ was placed in a 1-cm cuvette in the thermostated cell compartment of a Cary 118 spectrophotometer. The reaction was monitored by the increase in absorbance at 400 nm due to the product ylide complex. A plot of ln ($A_\infty - A_t$) vs. time gave a good straight line from which the first-order rate constant was determined (Table II). Reactions in the presence of free ligand were carried out in the same way.

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Registry No. $PtCl_2(CH_2CHMeCH_2)$, 79553-22-3; $PtCl_2$-(CHMeCH_2CH_2), 107270-83-7; $PtCl_2(CH_2CHBuCH_2)$, 79553-24-5; $PtCl_2(CH_2CMe_2CH_2)$, 107270-84-8; $PtCl_2(CHPhCH_2CH_2)$, 12348-06-0; $PtCl_2${CH(4-MeC_6H_4)CH_2CH_2}, 60379-99-9; $PtCl_2$-(CHMeCHMeCH_2), 71687-32-6; $PtCl_2$(CHMeCMe$_2$CH_2), 107270-85-9; C_5H_5N, 110-86-1; 2-MeC_5H_4N, 109-06-8; MeCN, 75-05-8; 2,6-$Me_2C_5H_3N$, 108-48-5; $PtCl_2(CH_2CHMeCH_2)L_2$ (L = C_5H_5N), 68111-87-5; $PtCl_2(CHMeCH_2CH_2)L_2$ (L = C_5H_5N), 68111-86-4; *trans*-[$PtCl_2${CH(L)CH_2CH_2Me}L] (L = 2-MeC_5H_4N), 79593-03-6; *trans*-[$PtCl_2$(CH_2=CHCH_2Me)L] (L = MeCN), 107246-58-2; *trans*-[$PtCl_2${CH(L)CH_2CH_2Bu}L] (L = 2-MeC_5H_4N), 79593-04-7; $PtCl_2(CH_2CMe_2CH_2)L_2$ (L = C_5H_4N), 68472-68-4; *trans*-[$PtCl_2${CH(L)CH_2cHMe$_2$}L] (L = 2-MeC_5H_4N), 107246-59-3;

trans-[$PtCl_2$(CH_2=$CHCHMe_2$)L] (L = 2,6-$Me_2C_5H_3N$), 74909-83-4; *trans*-[$PtCl_2$(CH_2=$CHCHMe_2$)L] (L = MeCN), 107270-93-9; *trans*-[$PtCl_2$($CH(L)CH_2CH_2Ph$)L] (L = 2-MeC_5H_4N), 74889-88-6; *trans*-[$PtCl_2$($CH(L)CH_2CH_2C_6H_4Me$)L] (L = 2-MeC_5H_4N), 107246-60-6; *trans*-[$PtCl_2$(CH_2=CMeEt)L] (L = 2-MeC_5H_4N), 82942-41-4; *trans*-[$PtCl_2$(CH_2=CMeEt)L] (L = MeCN), 107246-61-7; *trans*-[$PtCl_2$(CH_2=CMe-*i*-Pr)L] (L = C_5H_5N), 67235-52-3; *trans*-[$PtCl_2$(CH_2=CMe-*i*-Pr)L] (L = 2-MeC_5H_4N), 107246-62-8; $PhCHCD_2CH_2$, 88377-58-6; $PhCHCBr_2CH_2$, 3234-51-3; Bu_3SnD, 6180-99-0; $Me_2CCD_2CH_2$, 107270-86-0; $Me_2CCBr_2CH_2$, 32264-50-9; *trans*-[$CHMeCHMeCD_2$], 107270-87-1; *trans*-[$CHMeCHMeCBr_2$], 3591-58-0; *trans*-[$PtCl_2$($CH(L)CH_2CHMe_2$)L] (L = C_5H_5N), 77629-79-9; $PtCl_2$($CH_2CH(4\text{-}MeC_6H_4)CH_2$), 38922-12-2; *trans*-[$PtCl_2$($CH_2$=$CHCH_2$-4-$MeC_6H_4$)(2,6-$Me_2$(py))], 107246-63-9; CD_3CN, 2206-26-0; *trans*-[$PtCl_2$(CH_2=CMeEt)(CD_3CN)], 77629-76-6; *trans*-[$PtCl_2$(CH_2=$CHCHMe_2$)(CD_3CN)], 77629-75-5; *trans*-[$PtCl_2$(CH_2=CMeEt)py], 77629-80-2; *trans*-$PtCl_2py_2$, 14024-97-6; $Pt_2Cl_4(C_2H_4)_2$, 12073-36-8; CH_2=$CHCHMe_2$, 563-45-1; Pt_2Cl_4(CH_2=$CHCHMe_2$)$_2$, 88760-38-7; *trans*-[$PtCl_2$(CH_2=$CHCHMe_2$)(2-Me(py))], 107246-64-0; $PtCl_2(CD_2CHMeCHMe$, 107270-88-2; $PtCl_2(CD_2CHMeCHMe)py_2$, 107246-65-1; *trans*-[$PtCl_2$(CHD=CMeCHDMe)(2-Me(py))], 82942-32-3; CHD=CMeCHDMe, 82945-14-0; CHD=$CMeCDMe_2$, 82948-82-1; *trans*-$PtCl_2$(CHD=$CMeCDMe_2$)(py), 107246-66-2; *trans*-[$PtCl_2$($CH(L)CH_2CH_2Me$)L] (L = C_5H_5N), 77629-77-7; PrCHO, 123-72-8; $PtCl_2(CHPhCH_2CH_2)L_2$ (L = 2-MeC_5H_4N), 107246-67-3; $PtCl_2(CH_2CHPhCH_2)L_2$ (L = 2-MeC_5H_4N), 107246-68-4; $PtCl_2(CH_2CMe_2CH_2)L_2$ (L = 2-MeC_5H_4N), 107246-69-5; $PtCl_2$-$(CH_2CMe_2CH_2)L_2$ (L = 2,6-$Me_2C_5H_3N$), 107246-70-8; *trans*-[$PtCl_2$($CH(L)CH_2CHMe_2$)L] (L = 2,6-$Me_2C_5H_3N$), 74889-90-0; $PtCl_2(CH_2CD_2CHPh)$, 107270-89-3; $PtCl_2(CD_2CH_2CHPh)$, 107270-90-6; *trans*-[$PtCl_2$($CH(L)CD_2CH_2Ph$)L] (L = 2-MeC_5H_4N), 74889-89-7; *trans*-[$PtCl_2$($CH(L)CD_2CHMe_2$)L] (L = 2-MeC_5H_4N), 107246-71-9; $PtCl_2(CH_2CD_2CMe_2)$, 107270-91-7; $PtCl_2$-$(CH_2CMe_2CD_2)$, 107270-92-8; *trans*-[$PtCl_2$($CD(L)CH_2CHDPh$)L] (L = 2-MeC_5H_4N), 107246-72-0; *trans*-[$PtCl_2$($CD(L)CH_2CDMe_2$)L] (L = 2-MeC_5H_4N), 107246-73-1; *trans*-[$PtCl_2$($CH(L)CD_2CHMe_2$)L] (L = 2,6-$Me_2C_5H_3N$), 107246-74-2.

Synthesis of C-Silylated Phosphoranimines[1]

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The title compounds are derived from the phosphazene precursors Me_3SiN=$P(OCH_2CF_3)R^1R^2$ (1, R^1 = R^2 = Me; 2, R^1 = Ph, R^2 = CH_2CH=CH_2; 3, R^1 = R^2 = CH_2CH=CH_2) by a deprotonation/silylation process. Thus, treatment of 1 with *n*-BuLi at −78 °C in Et_2O solution generates the reactive intermediate Me_3SiN=$P(OCH_2CF_3)(Me)CH_2^-Li^+$ (1a) which, after quenching with appropriate chlorosilanes, affords the silylated phosphoranimines Me_3SiN=$P(OCH_2CF_3)(Me)CH_2SiMe_2R$ [4, R = Me; 5, R = Ph; 6, R = CH=CH_2; 7, R = H; 8, R = $(CH_2)_3CN$]. Similarly, the reaction of 1a with Me_2SiCl_2 or $(ClMe_2SiCH_2)_2$ in a 2:1 ratio yields the bis((phosphoranimino)silanes) [Me_3SiN=$P(OCH_2CF_3)(Me)CH_2]_2E$ (9, E = $SiMe_2$; 10, E = $SiMe_2CH_2CH_2SiMe_2$). Addition of MeLi to the crude Si–Cl product of the 1:1 reaction of 1a and Me_2SiCl_2 leads to the formation of 4. The deprotonation/silylation reactions of the allyl-substituted phosphoranimines 2 and 3 give the 3-silylpropenyl derivatives Me_3SiN=$P(OCH_2CF_3)(R)CH$=$CHCH_2SiMe_3$ (11, R = Ph; 12, R = CH_2CH=CH_2) with the *E* configuration about the C=C double bond. Application of a second silylation reaction to products 4 and 12 affords the disilylated derivatives Me_3SiN=$P(OCH_2CF_3)(Me)CH(SiMe_3)_2$ (13) and Me_3SiN=$P(OCH_2CF_3)(CH$=$CHCH_2SiMe_3)_2$ (14), respectively. Although the analogous reactions of the phosphoranimine anions with dichlorosiloxanes are generally unsatisfactory, the sequential treatment of $(ClSiMe_2)_2O$ with 1a and MeLi does yield the siloxy compound Me_3SiN=$P(OCH_2CF_3)(Me)CH_2SiMe_2OSiMe_3$ (15). These new silylated phosphoranimines are found to be much more thermally stable (to ca. 200–220 °C) than their unsubstituted precursors, and they do not yield poly(phosphazenes) upon decomposition under extreme conditions. Detailed characterization data, including multinuclear (^1H, ^{13}C, ^{31}P, and ^{29}Si) NMR spectra, of the silyl derivatives 4–15 are presented.

Introduction

The *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines such as Me_3SiN=$P(OCH_2CF_3)Me_2$ (1) are useful as precursors to poly(alkyl/arylphosphazenes) via a thermally induced condensation polymerization reaction.[3] In order to extend the scope and utility of this process, we are investigating various methods of introducing functional groups into both the phosphoranimine "monomers" as well as the preformed polymers. As reported recently, we have found that both the precursors (e.g., 1) and the polymers (e.g., [Ph(Me)-$PN]_n$) undergo facile deprotonation/substitution reactions in which phosphine-functionalized precursors[4] or silylated polymers,[5] respectively, are produced.

In this paper, we report the results of a more complete study of the deprotonation/silylation reactions of phos-

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