Chemistry of Platinacyclobutanes Derived from 1,2-Disubstituted Cyclopropanes[1,2]

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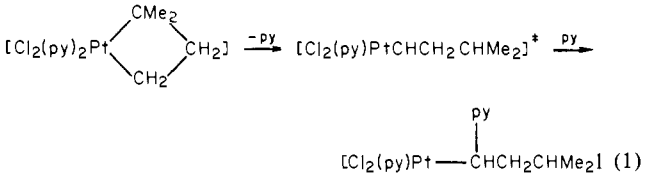
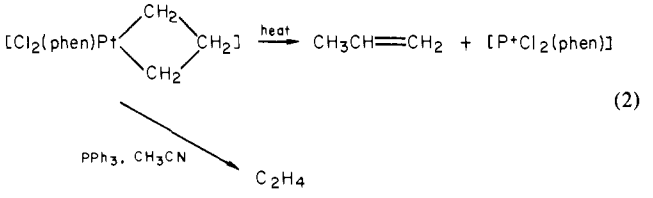
Abstract: Platinacyclobutanes have been prepared from 1,2-disubstituted cyclopropanes, *trans*-1,2-$R^1R^2C_3H_4$ ($R^1 = R^2$ = Me, Ph, 4-tolyl; R^1 = Me, R^2 = Ph; R^1 = Ph, R^2 = D), and from *cis*-1,2-$Ph_2C_3H_4$ and were characterized by ^1H and ^{13}C NMR spectroscopy. The isomer (IIb) was formed first from *trans*-1,2-di-4-tolylcyclopropane, and this underwent skeletal isomerization to an equilibrium mixture with Ie, and then treatment with PPh_3 gave back *trans*-1,2-di-4-tolylcyclopropane. Similar experiments with other derivatives show that formation of platinacyclobutanes from cyclopropanes, skeletal isomerization of platinacyclobutanes, and reductive elimination of cyclopropane derivatives from platinacyclobutanes all occur with retention of stereochemistry about the ring. Concerted mechanisms of reaction, rather than mechanisms involving zwitterionic intermediates or carbene–alkene complex intermediates, are proposed to account for these observations. Factors influencing the relative stabilities of isomeric metallacyclobutanes are discussed, particularly where relevant to proposed intermediates in alkene metathesis reactions.

Introduction

Metallacyclobutanes have been proposed as intermediates in alkene polymerization[4] and metathesis[5] and in ring-opening reactions[6] and retrocarbene additions[7] of cyclopropanes. The chemistry of platinacyclobutanes, which can be prepared by reaction of Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$, with cyclopropanes,[8] has given useful model reactions for several of these catalytic processes. For example, the α-elimination reaction (eq 1) aids an understanding of the possible role of metallacyclobutanes



in alkene polymerization, if the intermediate carbene can react with more alkene to regenerate a higher metallacyclobutane.[9] The reactions of eq 2 have relevance to alkene metathesis and rearrangements of strained-ring compounds to alkenes (phen = 1,10-phenanthroline).[10]



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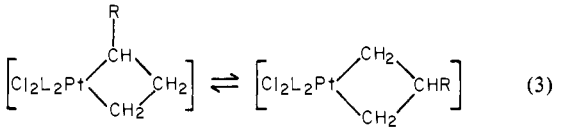
Of particular interest are the intramolecular skeletal rearrangements of eq 3 (e.g., R = Ph; L = pyridine).[11] The rearrangement has been shown to be intramolecular[11-14] and to occur after dissociation of a pyridine ligand, L. One possible mechanism involves breakdown to a carbene–alkene complex, followed by rotation of the alkene and formation of the isomeric platinacyclobutane. Such a mechanism would predict that cis–trans isomerization of substituents on the ring would accompany skeletal isomerization. We have made an effort to detect such cis–trans isomerization by study of platinacyclobutanes derived from cis- and trans-1,2-disubstituted cyclopropanes, and the results are given below. Preliminary accounts of some of this work have been published,[14,15] and other workers have recently published related results.[12,16,17]



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Results

Synthesis and Isomerization of Platinacyclobutanes. The reaction of *trans*-1,2-dimethylcyclopropane with Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$, gave a platinacyclobutane $\{[PtCl_2(CHMeCHMeCH_2)]_n\}$ which with pyridine gave Ia, L = C_5H_5N,[16] and with 1,10-phenanthroline gave Ia, L_2 = 1,10-phenanthroline. These complexes were thermally stable, but on treatment of the initial oligomeric platinacyclobutane with either bulky ligands (2-methylpyridine) or weak nitrogen-donor ligands (CD_3CN or PhCN) only the alkene complexes *trans*-$[PtCl_2(L)(CH_2{=}CMeEt)]$ were isolated. However at low temperatures

(1) Part 9 of the series: Reactions and Properties of Some Trimethyleneplatinum(IV) Complexes. For part 8, see ref 2.
(2) D. C. L. Perkins, R. J. Puddephatt, M. C. Rendle, and C. F. H. Tipper, *J. Organomet. Chem.*, **195**, 105 (1980).
(3) (a) University of Western Ontario. (b) University of Liverpool.
(4) K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978).
(5) R. H. Grubbs, *Prog. Inorg. Chem.*, **24**, 1 (1978). N. Calderon, J. P. Lawrence, and E. A. Ofstead, *Adv. Organomet. Chem.*, **17**, 449 (1979).
(6) K. C. Bishop III, *Chem. Rev.* **76**, 461 (1976).
(7) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 6057 (1976).
(8) F. J. McQuillin and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 2123 (1972).
(9) R. J. Al-Essa and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 45 (1980).
(10) P. W. Hall, R. J. Puddephatt, K. R. Seddon, and C. F. H. Tipper, *J. Organomet. Chem.*, **81**, 423 (1974); F. Iwanciw, M. A. Quyser, R. J. Puddephatt, and C. F. H. Tipper, *ibid.*, **113**, 91 (1976); D. C. L. Perkins, R. J. Puddephatt, and C. F. H. Tipper, *ibid.*, **54**, C16 (1978); D. C. L. Perkins, R. J. Puddephatt, M. C. Rendle, and C. F. H. Tipper, *ibid.*, submitted for publication.
(11) R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Chem. Soc., Chem. Commun.*, 626 (1976); R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Am. Chem. Soc.*, **101**, 364 (1979).
(12) C. P. Casey, D. M. Scheck, and A. J. Shusterman, *J. Am. Chem. Soc.*, **101**, 4233 (1979); N. Dominelli and A. C. Oehlschlager, *Can. J. Chem.*, **55**, 364 (1977).
(13) T. H. Johnson, *J. Org. Chem.*, **44**, 1356 (1979).
(14) R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *Inorg. Chim. Acta*, **34**, L187 (1979).
(15) R. J. Al-Essa, R. J. Puddephatt, C. F. H. Tipper, and P. J. Thompson, *J. Organomet. Chem.*, **157**, C40 (1978).
(16) B. M. Cushman, S. E. Earnest, and D. B. Brown, *J. Organomet. Chem.*, **159**, 431 (1978).
(17) T. H. Johnson, T. F. Baldwin, and K. C. Klein, *Tetrahedron Lett.*, 1191 (1979).
(18) This complex was prepared independently by Brown and co-workers.[16]

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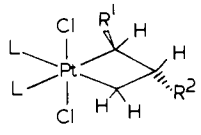
Table I. ^{1}H NMR Spectra of Complexes $[PtCl_2(trans\text{-}CH^1R^1CH^2R^2CH_2{}^3)L_2]$ (A) and $[PtCl_2(trans\text{-}CHR^1CH_2{}^2CHR^1)L_2]$ (B)

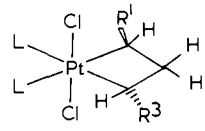
complex type	R^1	R^2	L	$\delta(R^1)$	$\delta(R^2)$	$\delta(H^1)$	$^3J(H^1H^2)$, Hz	$^2J(PtH^1)$, Hz	$\delta(H^2)$	$\delta(H^3)$	$^3J(H^2H^3)$, Hz	$^2J(PtH^3)$, Hz	other
A	Me	Me	C_5H_5N	0.58 d[a]	0.94 d[b]	2.98 dq		88	2.95 m	2.28 m[c]	8	79.5	
										2.32 m[c]	8	79	
A	Me	Me	2-MeC_5H_4N	0.40 d[d]	0.83 d[e]	*f*			*f*	*f*			$\delta(MeC_5H_4N)$
A	Me	Me	phen	1.15 d[g]	1.05 d[h]	*f*			*f*	*f*			
A	Me	Me	CD_3CN	0.60 d[i]	0.73 d[j]	*f*			*f*	*f*			
A	Me	Me	PhCN	0.60 d[k]	0.78 d	*f*			*f*	*f*			
A	Me	Ph	C_5H_5N	0.61 d[m]		*f*			*f*	*f*			
A	Ph	Me	C_5H_5N		0.96 d[n]	4.56 d	10	99	*f*	2.67 m	9	80	
										3.05 m	9	80	
A	Ph	Ph	C_5H_5N			5.18 d	10	98	4.81	3.20	9	80	
A	Ph	Ph	*t*-BuC_5H_4N			5.13 d	10	98	4.78	3.26 d	8.6	80.5	δ(*t*-Bu) 1.35
A	4-tolyl	4-tolyl	*t*-BuC_5H_4N	2.39 s[o]	2.31 s[o]	5.11 d	10	97	4.76	3.27 d	8.5	80.5	δ(*t*-Bu) 1.34
B	4-tolyl		*t*-BuC_5H_4N	2.26 s[o]		5.29 t	8.5	102	3.29 t				
A[p]	Ph	D	C_5H_5N			4.91 d	9.5	100	3.35 m	2.94 m		80	
B[p]	Ph	D	C_5H_5N			4.92 dd	8.5, 9.5	100	3.35 m	2.94 m		80	
A	D	Ph	C_5H_5N			2.94 d	9	83	4.10 g	2.94 d	9	83	

[a] $^3J(H^1R^1) = 6.5$ Hz, $^3J(PtR^1) = 22.8$ Hz. [b] $^3J(H^2R^2) = 5.8$ Hz, $^4J(PtR^2) = 7.2$ Hz. [c] AB pattern. [d] $^3J(H^1R^1) = 6.3$ Hz, $^3J(PtR^1) = 32$ Hz. [e] $^3J(H^2R^2) = 6$ Hz. [f] Not resolved. [g] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 22$ Hz. [h] $^3J(H^2R^2) = 6$ Hz. [i] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 37$ Hz. [j] $^3J(H^2R^2) = 6$ Hz, $^4J(PtR^2) = 14$ Hz. [k] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 38$ Hz. [l] $^3J(H^2R^2) = 6$ Hz. [m] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 24$ Hz. [n] $^3J(H^2R^2) = 6$ Hz. [i] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 37$ Hz. [j] $^3J(H^2R^2) = 6$ Hz, $^4J(PtR^2) = 14$ Hz. [k] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 38$ Hz. [l] $^3J(H^2R^2) = 6$ Hz. [m] $^3J(H^1R^1) = 6$ Hz, $^3J(PtR^1) = 24$ Hz. [n] $^3J(H^2R^2) = 3$ Hz. [o] Me resonance. [p] Present as 1:1 mixture of A and B.

the platinacyclobutane complexes (Ia), L = CD_3CN, PhCN, or 2-MeC_5H_4N, were formed and identified by the ^{1}H NMR spectra. In no case was the alternative isomer (II), $R^1 = R^3$ = Me, formed in significant amounts. In our hands, *cis*-1,2-dimethylcyclopropane failed to react with Zeise's dimer in tetrahydrofuran at 50 °C.



Ia, $R^1 = R^2$ = Me
Ib, R^1 = Me, R^2 = Ph
Ic, R^1 = Ph, R^2 = Me
Id, $R^1 = R^2$ = Ph
Ie, $R^1 = R^2$ = 4-MeC_6H_4
If, R^1 = Ph, R^2 = D
Ig, R^1 = D, R^2 = Ph

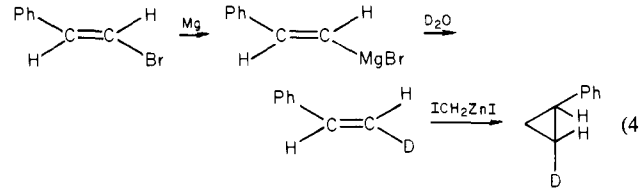


IIa, $R^1 = R^3$ = Ph
IIb, $R^1 = R^3$ = 4-MeC_6H_4
IIc, R^1 = Ph, R^3 = D

A similar sequence of reactions with *trans*-1-methyl-2-phenylcyclopropane gave a mixture of Ib and Ic, L = C_5H_5N, in relative amounts 1:2.8 ± 0.2. The ratio of isomeric products did not change on allowing a solution in $CDCl_3$ to stand for 2 weeks at room temperature, but slow thermal decomposition occurred. No complex (II) could be detected by NMR spectroscopy.

1,2-Diarylcyclopropanes reacted only slowly with Zeise's dimer, but stable platinacyclobutanes could be formed in several cases. *trans*-1,2-Di-4-tolylcyclopropane gave initially almost pure IIb, L = 4-*t*-BuC_5H_4N, but this underwent skeletal isomerization to give an equilibrium mixture of IIb and Ie in relative amounts, ca. 1:4. The isomerization was complete in 4 days at room temperature in $CDCl_3$ solution. The ligand 4-*t*-BuC_5H_4N was used, so as to increase the solubility and hence facilitate characterization by NMR spectroscopy. The similar complexes with pyridine ligands are only sparingly soluble. Similar reactions were found with complexes derived from *trans*-1,2-diphenylcyclopropane. However, the initial product was always a mixture of IIa and Id, L = C_5H_5N or 4-*t*-BuC_5H_4N, and further isomerization of IIa to Id then occurred slowly until the equilibrium mixture was obtained (IIa:Id, ca. 1:6). *cis*-1,2-Diphenylcyclopropane reacted even more sluggishly with Zeise's dimer, and considerable decomposition, apparently giving diphenylallyl derivatives of platinum, occurred. However, a platinacyclobutane probably containing $[PtCl_2(CHPhCH_2CHPh)(C_5H_5N)_2]$ (the ^{1}H NMR spectrum contained a *triplet* signal at δ 5.1 due to CHPh protons) was obtained in impure form. No isomerization was observed but may have been missed due to poor quality of the NMR spectra obtained.

trans-1-phenyl-2-deuteriocyclopropane (with impurity of the cis isomer) was prepared by methylene addition to largely *trans*-β-deuteriostyrene, prepared by the reaction sequence of eq 4.



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In our hands, some trans → cis isomerization always occurred during the synthesis of *trans*-β-deuteriostyrene and our best sample contained 91% trans and 9% cis isomer. The methylene addition occurred without further trans → cis isomerization. From this cyclopropane, the complexes If and IIc, L = C_5H_5N, were prepared (in equimolar amounts as predicted from statistical considerations). These platinacyclobutanes then rearranged to a mixture of Ig with If and IIc as described previously for the derivatives prepared from unlabeled phenylcyclopropane.[11] Casey and co-workers have independently found similar reactions in complexes derived from *cis*-1-phenyl-2-deuteriocyclopropane.[12]

Characterization of Platinacyclobutanes. ^{1}H NMR spectra of the platinacyclobutanes were often complex (Table I), but the positions of substituents on the ring could usually be deduced by using the following criteria. (1) Ring hydrogen atoms give a coupling $^2J(PtH)$ of 78–105 Hz when on the carbons α to platinum but show no coupling to ^{195}Pt when on the β-carbon. (2) The proton of an α-benzylidene group, PtC*H*Ar, appears at low field ($\delta \sim 5$), well separated from other resonances. It appears as a doublet for isomers of type I but a triplet for II, when R_1 = Ar. (3) Protons of methyl substituents on the ring give a coupling $^3J(PtH)$ of 20–40 Hz when on the carbons α to platinum, but $^4J(PtH)$ is <10 Hz for a methyl group on the β-carbon atom.

In some cases proton-decoupled ^{13}C NMR spectra were needed to determine the sites of ring substituents. The spectra are particularly simple and results are unambiguous.[11] The following criteria are useful. (1) When $R_1 = R_2$ (or R_3), isomer I gives three resonances due to ring carbons but II gives only two resonances. This criterion is clearly not useful when $R_1 \neq R_2$ (or R_3). (2) Ring carbon atoms give $^1J(PtC)$ of 330–390 Hz but $^2J(PtC)$ of 98–130 Hz. (3) CH_2 groups can be distinguished from CHR groups by recording the off-resonance decoupled ^{13}C NMR spectrum. The CH_2 group gives a triplet while the CHR group gives a doublet.

A further aid to assignment when mixtures of isomers are formed initially is obtained if skeletal isomerization occurs, since

Table II. ^{13}C NMR Spectra of Complexes $[PtCl_2(trans\text{-}C^1HR^1C^2HR^2C^3H_2)L_2]$ (A) and $[PtCl_2(trans\text{-}C^1HR^1C^2H_2C^1HR^1)L_2]$ (B)[a]

complex												
type	R^1	R^2	L	$\delta(R^1)$	$J(PtR^1)$	$\delta(R^2)$	$J(PtR^2)$	$\delta(C^1)$	$^1J(PtC^1)$	$\delta(C^2)$	$^2J(PtC^2)$	$\delta(C^3)$	$J(PtC^3)$
A	Me	Me	C_5H_5N	20.9 q[d]	29	21.7 q[d]	68	10.9 d	336	46.4 d	98	−2.6 t	347
A	Me	Ph	C_5H_5N	21.1	30			10.6	360	57.5	100	−2.9	370
A	Ph	Me	C_5H_5N			22.8	74	16.9	333	41.2	103	−0.2	364
B	Ph	Ph	$t\text{-}BuC_5H_4N$[b]					15.1	343	50.6	105	−1.8	377
B	Ph		$t\text{-}BuC_5H_4N$[b]					6.0	340	41.2	130		
A	4-tolyl	4-tolyl	$t\text{-}BuC_5H_4N$[c]	20.9	0	20.9	0	15.7	341	50.5	105	−1.6	383
B	4-tolyl		$t\text{-}BuC_5H_4N$[c]	21.4	0			6.3	338	41.6	125		

[a] Solvent $CDCl_3$. [b] $\delta(t\text{-Bu})$ 30.1 (Me), 34.6 (C). [c] $\delta(t\text{-Bu})$ 30.1 (Me), 34.5 (C). [d] The assignments for R^1 and R^2 may be reversed.

Table III. Products Released from Platinacyclobutanes $[PtCl_2(CHR^1CHR^2CHR^3)L_2]$ by Reaction with CN^- or PPh_3

complex					% of product $(CHR^1CHR^2CHR^3)$	
R^1	R^2	R^3	L	reagent	cis	trans
Ph[a]	Ph[a]	H		CN^-	0	100
Ph[a,d]	Ph[a,d]	H	C_5H_5N	CN^-	14	86
Ph[a]	Ph[a]	H	$4\text{-}MeC_5H_4N$	CN^-	10	90
Ph[a]	Ph[a]	H	$^1/_2$ tmed[c]	CN^-	0	100
Ph[a,d]	Ph[a,d]	H	C_5H_5N	PPh_3	0	100
Ph[b]	H	Ph[b]	C_5H_5N	CN^-	91	9
Ph[b,d]	H	Ph[b,d]	C_5H_5N	PPh_3	100	0
$4\text{-}MeC_6H_4$[a,e]	H	$4\text{-}MeC_5H_4N$[a,e]	$4\text{-}t\text{-}BuC_5H_4N$	PPh_3	4	96
$4\text{-}MeC_6H_4$[a,f]	$4\text{-}MeC_6H_4$[a,f]	H	$4\text{-}t\text{-}BuC_5H_4N$	PPh_3	4	96
Me[a]	Ph[a]	H	C_5H_5N	PPh_3	0	100
Ph[a]	Me[a]	H				
Me[a]	Ph[a]	H	C_5H_5N	$AsMe_3$	0	100
Ph[a]	Me[a]	H				
Me[a]	Me[a]	H	C_5H_5N	PPh_3	0	100
Ph[g,h]	D[g,h]	H	C_5H_5N	PPh_3	9	91
D[g,i]	Ph[g,i]	H	C_5H_5N	PPh_3	9	91

[a] Prepared from *trans*-1,2-disubstituted cyclopropane. [b] Prepared from *cis*-1,2-disubstituted cyclopropane. May also contain isomer with $R_1 = R_2 = Ph$, $R_3 = H$. [c] tmed = 1,2-bis(dimethylamino)ethane. [d] Identical result found for freshly prepared sample and for sample heated in $CHCl_3$ for 2 days at 45 °C. [e] Freshly prepared sample, contains a trace of isomer with $R^1 = R^2 = 4\text{-}MeC_6H_4$, $R^3 = H$. [f] Equilibrated sample, contains some of isomer with $R^1 = R^3 = 4\text{-}MeC_6H_4$, $R^2 = H$. [g] Mixture of isomers. Prepared from 91% *trans*-, 9% *cis*-1-phenyl-2-deuteriocyclopropane. [h] Initially prepared sample, contains equal amount of complex with $R^1 = Ph$, $R^2 = H$, $R^3 = D$. [i] Equilibrium mixture with above compounds.

peaks which grow or decrease in intensity as isomerization proceeds can be assigned to a specific isomer (e.g., Figure 2). The data given in Tables I and II and in Figures 1 and 2 illustrate how structural assignments are made. Once assignments are made, relative abundances of isomers can be obtained by integration of the ^1H NMR spectra.

The stereochemistry about the ring was usually obtained by displacing the cyclopropane from platinum by reaction with a soft ligand and then determining the stereochemistry of the cyclopropane by GLC or NMR techniques. Results are given in Table III. Reactions of the platinacyclobutanes derived from *trans*-1,2-diphenylcyclopropane with cyanide ion were studied first, but considerable amounts of *cis*-1,2-diphenylcyclopropane were sometimes obtained, the amount depending on the particular complex and on the reaction conditions. The platinacyclobutanes could not contain such large amounts of other isomers, since they would have been detected by NMR spectroscopic studies (for example, the cis and trans isomers would give separate resonances in the ^{13}C NMR spectra). Thus it became clear that trans → cis isomerization occurred during the reductive elimination of the cyclopropane derivative from platinum. The isomerization was greatest when cyanide in aqueous solution was added to the platinacyclobutane in an immiscible organic solvent. Fortunately, treatment of the complexes with triphenylphosphine gave pure *trans*-1,2-diphenylcyclopropane along with $[PtCl_2(PPh_3)_2]$, and this method of releasing the cyclopropane was used generally. In almost all cases the parent cyclopropane was recovered unchanged, from both initially prepared samples of platinacyclobutanes and samples heated to equilibration or, when isomerization was not observed, heated under conditions where the equilibration was known to occur in similar complexes.[11,15] The only exception arose in the platinacyclobutane from *trans*-1,2-di-4-tolylcyclopropane where a small amount (4%) of the cis isomer was formed (Table III). It is possible that 4% of the cis isomer could be present in the platinacyclobutane, since this would probably not be seen in the NMR spectra of mixtures, but we believe that isomerization most probably occurs on liberation with triphenylphosphine. Since the proportion of the cis isomer from initially formed and isomerized platinacyclobutanes was the same, it is unlikely that the cis–trans interconversion occurs during the skeletal isomerization, but the possibility that 4% trans → cis isomerization occurs during the initial reaction of the cyclopropane with Zeise's dimer cannot be excluded.

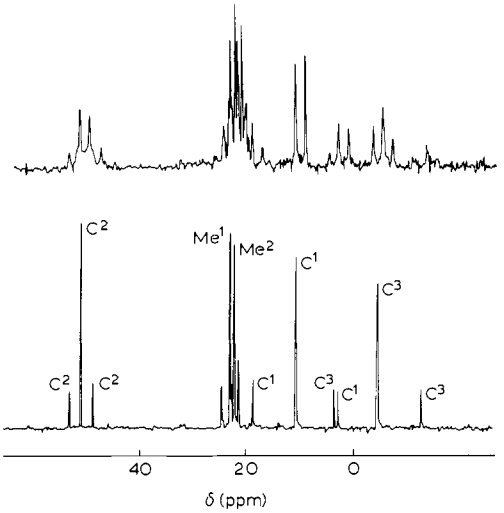


Figure 1. ^{13}C NMR spectra (25.2 MHz) of $[PtCl_2(C^1HMe^1C^2HMe^2C^3H_2)(C_5H_5N)_2]$: (a) below, ^1H-decoupled spectrum; (b) above, off-resonance decoupled spectrum.

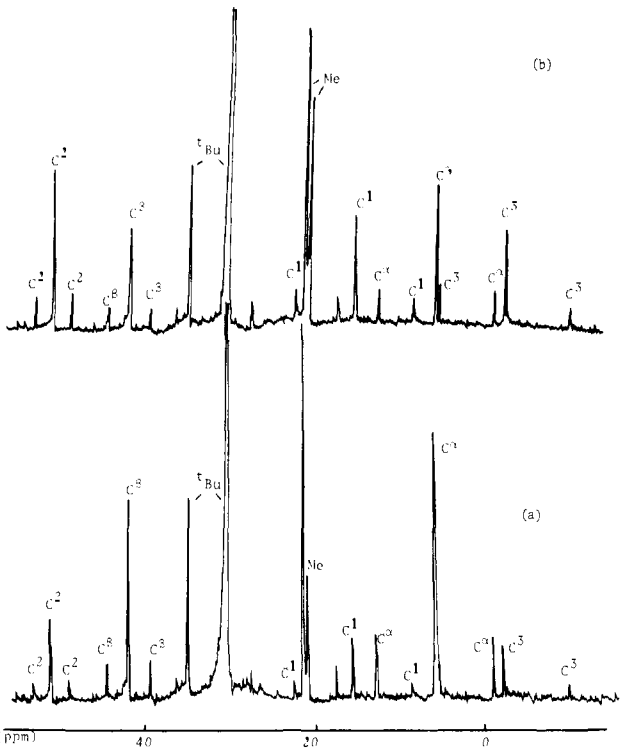


Figure 2. ^{13}C NMR spectra (25.2 MHz) of $\{PtCl_2[C^1H(4\text{-}MeC_6H_4)C^2H(4\text{-}MeC_6H_4)C^3H_2](4\text{-}t\text{-}BuC_5H_4N)_2\}$ (Ie) and $\{PtCl_2[C^\alpha H(4\text{-}MeC_6H_4)C^\beta H_2C^\alpha H(4\text{-}MeC_6H_4)](4\text{-}t\text{-}BuC_5H_4N)_2\}$ (IIb): (a) first-formed mixture, largely IIb; (b) spectrum after 1 day, largely Ie.

The assignment of stereochemistry to the platinacyclobutanes on the basis of the cyclopropane derivatives recovered by treatment with triphenylphosphine is open to criticism, since the parent cyclopropane would also be recovered in a process involving *inversion* of stereochemistry at both ring opening and reductive elimination of cyclopropane stages. However this sequence can be positively eliminated for reactions of *trans*-1,2-diarylcyclopropanes (and hence is considered most unlikely in other cases) by the following evidence. First, isomer Id, L = pyridine, has been fully characterized by X-ray crystallography to be formed from *trans*-1,2-diphenylcyclopropane with retention of stereochemistry about the ring.[32] Second, isomer IIb, L = 4-*tert*-butylpyridine, can be shown to be the initial product formed from *trans*-1,2-di-4-tolylcyclopropane by the ^1H NMR spectrum. Thus the ring CH_2 protons appear as a sharp triplet in the ^1H NMR spectrum δ 3.29 (^3J(HH) = 8.5 Hz, Table I), showing these hydrogen atoms to be equivalent as expected for the trans isomer (IIb) but not for the cis isomer. The cis isomer would give two considerably more complex resonances. Now, on insertion of platinum into the most substituted bond of *trans*-1,2-ditolylcyclopropane, a double inversion process would give IIb as observed but a single inversion would give the cis isomer. Skeletal isomerization of IIb with retention of stereochemistry would then give Ie as observed, but reductive elimination with double inversion from Ie would give *cis*-1,2-ditolylcyclopropane which was actually formed in only trace amounts. Similarly, the chemistry of the complexes derived from *trans*-1-phenyl-2-deuteriocyclopropane can only be explained if ring-opening, skeletal isomerization and reductive elimination of cyclopropane all occur with retention of stereochemistry.

Since the cis and trans couplings ^3J(HH) between ring protons are similar, it is generally not possible to deduce the stereochemistry about the PtC_3 ring by using ^1H NMR spectroscopy. However, in the platinacyclobutanes derived from *trans*-1-phenyl-2-deuteriocyclopropane, some useful results were obtained. The initially prepared 1:1 mixture of If and IIc gave a resonance centered at 4.9 ppm for the benzylidene proton (Figure 3). The resonance for IIc appeared as a doublet of doublets with ^3J(HH) values of 8.5 and 9.5 Hz, whereas that for If appeared as a doublet with ^3J(PtH) = 9.5 Hz. With the assumption that the insertion

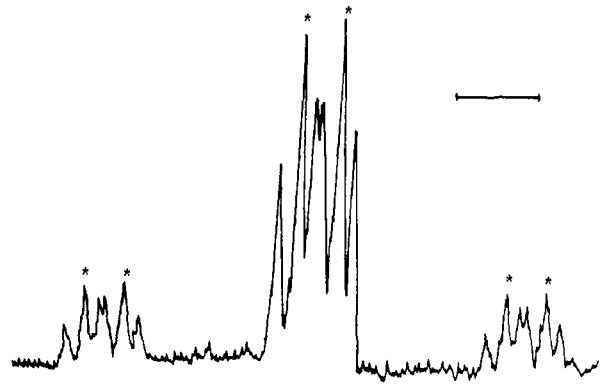
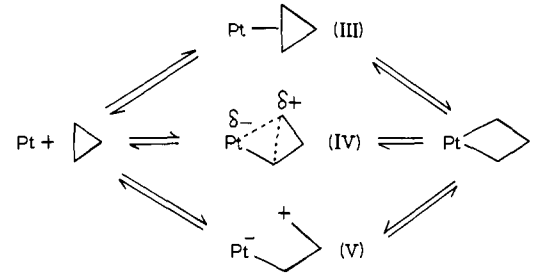


Figure 3. ^1H NMR spectrum of the benzylidene proton in $[PtCl_2(trans\text{-}CHPhCH_2CHD)(C_5H_5N)_2]$ (IIc) and $[PtCl_2(trans\text{-}CHPhCHDCH_2)(C_5H_5N)_2]$ (If). Peaks marked asterisk are due to If, and the bar represents 20 Hz.

Scheme I. Possible Mechanisms of Formation and Decomposition of Platinacyclobutanes



occurs with retention of stereochemistry, the larger coupling is therefore assigned as the trans coupling. After isomerization to the equilibrium mixture containing Ig, this signal was unchanged showing that the phenyl and deuterium in If remain mutually trans and hence that the isomerization If ⇌ IIc ⇌ If does not lead to cis–trans isomerization about the ring. We estimate that 10% of trans–cis isomerization could be detected.

Discussion

The above reactions give useful information about the mechanisms by which cyclopropanes add to or are eliminated from platinum, about the mechanism of skeletal isomerization of platinacyclobutanes and about the factors influencing the relative stabilities of isomeric platinacyclobutanes. These will be dealt with in turn.

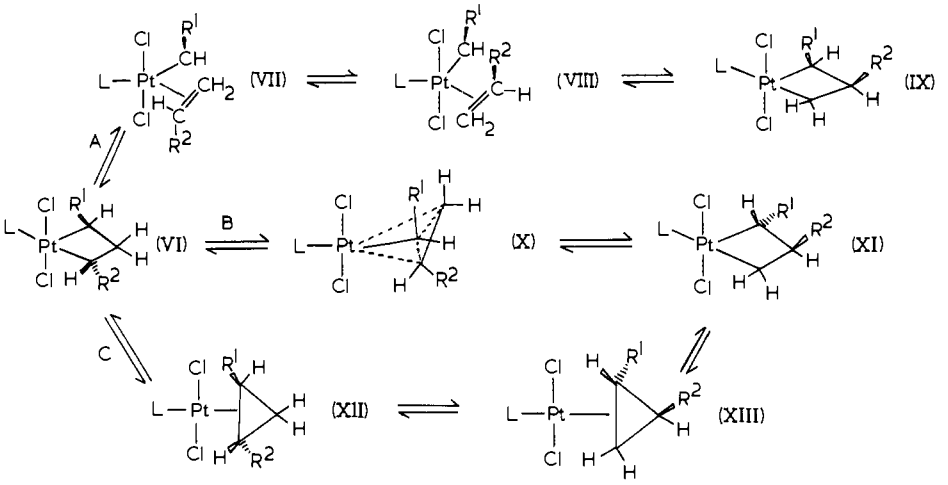
Addition and Elimination of Cyclopropanes to and from Platinum. The mechanisms which have been seriously considered for these reactions are shown in Scheme I ($Pt = PtCl_2L_n$; L = ligand; n = 1 or 2).[8,19,20]

An intermediate such as V would be able to undergo rotation about the C–C bonds, and this would lead to cis–trans isomerization about the ring in complexes derived from cis- or trans-1,2-disubstituted cyclopropanes. Since this form of isomerization did not occur in general, this intermediate can be excluded. However, in the reactions using cyanide to displace the cyclopropane derivatives from platinum (Table III) some cis–trans isomerization was observed and the intermediate (V) may well be implicated under these conditions.

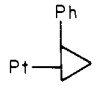
The observation that platinum inserts into the most substituted bond of *trans*-1,2-di-4-tolylcyclopropane is surprising. It has been noted previously that platinum inserts into the most substituted bond of phenylcyclopropane,[11] and this was rationalized either

(19) R. D. Gillard and M. F. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 102 (1973).
(20) R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organomet. Chem.* **150**, 295 (1978).

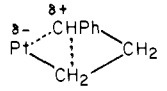
Scheme II. Possible Mechanisms of Isomerization of Platinacyclobutanes



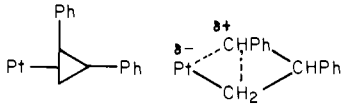
in terms of the aryl group coordinating to platinum first and hence forming the edge complex



with the phenyl group α to platinum, or in terms of an intermediate of type IV which would give the most stable carbocation[21]



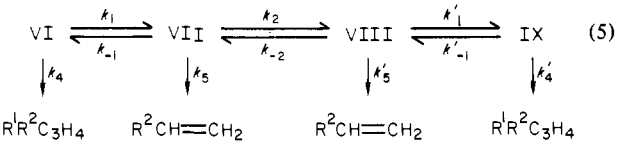
By similar reasoning, the preferred intermediates from diphenylcyclopropane would be expected to be



respectively, and insertion into the least substituted bond would be expected. The ring opening of cyclopropanes by other electrophiles does not always occur in a predictable manner.[21] For example, mercury(II) reacts with *cis*-1,2-diphenylcyclopropane at the most substituted bond but with the trans isomer at the least substituted bond.[23]

Skeletal Isomerization of Platinacyclobutanes. Three mechanisms have been considered for the skeletal isomerization and are shown in Scheme II.[11-14] It is known that pyridine dissociation precedes isomerization,[11] and the first intermediate (VI) is written as a square-pyramidal rather than trigonal-bipyramidal species in accordance with predictions and known structures for d^6 complexes.[24]

In mechanism A the ring breaks down to give a trigonal-bipyramidal carbene–alkene–platinum(II) species, VII, which undergoes rotation about the platinum–alkene bond to give VIII which then cyclizes to give IX. In the simplest mechanism, there could, but not necessarily, be cis–trans isomerization about the ring as illustrated in Scheme II. The results clearly show that such cis–trans isomerization does not occur, a result which has independently been observed by Casey and co-workers.[12] For this mechanism to be correct, the alkene and carbene ligands in VII must rotate in unison in order for the substituents R^1 and R^2 to remain mutually trans. There is a little data about barriers to rotation about platinum–alkene or platinum–carbene bonds in five-coordinate complexes but, in the more usual square-planar complexes, rotation about platinum–alkene bonds occurs more readily than about platinum–carbene bonds.[26] Similar five-coordinate intermediates are involved in the skeletal isomerization reactions[11] and in the thermal decomposition of platinacyclobutanes,[10] and a simplified kinetic analysis is given in eq 5. (See Scheme II for structures; $R^1R^2C_3H_4$ may be a cyclopropane or alkene derivative.)



(5)

Since the skeletal isomerization reactions are considerably faster than the thermal decomposition reactions, clearly the rate constants k_1, k_{-1}, k_2, k_{-2}, k'_1, and k'_{-1} are considerably greater than k_4, k'_4, k_5, and k'_5. In addition, if mechanism A is correct, then k_4[VI] and k'_4[IX] must be much greater than k_5[VII] and k'_5[VIII], since the alkene $R^2CH{=}CH_2$ is only rarely a product of thermal decomposition of platinacyclobutanes. Five-coordinate alkene complexes of platinum(II), which may be considered as models for VII and VIII, are known, but, unless the alkene carries electronegative substituents or there is a chelate ligand present, ligand dissociation is usually rapid[25] and k_5 and k'_5 would be expected to be comparable in magnitude with k_4 and k'_4. For mechanism A to be correct it seems likely then that the stationary state concentrations of the carbene–alkene intermediates, VII and VIII, must be much lower than those of VI and IX.

Mechanism C involves reaction to give an edge complex, XII, followed by "edge" to "edge" isomerization to give XIII and then ring opening to give XI. Intermediates analogous to XII and XIII have been proposed during formation or thermal decomposition of platinacyclobutanes,[10,20] and the mechanism would lead to retention of stereochemistry about the ring, as observed.

Mechanism B is a concerted process in which the platinum atom interacts directly with the β-carbon atom, and a strongly puckered ring results in which the necessary C–C bond cleavage and for-

(21) That the charge separation in such a species is probably small is indicated by dependence of rate of ring opening on X in the cyclopropanes $4\text{-}XC_6H_4C_3H_5$. For platinacyclobutane formation $k(X{=}EtO)/k(X{=}H) \approx 8$,[20] while for ring opening by mercury(II) acetate, where a large charge separation is assumed, $k(X{=}MeO)/k(X{=}H) \approx 350$. R. J. Quellette, R. D. Robins, and A. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 1619 (1968). The C–C bonds adjacent to the phenyl group are weaker than the unsubstituted C–C bond in phenylcyclopropane, and this could also affect the point of insertion.

(22) A. DeBoer and C. H. DePuy, *J. Am. Chem. Soc.*, **92**, 4008 (1970). L. N. Ferguson, "Highlights of Alicyclic Chemistry", Part I, Franklin, New Jersey, 1973, pp 224–230.

(23) Yu. S. Shabarov and S. N. Bernenko, *Zh. Obshch. Khim.*, **43**, 2330 (1973); Yu. S. Shabarov, L. D. Sychkova, S. G. Bandaev, and O. A. Subbotin, *ibid.*, **45**, 2300 (1975).

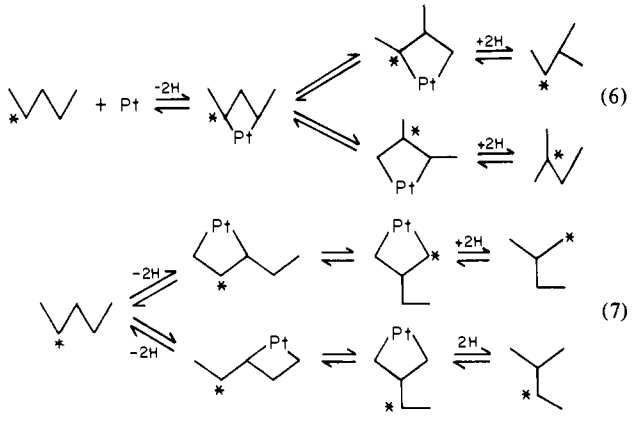
(24) M. Elian and R. Hoffmann, *Inorg. Chem.*, *14*, 1058 (1975); H. D. Empsall, E. M. Hyde, E. Mentzner, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 2285 (1977).

(25) H. C. Clark and L. E. Manzer, *J. Am. Chem. Soc.*, **95**, 3813 (1973); G. Natile, L. Maresca, L. Cattalini, U. Belluco, P. Uguagliati, and U. Croatto, *Inorg. Chim. Acta*, **20**, 49 (1976); I. Al-Najjar and M. Green, *J. Chem. Soc., Chem. Commun.*, 212 (1977); N. Chaudhury, M. G. Kekre, and R. J. Puddephatt, *J. Organomet. Chem.*, **73**, C17 (1974).

(26) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971); J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1776 (1972).

mation can occur together. The proposed intermediate X bears a strong resemblance to the carbene–alkene complex (VII) but, since complete C–C bond cleavage does not occur in mechanism B, the stereochemistry about the ring is retained.[27] The hypothetical intermediate needed to interconvert the "edge complexes" XII and XIII would also need to have the cyclopropane essentially sideways on to platinum and would also bear a strong resemblance to X. In this sense mechanism B may be considered to be intermediate between mechanisms A and C. Theoretical studies would be valuable to assess the relative energies of the proposed intermediates. As a further analogy with conventional cyclopropane chemistry, XII and XIII are "edge-metalated" cyclopropanes while X is closer to a "corner-metalated" cyclopropane but with additional interaction between the metal and the other two carbon atoms.[22]

These skeletal isomerization reactions have relevance to the mechanism of alkene metathesis and also to the isomerization and cracking hydrocarbons by the bond-shift process over heterogeneous platinum catalysts. Species resembling platinacyclobutanes but with several platinum atoms involved have been proposed,[28] but a simpler scheme can be proposed on the basis of the known isomerization of monomeric platinacyclobutanes. This is shown in eq 6 and 7 to interpret the labeling experiments of Gault on pentane to isopentane reaction (the asterisk = ^{13}C labeled carbon).[28,29]



In a typical isomerization the ratio of 2-methylbutane-*1*-^{13}C:-*2*-^{13}C:*3*-^{13}C was 0.12:0.40:0.48, which is consistent with the reactions of eq 5 and 6 occurring at a relative rate of ca. 3.3:1. The isomerization of 2-methylbutane or 2-methylpentane over platinum[28] can be interpreted in a similar way, and again the initial platinacyclobutane appears to be formed preferentially by attack of platinum at tertiary > secondary > primary CH bonds.

Cracking of hydrocarbons could also involve C–C cleavage within the platinacyclobutane intermediates, by a mechanism analogous to that currently accepted for alkene metathesis and shown to be possible in model platinacyclobutanes.[10]

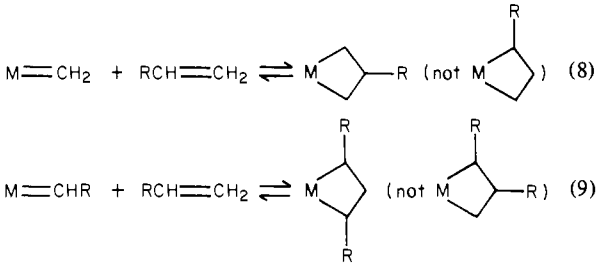
Relative Stabilities of Isomeric Platinacyclobutanes. Although skeletal isomerization of platinacyclobutanes is not always observed experimentally, there is strong evidence arising from the chemistry that such reactions are general for all platinacyclobutanes.[9,11-15,30] When the platinacyclobutane ring carries alkyl substituents, the isomerization appears to be rapid and a thermodynamic equilibrium is always present[15] whereas, with aryl substituents, the isomerization is often slow enough to be observed experimentally.[11-14] Table IV gives a list of known equilibrium constants, and some general comments are given below.

In general, aryl groups have a higher tendency than alkyl groups to occupy the α position on the ring, and this must be an electron effect. As examples to illustrate this effect, the complexes from trans-1,2-disubstituted cyclopropanes exist as a mixture of 1,3- and 1,2-disubstituted (propane-1,3-diyl)platinum complexes with phenyl substituents but only the 1,2-isomer with methyl substituents, and the platinacyclobutane from *trans*-1-methyl-2-phenylcyclopropane exists largely as the (*trans*-1-phenyl-2-methylpropane-1,3-diyl)platinum isomer.

Steric effects favor the isomer with the bulky substituents(s) in the β position. Thus in platinacyclobutanes from alkylcyclopropanes, only with the methyl derivative is the (1-methylpropane-1,3-diyl)platinum isomer sufficiently abundant in the equilibrium mixture to be detected.[8,9,16]

In order to investigate the steric effects more fully, we have studied space-filling models of platinacyclobutanes $[PtCl_2(C_5H_5N)_2(Ph_2C_3H_4)]$.[31] The α-phenyl substituent must mesh with the pyridine ligands and has little rotational freedom. The *trans*-1,2-diphenyl isomer appears most stable, and the β-phenyl group has some rotational freedom as expected from the X-ray structure determination where two isomers with the β-phenyl group parallel or perpendicular to the ring were found.[32] The *cis*- and *trans*-1,3-diphenyl isomers are less stable due to increased steric interactions of α-phenyl groups with the pyridine and chloride ligands and not due to 1,3-transannular interactions which have often been assumed to dominate in other metallacyclobutanes.[33] Due to the presence of long Pt–C bonds, the transannular bond distances in platinacyclobutanes are longer than in cyclobutane and hence the transannular steric interactions are also less than in cyclobutanes. We were unable to make the *cis*-1,2-diphenyl isomer due to strong steric effects between the ring substitutents and between ring substituents and pyridine and chloride ligands. Overall, the steric effects predicted are cis-1,2 ≫ cis-1,3 > trans-1,3 > trans-1,2, and this is fully consistent with the experimental results.

The selectivity and stereochemistry of alkene metathesis have often been discussed in terms of relative stabilities of possible intermediate metallacyclobutanes.[5,33] For example, it is known that terminal alkenes undergo degenerate metathesis very much faster than productive metathesis. The chain-carrying carbene could be M=CH_2 or M=CHR, and the reactions of eq 8 and 9 would lead to degenerate metathesis only.[34]



If the selectivity is determined by the thermodynamic stability of the metallacyclobutane, the reaction of eq 8 would be predicted to occur as shown, but we would predict that the reaction of eq 9 would give M(*trans*-CHRCHRCH$_2$) as the most stable metallacyclobutane and this would lead to productive metathesis,

(27) A related argument has been proposed by others.[12]

(28) F. Garin and F. G. Gault, *J. Am. Chem. Soc.*, **97**, 4466 (1975); A. O'Cinneide and F. G. Gault, *J. Catal.*, **37**, 311 (1975). The addition and loss of 2 H atoms is common at Pt surfaces and formally involves insertion of Pt into CH bonds followed by migration of H atoms on the surface. Electronic differences between the platinum(IV) metallacyclobutanes studied here and the proposed Pt(II) species in the catalysis weaken this analogy.

(29) A very similar mechanism has recently been proposed by Parshall and co-workers. The only significant difference is that Parshall assumes mechanism A for the skeletal isomerization step, whereas we feel that the balance of evidence does not favor this mechanism. G. W. Parshall, T. Herskovitz, F. N. Tebbe, A. D. English, and J. V. Zeile in "Fundamental Research in Homogeneous Catalysis", Vol. 3, M. Tsutsui, Ed., Plenum Press, New York, 1979.

(30) B. M. Cushman and D. B. Brown, *J. Organomet. Chem.*, **152**, C42 (1978); T. H. Johnson and S.-S. Cheng, *J. Am. Chem. Soc.*, **101**, 5277 (1979).

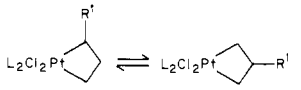
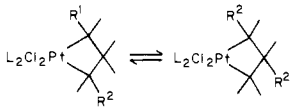
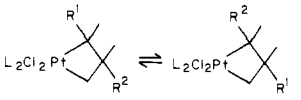
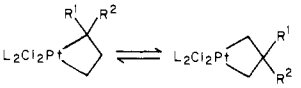
(31) Using CPK models with bond angles at platinum the same as found for $[PtCl_2(trans\text{-}CHPhCHPhCH_2)(C_5H_5N)_2]$.[32]

(32) J. A. McGinnety, *J. Organomet. Chem.*, **59**, 429 (1973).

(33) For summaries see: T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975); C. P. Casey, L. D. Albin, and T. J. Burkhardt, *ibid.*, **99**, 2533 (1977); M. Leconte and J. M. Basset, *ibid.*, **101**, 7296 (1979); C. P. Casey, S. W. Polichnowski, A. J. Shusterman, and C. R. Jones, *ibid.*, **101**, 7282 (1979). The last two articles discuss alternative interactions also.

(34) M. T. Mocella, M. A. Busch, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1283 (1976).

Table IV. Equilibrium Constants, K, for Isomerization of Platinacyclobutanes

reaction	L	R^1	R^2	K
	CD_3CN	Me		2.4
	C_5H_5N	Me		5.7
	C_5H_5N	Et		*a*
	C_5H_5N	Ph		2.3
	$2\text{-}MeC_5H_4N$	Ph		*a*
	$4\text{-}MeC_5H_4N$	Ph		1.2
	C_5H_5N	$4\text{-}MeC_6H_4$		20
	C_5H_5N	$2\text{-}MeC_6H_4$		*a*
	C_5H_5N	$4\text{-}MeOC_6H_4$		20
	C_5H_5N	Me	Me	*a*
	$4\text{-}t\text{-}BuC_5H_4N$	Ph	Ph	6
	$4\text{-}t\text{-}BuC_5H_4N$	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	4
	C_5H_5N	Ph	Me	*a*
	C_5H_5N	Me	Ph	2.8
	C_5H_5N	Me	Me	*a*

[a] Large K, minor isomer not detected.

Table V. Analytical Data for the Complexes

complex	C		H		N	
	calcd	found	calcd	found	calcd	found
$[PtCl_2(CHMeCHMeCH_2)(C_5H_5N)_2]$	36.4	36.3	4.0	4.0	5.7	5.5
$[PtCl_2(CHMeCHMeCH_2)(phen)]$[a]	39.5	39.4	3.5	3.7	5.4	5.7
$[PtCl_2(CHPhCHMeCH_2)(C_5H_5N)_2]$	43.2	42.7	4.0	3.5	5.0	5.3
$[PtCl_2(trans\text{-}CHPhCH_2CHPh)]$	39.1	39.3	3.0	3.4		
$[PtCl_2(CHPhCH_2CHPh)(C_5H_5N)_2]$	48.5	48.7	3.9	3.9	4.5	4.1
$[PtCl_2(CHPhCH_2CHPh)(t\text{-}BuC_5H_4N)_2]$	54.2	54.2	5.5	5.3	3.8	3.7
$\{PtCl_2[CH(tol)CH_2HC(tol)](t\text{-}BuC_5H_5N)_2\}$[b]	55.5	55.0	5.8	5.9	3.7	3.8

[a] phen = 1,10-phenanthroline. [b] tol = $4\text{-}MeC_6H_4$.

giving *trans*-CHR=CHR as well as $RCH{=}CH_2$ on decomposition. We might then predict that $M{=}CH_2$ is the chain-carrying carbene complex. As a cautionary note, it should be noted that skeletal isomerization of platinacyclobutanes usually occurs faster than decomposition of organic fragments and that the organic products often appear to be formed from the *least* stable platinacyclobutane which can be formed.[9,15,16,35]

However, the platinacyclobutanes are useful in allowing the model of selectivity of alkene metathesis on the basis of the stability of isomeric metallacyclobutanes with chain-carrying M=CHR groups to be rejected.

Many of the differences between the reactions of platinacyclobutanes and presumed tungstacyclobutanes formed in alkene metathesis reactions may be due to the different relative stabilities with respect to carbene–alkene complexes. Thus in platinum complexes it seems that the metallacyclobutane is the more stable (eq 5 and subsequent discussion), but in tungsten complexes it is possible that the carbene–alkene complex is the more stable. If this is the case, then platinacyclobutanes will not be good models for intermediates in alkene metathesis reactions.

Experimental Section

Synthesis of Cyclopropane Derivatives. *trans*-1-Methyl-2-phenylcyclopropane was prepared from *trans*-β-methylstyrene by using the Simmons–Smith reaction described previously.[11] Largely *trans*-1-phenyl-2-deuteriocyclopropane (91% trans, 9% cis) was obtained by methylene addition.[11] *cis*- and *trans*-1,2-diphenylcyclopropane were prepared by the method of Beech et al.[37] and were separated by vacuum distillation with the use of a spinning band column. *cis*- and *trans*-1,2-di-4-tolylcyclopropane were prepared in a similar way and were separated by fractional crystallization. In each case isomeric purity was confirmed by using GLC. *cis*- and *trans*-1,2-dimethylcyclopropane were commercial samples and were used without further purification.

Dichloro(*trans*-1,2-dimethylpropane-1,3-diyl)platinum(IV). This was obtained by reaction of $[Pt_2Cl_4(C_2H_4)_2]$ (0.5 g) in tetrahydrofuran (7 cm^3) with *trans*-1,2-dimethylcyclopropane (0.7 cm^3) at 50 °C for 7 h, in a flask fitted with a condenser cooled to −78 °C to prevent escape of the volatile cyclopropane. Evaporation of the solvent gave the product as a yellow solid.

Stable complexes were prepared by suspending this product (0.1 g) in CH_2Cl_2 (3 mL) and then adding the ligand slowly until a clear solution was obtained. The products were crystallized from CH_2Cl_2/pentane as white solids: $[PtCl_2(CHMeCHMeCH_2)(C_5H_5N)_2]$, mp 133 °C dec, Anal. for C, H, N; $[PtCl_2(CHMeCHMeCH_2)(phen)]$ (phen = 1,10-phenanthroline), mp 252 °C dec, Anal. for C, H, N.

When complexes were not thermally stable (L = CD_3CN, PhCN, or $2\text{-}MeC_5H_4N$), they were prepared in $CDCl_3$ solution by addition of ligand to a suspension of $\{[PtCl_2(CHMeCHMeCH_2)]_n\}$ (0.05 g) in $CDCl_3$ (0.4 cm^3) at −78 °C and were identified by low-temperature NMR spectroscopy.

Dichloro(*trans*-methylphenylpropane-1,3-diyl)platinum(IV). This was prepared from $[Pt_2Cl_4(C_2H_4)_2]$ (0.4 g) in tetrahydrofuran (7 mL) and *trans*-1-methyl-2-phenylcyclopropane (0.8 g) by reaction at 40 °C for 3 h. The product was obtained as a yellow solid on evaporation of the solvent. The pyridine complex $[PtCl_2(CHPhCHMeCH_2)(C_5H_5N)_2]$ was prepared as described above; mp 122 °C dec, Anal. for C, H, N.

Dichloro(*trans*-diphenylpropane-1,3-diyl)platinum(IV). A suspension of $[Pt_2Cl_4(C_2H_4)_2]$ (1.4 g) in anhydrous ether (30 cm^3) was heated under reflux with excess *trans*-1,2-diphenylcyclopropane (1.4 g) for 9 days, after

(35) T. H. Johnson and E. C. Hefty, *J. Org. Chem.*, **44**, 4896 (1979).
(36) J. M. Church, F. C. Whitmore, and R. V. McGrew, *J. Am. Chem. Soc.*, **56**, 178 (1973).
(37) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

which time the absence of Zeise's dimer was confirmed by ^1H NMR spectroscopy. The time needed for reaction varied with the amount of Zeises' dimer used; thus in reaction with $[Pt_2Cl_4(C_2H_4)_2]$ (0.2 g) and *trans*-1,2-diphenylcyclopropane (0.4 g) in ether (15 cm^3) the reaction was complete in 24 h. The insoluble product was filtered off, washed with ether, and dried under vacuum; yield 86%, Anal. for C, H.

Similarly, crude dichloro(*cis*-diphenylpropane-1,3-diyl)platinum(IV) was prepared from $[Pt_2Cl_4(C_2H_4)_2]$ (0.3 g) and *cis*-1,2-diphenylcyclopropane (0.5 g) in refluxing ether (20 cm^3) for 7 days.

Dichlorobis(pyridine)(*trans*-diphenylpropane-1,3-diyl)platinum(IV). Dichloro(*trans*-diphenylpropane-1,3-diyl)platinum(IV) (0.15 g) suspended in CH_2Cl_2 (5 cm^3) was treated with pyridine (ca. 0.2 g) until a clear solution was obtained. The solvent was evaporated, and the *product* was washed with pentane and dried under vacuum: yield 67%, mp 108 °C dec, Anal. for C, H, N.

Dichlorobis(4-*tert*-butylpyridine)(*trans*-diphenylpropane-1,3-diyl)platinum(IV). This was prepared in a similar way but was purified by chromatography through silica gel, eluting with CH_2Cl_2: yield 86%, Anal. for C, H, N.

Dichlorobis(4-*tert*-butylpyridine)(*trans*-1,3-di-4-tolylpropane-1,3-diyl)platinum(IV). A suspension of $[Pt_2Cl_4(C_2H_4)_2]$ (0.8 g) in anhydrous ether (30 cm^3) was heated under reflux for 3 days with *trans*-1,2-di-4-tolylcyclopropane (0.8 g). The precipitate was filtered off and suspended in CH_2Cl_2 (10 cm^3) and 4-*tert*-butylpyridine was added dropwise with stirring until a clear solution was obtained. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography through silica gel, eluting with CH_2Cl_2, and was isolated as a pale yellow solid: yield 0.82 g (80%), mp 290 °C dec, Anal. for C, H, N.

Reactions with Cyanide and Triphenylphosphine. A solution of dichlorobis(pyridine)(*trans*-diphenylpropane-1,3-diyl)platinum(IV) (25 mg) in $CHCl_3$ (3 cm^3) was heated at 45 °C for 2 days. The product was isolated and redissolved in $CHCl_3$ and then an aqueous solution of potassium cyanide (3 cm^3, 0.05 M) was added. The mixture was shaken for several minutes, then the organic layer was separated, dried with $MgSO_4$, and filtered. Analysis of the filtrate by GLC showed the presence of *trans*- and *cis*-1,2-diphenylcyclopropane in relative amounts 86% and 14%, respectively.

In reactions with triphenylphosphine, the phosphine (2 mol) was added to the platinacyclobutane (1 mol) in $CHCl_3$. The precipitate of $[PtCl_2(PPh_3)_2]$ was removed by filtration, and the filtrate was analyzed as above.

1-Phenyl-2-deuteriocyclopropane was analyzed, after displacement from the platinum complexes by triphenylphosphine, by NMR spectroscopy. The methylene groups of the cyclopropane give signals at 0.64 ppm (H atoms cis to Ph) and at 0.88 ppm (H atoms trans to Ph). In our best sample of the parent cyclopropane this ratio is 1.75:1 from which the ratio *trans*-:*cis*-1-phenyl-2-deuteriocyclopropane = 91:9. The same ratio was found in the cyclopropane formed from the initially formed and the isomerized platinacyclobutanes. Similarly, a sample containing 80% trans and 20% cis isomer gave the identical mixture on reaction of isomerized platinacyclobutane with PPh_3.

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Response of *syn*-1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene and Related Molecules to Oxidation with Ozone, Singlet Oxygen, and Triplet Oxygen. Strain and Steric Effects as Controllers of Reactivity

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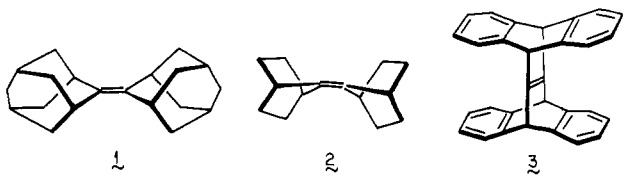
Abstract: The title compound (**4**), its 2,3-benzo derivative (**5**), and dimethyl *syn*-1,4,5,8-tetrahydro-1,4:5,8-dimethanonaphthalenedicarboxylate (**6**) have been synthesized and their reactivity toward various oxygenating agents evaluated. Whereas **4** is unreactive toward triplet oxygen, **5** experiences 80% conversion to exo epoxide **19** (55%) and diketone **20** (45%) during 28 h in benzene solution at 10 °C. By way of comparison, diester **6** is exceptionally reactive in air, giving chiefly epoxide **21**. The stereochemistry of **21** was suggested by ^{13}C NMR spectroscopy and substantiated by photocyclization to cage diester **22**. In the presence of ozone, **4** is transformed almost completely to diperoxy diketone **25** without regard for solvent polarity (pentane or ethyl acetate). When the ozonolysis is conducted in the presence of TCNE, diketone **26** is formed uniquely. To further test the ability of **4** to undergo 1,3-dipolar cycloaddition, we treated the olefin with phenyl azide. Triazoline **27** was produced; irradiation of this adduct gave aziridine **28**. Under conditions of photooxygenation with methylene blue and tetraphenylporphin as sensitizer, **4** is slowly converted to diketone **26**. With polymer-bound rose bengal as the sensitizer, photoepoxidation also is observed. Conclusions dealing with the mechanistic aspects of these reactions are presented and references are made to the possible usefulness of these uniquely structured molecules in the elucidation of transition-state geometries.

A few uniquely constructed olefinic compounds are now known in which attack by a given reagent is severely restricted to approach along a very limited number of geometric planes. As a result, usually preferred modes of reaction may be rendered inoperative and important mechanistic information may consequently be made evident. For example, the special structural features of biadamantylidene (**1**)[1] and 7,7′-binorbornylidene (**2**)[2] provide π-bond



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faces which are most open and accessible if perpendicular ($\pi^2s + \pi^2a$) attack takes place.[3] In dehydrojanusene (**3**),[4] the presence

(1) (a) Wierenga, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169. (b) Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381. (c) Numan, H.; Wierenga, J. H.; Wynberg, H.; Hess, J.; Vos, A. *J. Chem. Soc., Chem. Commun.* **1977**, 591. (d) Schuster, G. B.; Turro, N. J.; Steinmetzer, H. C.; Schaap, A. P.; Faler, G.; Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 7110. (e) Wynberg, H.; Numan, H. *Ibid.* **1977**, *99*, 603.

(2) Bartlett, P. D.; Ho, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 627.

(3) Additional examples include fenchylidene–fenchane, camphenylidene–camphenilane, and camphenylidene–adamantane: McCapra, F.; Beheshti, I. *J. Chem. Soc., Chem. Commun.* **1977**, 517.

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