Skeletal Isomerization of Platinacyclobutanes and Its Relevance to the Mechanism of Olefin Metathesis[1]

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Abstract: Skeletal isomerization of platinacyclobutane complexes is demonstrated, of the general form $[PtCl_2(CHRCH_2CH_2)L_2]$ (III) $\rightleftharpoons$ $[PtCl_2(CH_2CHRCH_2)L_2]$ (IV), R = aryl; L = nitrogen-donor ligand or tetrahydrofuran. Factors influencing the magnitude of the equilibrium constants for the reactions are discussed and steric effects are found to be dominant in favoring isomer IV. Isomerization is retarded by added ligand L and, when R = 4-tolyl and L = pyridine, the approach to equilibrium follows first-order kinetics and a linear correlation between the reciprocal of the observed rate constants and $[C_5H_5N]$ is demonstrated. A mechanism involving reversible dissociation of ligand, L, followed by skeletal isomerization of the resulting five-coordinate platinum(IV) complex is proposed. The relevance of this work to the mechanism of olefin metathesis is discussed. Methods of characterization of isomeric platinacyclobutanes using ^{13}C and ^1H NMR spectroscopy are presented.

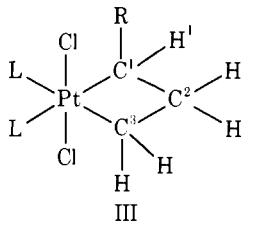
Introduction

There has been considerable interest in the chemistry of transition metallocyclobutane complexes recently, since they have been invoked as intermediates in several transition metal catalyzed reactions.[3] For example, although the mechanism of olefin metathesis is not yet certain,[4] one proposed mechanism involves the interconversion of carbene-metal-olefin complexes and metallocyclobutanes as shown in Scheme I.[5]

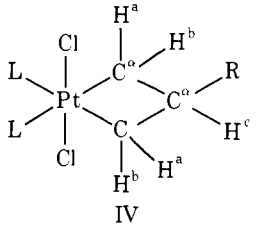
In catalytic systems the intermediates I and II will of course be short lived, but, in systems where the metallocyclobutanes are stable, isomerization I $\rightleftharpoons$ II might be expected to occur readily if this mechanism is correct. We have investigated this form of isomerization for the platinum(IV) derivatives, which may be prepared directly from arylcyclopropanes (eq 1).[6]

$$2[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2] + 4RCH\langle{}^{CH_2}_{CH_2}\rangle \longrightarrow [\{PtCl_2(C_3H_5R)\}_4] + 4C_2H_4 \quad (1)$$

The initially formed tetramers are difficult to characterize but they can readily be converted to the more stable and more soluble pyridine complexes, which may have either structure III or IV, L = C_5H_5N.



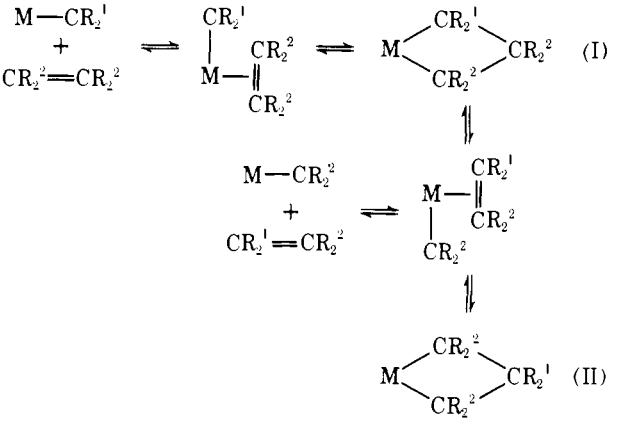
III



IV

When we began this work, there was already some indication that isomerization III $\rightleftharpoons$ IV might occur. Thus, treatment of the tetramer, $[\{PtCl_2(PhC_3H_5)\}_4]$, derived from phenylcyclopropane with hydrogen gave 56% 1-phenylpropane, 30% 1-cyclohexylpropane, and 14% 2-phenylpropane which, if hydrogenolysis occurs without isomerization, would indicate that the tetramer contained 86% 1-phenylpropane-1,3-diylplatinum(IV) and 14% 2-phenylpropane-1,3-diylplatinum(IV) linkages.[7] However, direct characterization of the pyridine adduct by NMR spectroscopy showed it to consist largely of the isomer with structure IV. The authors believed that isomerization III $\rightleftharpoons$ IV was unlikely and hence that the tetramer also contained the 2-phenylpropane-1,3-diylplatinum(IV) structure, and that isomerization occurred during hydrogenolysis. In a preliminary communication[8] we reported that these data are explained instead by the isomerization III $\rightleftharpoons$ IV, a form of skeletal isomerization which has not previously been observed in organometallic chemistry, and we now present more details of this reaction.

Scheme I



Results

The experimental evidence for skeletal isomerization of platinacyclobutane complexes derived from phenylcyclopropane will be presented first, followed by similar reactions of compounds derived from other arylcylopropanes and then by mechanistic studies of these reactions.

Preparation and Characterization of Platinacyclobutanes from Phenylcyclopropane. Tetrameric $[\{PtCl_2(C_3H_5Ph)\}_4]$ was prepared by reaction of phenylcyclopropane with $[\{PtCl_2(C_2H_4)\}_2]$ in diethyl ether or tetrahydrofuran at 40 °C, using the shortest possible reaction times in order to minimize isomerization of the initially formed isomer. The formation of monomeric derivatives from this tetramer is illustrated in Scheme II. Again the mildest conditions were used to minimize isomerization. For example, the complex III, R = Ph; L = C_5H_5N, was prepared by suspending the tetramer in dichloromethane, adding sufficient pyridine to give a clear solution, and then immediately evaporating the solvent under vacuum and washing the product with *n*-pentane. The complex was

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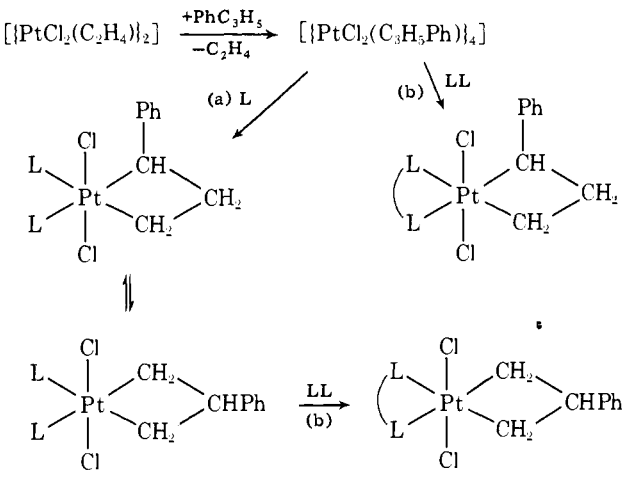
Scheme II

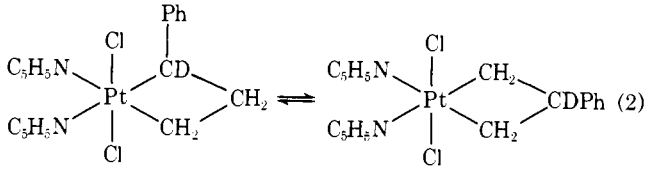


(a) L = C_5H_5N or 4-MeC_5H_4N
(b) LL = $Me_2NCH_2CH_2NMe_2$ or 2,2'-bipyridyl

then characterized spectroscopically without further purification.

The ^1H and ^{13}C NMR spectra were particularly valuable in characterizing the complexes. Thus Figure 1a shows the ^1H NMR spectrum of the initially formed complex III, R = Ph; L = C_5H_5N, and the characteristic feature in a complex spectrum is the triplet at δ 4.93 due to H^1 with satellites due to coupling with ^{195}Pt, $^2J(PtH)$ = 101 Hz. The peaks in the ^1H NMR spectrum due to this isomer slowly decayed and new peaks appeared until the spectrum in Figure 1b was obtained. This spectrum is largely due to isomer IV, R = Ph; L = C_5H_5N, and is characterized by an intense doublet due to protons H^a and H^b (whose chemical shifts are almost identical), with satellites due to coupling with ^{195}Pt, $^2J(PtH)$ = 82 Hz. By integration of the NMR spectrum, an approximate value of the equilibrium constant for the isomerization III $\rightleftharpoons$ IV could be obtained, and is included together with the ^1H NMR data in Table I.

In order to prove that a skeletal isomerization of the platinacyclobutane ring rather than a phenyl migration was involved in these reactions, the similar isomerization of the analogous complex derived from 1-deuterio-1-phenylcyclopropane was studied. Figure 1c shows the ^1H NMR spectrum of the equilibrium mixture of isomers and, from the absence of a signal due to H^c of IV, R = Ph; L = C_5H_5N, and the collapse of the doublet due to H^a and H^b to a singlet, this clearly shows that the isomerization occurs as shown in eq 2.



(2)

The isomerization III $\rightleftharpoons$ IV, R = Ph; L = C_5H_5N, could be followed more clearly using ^{13}C NMR spectroscopy.[9] Thus isomer III gives three resonances in the ^{13}C NMR spectrum due to the metallocyclobutane carbon atoms C^1, C^2, and C^3 whereas in IV the two carbon atoms bound directly to platinum are equivalent and only two resonances due to C^α and C^β are observed. Figure 2 shows the change in the ^{13}C NMR spectrum when III isomerizes to IV, R = Ph; L = C_5H_5N, and, since each carbon atom gives rise to a singlet with satellites due to coupling with ^{195}Pt, the evidence for the isomerization is clear-cut. Full details of the ^{13}C NMR spectra are given in Table II. The only problem in studying the isomerization reactions using ^{13}C NMR spectroscopy is that some isomerization occurred during the time required to accumulate the spectrum of III.

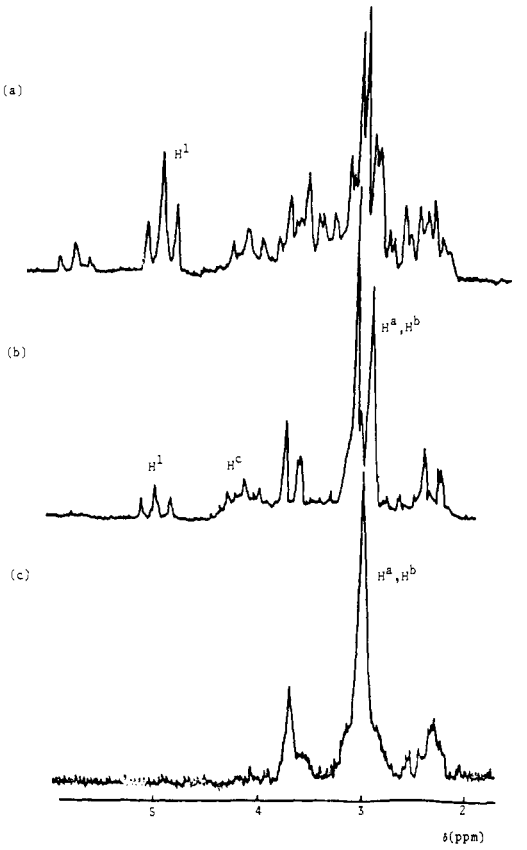


Figure 1. ^1H NMR spectra (60 MHz) in $CDCl_3$ of complexes $[PtCl_2(PhC_3H_5)(C_5H_5N)_2]$: (a) first-formed isomer, largely III; (b) equilibrium mixture of III and IV; (c) equilibrium mixture of products of eq 2.

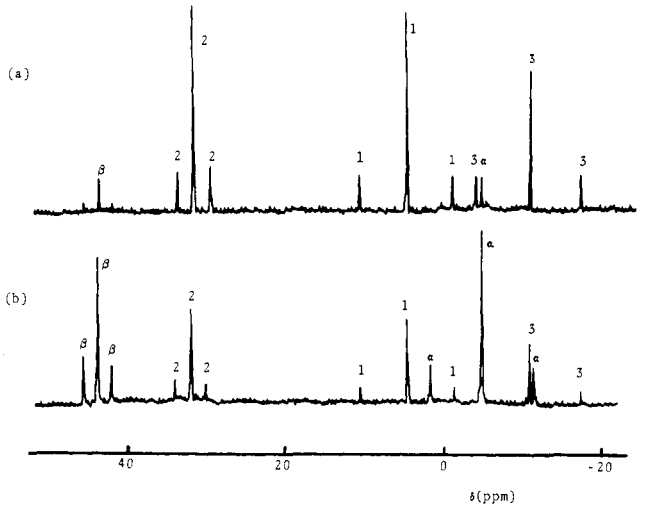


Figure 2. ^{13}C NMR spectra (25.3 MHz) in $CDCl_3$ of complexes $[PtCl_2(PhC_3H_5)(C_5H_5N)_2]$: (a) first-formed isomer, largely III; (b) equilibrium mixture of III and IV.

Very similar results were obtained for the isomerization of III $\rightleftharpoons$ IV, R = Ph; L = 4-MeC_5H_4N or C_5H_5N, both systems reaching equilibrium at 50 °C in ca. 45 min. However, treatment of $[\{PtCl_2(C_3H_5Ph)\}_4]$ with 2-methylpyridine gave a complex which was difficult to purify, but which, on the evidence of the NMR spectrum, had structure IV, R = Ph; L = 2-MeC_5H_4N. Thus it seems that the bulkier ligand 2-methylpyridine causes rapid isomerization III $\rightleftharpoons$ IV and that the equilibrium is displaced toward isomer IV.

Table I. ^{1}H NMR Data for Complexes III and IV[a] and Equilibrium Constants, K, for Reaction III $\rightleftharpoons$ IV

		isomer III[b]			isomer IV				
R	L	$\delta(H^1)$, ppm	$^3J(H^1H^2)$, Hz	$^2J(PtH^1)$, Hz	$\delta(H^aH^b)$, ppm	$^3J(H^aH^c)$, Hz	$^2J(PtH^a)$, Hz	$\delta(H^c)$, ppm	K[c]
C_6H_5	C_5H_5N	4.93	9	101	2.95	9	82	4.05	2.3
C_6H_5	4-MeC_5H_4N	4.88[d]	9	100	2.94[e]	9	81	4.05	1.2
C_6H_5	2-MeC_5H_4N				3.05[f]	9	80	3.60	*g*
C_6H_5	C_4D_8O[h]	5.17	9	113	3.10	8	*i*	*i*	
C_6H_5	$^1/_2$ tmed	5.10[j]	9	101	3.43[k]	8	84	4.07	
4-MeC_6H_4	C_5H_5N	4.90[l]	8	102	3.00[m]	10	80	3.67	20
4-MeC_6H_4	C_4D_8O	5.00[n]	8	120	3.07[o]	10	80	*i*	
2-MeC_6H_4	C_5H_5N	4.90[p]	10	*g*	2.97[q]	9	80	3.60	*g*
4-$MeOC_6H_4$	C_5H_5N	5.03[r]	9	100	2.96[s]	9	83	*i*	20
4-$EtOC_6H_4$	C_5H_5N	4.90[t]	9	100	2.90[u]	10	82	3.65	

[a] Solvent $CDCl_3$ unless otherwise stated. [b] Peaks due to $C^2H_2C^3H_2$ protons appeared as complex multiplet in region δ 2–4.4. [c] In $CDCl_3$ at 35 °C. [d] δ(MeC) 2.31 ppm, s. [e] δ(MeC) 2.40 ppm, s. [f] δ(MeC) 2.90 ppm, s. [g] Too large to be determined; isomer III not detected. [h] Solvent C_4D_8O. [i] Not resolved. [j] Solvent C_6D_6, δ(MeN) 2.44 ppm, ^3J(PtH) = 14 Hz; $\delta(CH_2N)$ 1.85, 1.72 ppm, ^3J(PtH) = 12 Hz. [k] Solvent C_6D_6, δ(MeN) 1.93, 1.95 ppm, ^3J(PtH) = 12 Hz; $\delta(CH_2N)$ 1.64 ppm, ^3J(PtH) = 7 Hz. [l] δ(MeC) 2.13 ppm, s. [m] δ(MeC) 2.33 ppm, s. [n] δ(MeC) 2.10 ppm, J(PtH) = 8 Hz, solvent C_4D_8O. [o] δ(MeC) 2.28 ppm, s. [p] δ(MeC) 2.44 ppm, s. [q] δ(MeC) 2.40 ppm, s. [r] δ(MeO) 3.86 ppm, s. [s] δ(MeO) 3.90 ppm, s. [t] δ(Me) 1.40 ppm, $\delta(CH_2O)$ 4.02 ppm, ^3J(HH) = 7 Hz. [u] δ(Me) 1.40 ppm, $\delta(CH_2O)$ 4.04 ppm, ^3J(HH) = 7 Hz.

Table II. ^{13}C NMR Data for Complexes III and IV[a]

		isomer III						isomer IV			
R	L	$\delta(C^1)$, ppm	$^1J(PtC^1)$, Hz	$\delta(C^2)$, ppm	$^2J(PtC^2)$, Hz	$\delta(C^3)$, ppm	$^1J(PtC^3)$, Hz	$\delta(C^\alpha)$, ppm	$^1J(PtC^\alpha)$, Hz	$\delta(C^\beta)$, ppm	$^2J(PtC^\beta)$, Hz
C_6H_5	C_5H_5N	5.63	338	35.1	112	−11.3	355	−4.88	359	48.10	101
C_6H_5	4-MeC_5H_4N	4.29[b]	330	37.6	114	−11.8	372	−5.13[c]	358	48.11	99
C_6H_5	$^1/_2$ tmed	7.15[d]	329	38.0	112	−7.6	359	−3.10[e]	370	*f*	*f*
4-MeC_6H_4	C_5H_5N	5.80[g]	323	35.3	112	−11.5	366	−4.30[h]	370	47.8	99
4-MeC_6H_4	C_4D_8O	6.07[i]	397	34.9	127	−13.9	429	−7.57[j]	418	47.0	111
4-$EtOC_6H_4$	C_5H_5N	5.75[k]	320	35.5	115	−11.9	360	−4.30[l]	360	46.97	105

[a] Solvent $CDCl_3$ unless otherwise stated. [b] $\delta(CH_3C)$ 21.04 ppm. [c] $\delta(CH_3C)$ 21.04 ppm. [d] $\delta(CH_3N)$ 50.23, 49.79, 49.55, 49.33 ppm; $\delta(CH_2N)$ 62.35, 60.06 ppm. [e] $\delta(CH_2N)$ 61.54 ppm. [f] Obscured by CH_3N peaks. [g] $\delta(CH_3C)$ 21.05 ppm. [h] $\delta(CH_3C)$ 21.43 ppm. [i] $\delta(CH_3)$ 19.91 ppm. [j] $\delta(CH_3)$ 20.5 ppm. [k] $\delta(CH_3)$ 14.53 ppm; $\delta(CH_2O)$ 63.06 ppm. [l] $\delta(CH_3)$ 14.72 ppm; $\delta(CH_2O)$ 63.15 ppm.

In contrast, with the bidentate ligand N,N,N′,N′-tetramethylethylenediamine (tmed), the compound $[\{PtCl_2(C_3H_5Ph)\}_4]$ gave a derivative characterized as isomer III, R = Ph; L_2 = tmed, with only a trace of isomer IV, and no further isomerization III $\rightleftharpoons$ IV occurred at 50 °C. Treatment of the equilibrium mixture of III and IV, R = Ph; L = C_5H_5N, with tmed gave largely IV, R = Ph; L_2 = tmed, and again no further isomerization occurred at 50 °C. Thus the isomerization does not readily occur for derivatives with the bidentate ligand. Compounds III and IV, R = Ph; L_2 = 2,2′-bipyridine, were also prepared using the two preparative routes outlined above (Scheme II), but unambiguous structural characterization was hindered by the low solubility of the complexes in suitable NMR solvents. A feature of interest of the complex III, R = Ph; L_2 = tmed, is that all four MeN groups, as well as the two CH_2N groups, are expected to be nonequivalent and indeed four CH_3N and two CH_2N resonances were found in the ^{13}C NMR spectrum (Table II).

Platinacyclobutanes from Other Arylcyclopropanes. Using similar preparative methods, platinacyclobutane complexes have been prepared from the arylcyclopropanes RC_3H_5 with R = 4-MeC_6H_4, 2-MeC_6H_4, 4-$MeOC_6H_4$, and 4-$EtOC_6H_4$. In all cases where R = 4-XC_6H_4, the initially formed pyridine adducts were shown to exist largely as isomer III, L = C_5H_5N, and to isomerize in solution to give an equilibrium mixture with isomer IV predominating. However, when R = 2-MeC_6H_4, the complex obtained first was largely IV, L = C_5H_5N, and the small proportion of isomer III present decreased still further over a period of 1 day as further isomerization occurred. The compounds were again characterized by the ^{1}H and ^{13}C NMR spectra (Tables I and II).

Approximate equilibrium constants for the reactions III $\rightleftharpoons$ IV were determined by integration of the NMR spectra and are given in Table I. In all cases substitution of an electron-releasing group X in the substituent R = 4-XC_6H_4 led to an increase in the magnitude of the equilibrium constant compared with the case when X = H. We have been unable to prepare similar compounds with electron-withdrawing substituents X, but such substituents would be expected to favor isomer III.[10] Substitution in the ortho position of the aryl group evidently favors isomer IV. Attempts were made to study the temperature dependence of the equilibrium constants and hence to obtain thermodynamic parameters for the reactions III $\rightleftharpoons$ IV. These attempts have not been successful owing to experimental difficulties, but the qualitative observation is that increasing the temperature leads to an increase in the equilibrium constant. Thus an equilibrium mixture of isomers III and IV, R = 4-$MeOC_6H_4$; L = C_5H_5N, obtained at 35 °C ($K \sim 20$) was stored at 0 °C for 1 month, after which time the NMR spectrum showed the ratio of IV:III to be ~5. Though it is not certain that equilibrium had been reached, it is clear that at the lower temperature isomer III was more stable relative to IV than at the higher temperature, and hence that for the reaction III $\rightleftharpoons$ IV, R = 4-$MeOC_6H_4$; L = C_5H_5N, $\Delta H°$ is positive and therefore $\Delta S°$ is positive.[11]

The tetramers $[\{PtCl_2(C_3H_5R)\}_4]$ dissolve in tetrahydrofuran and, when R = Ph, the compound has been shown to be present as a monomer, presumably $[PtCl_2(C_3H_5R)(C_4H_8O)_2]$.[2] These compounds also undergo slow isomerization III $\rightleftharpoons$ IV, L = C_4H_8O, in solution as was readily shown by studying changes in the NMR spectra of freshly prepared tetramers in tetrahydrofuran-d_8 (Tables I and II). The reaction was most readily studied for the case with R = 4-MeC_6H_4 when the methyl resonances were clearly separated for the two isomers III and IV as shown in Figure 3. Of particular interest is the observation that long-range coupling between ^{195}Pt and

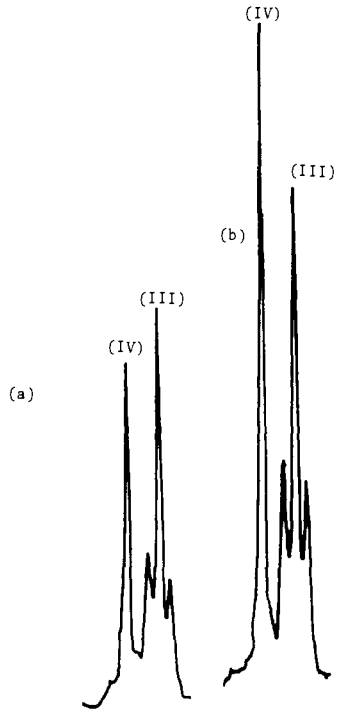


Figure 3. ^{1}H NMR spectra (60 MHz) in tetrahydrofuran-d_8 of $[PtCl_2(4\text{-}MeC_6H_4C_3H_5)]$ showing only the methyl group resonances of the tolyl groups: (a) first-formed mixture of isomers III and IV, L = THF-d_8; (b) spectrum after 24 h recorded at higher sensitivity. Low-field singlet due to isomer IV; high-field singlet with ^{195}Pt satellites due to isomer III.

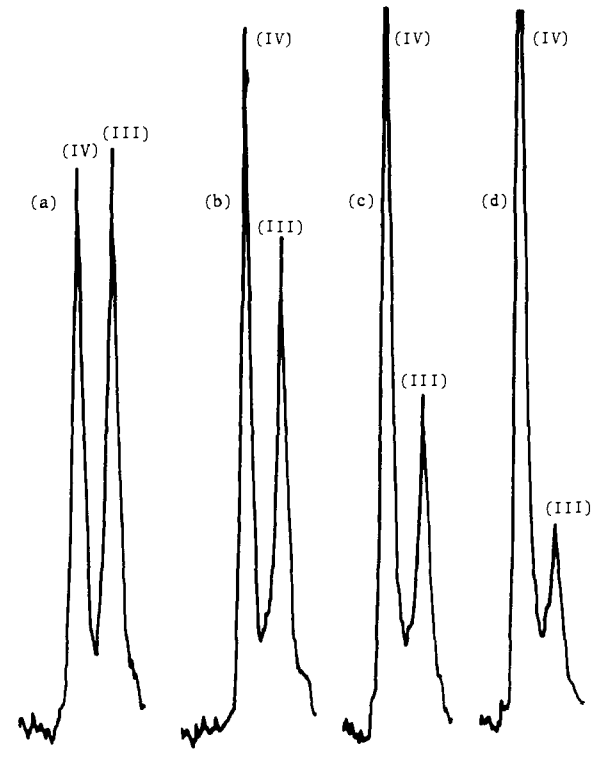
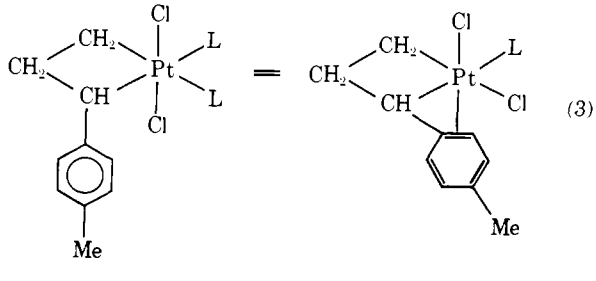


Figure 4. ^{1}H NMR spectra (60 MHz) in $CDCl_3$ at 50 °C for complexes III and IV, R = 4-tolyl; L = C_5H_5N, after (a) 20, (b) 70, (c) 150, (d) 400 min. The methyl resonance of the tolyl group of isomer III is at high field in each case.

the methyl protons of the tolyl group was observed for isomer III, L = C_4D_8O, but not for isomer III, L = C_5H_5N, or for IV, L = C_4D_8O or C_5H_5N. It is possible that direct interaction between the aryl group and platinum in isomer III, L = C_4D_8O, may occur, as has been observed in some coordinatively unsatured benzyl derivatives of transition metals,[12] and explain this long-range coupling. Also, the aryl protons for 4-tolylcyclopropane and IV, R = 4-tolyl; L = C_4D_8O, occur as a single peak in the 60-MHz NMR spectrum [at δ 7.10, ^5J(PtH)-14 Hz for IV] but for III, R = tolyl; L = C_4D_8O, an AB quartet was observed, δ (H^A) 7.57 ppm, ^4J(PtH) = 9 Hz; δ (H^b) 6.96 ppm. The downfield shift of the hydrogen atoms ortho to the ring for isomer III could be attributed to an interaction of the aryl group with platinum, though it might also be due to diamagnetic shielding effects. However, the relatively high values of the coupling constants between ^{195}Pt and the carbon and hydrogen atoms of the platinacyclobutane ring in III and IV when L = tetrahydrofuran compared with similar values when L = pyridine (Tables I and II) suggests the presence of a normal metallocyclobutane ring, in which the carbon atoms of the platinacyclobutane ring directly bound to platinum are trans to a ligand of low trans influence such as tetrahydrofuran.[9,13] Thus any direct interaction between platinum and the aryl group must be weak, but a rapid reversible equilibrium involving displacement of a weakly bound tetrahydrofuran ligand is tentatively suggested.



(3)

Kinetic Studies of the Isomerization. Preliminary studies showed that the isomerization III ⇌ IV, L = C_5H_5N; R = Ph, was strongly retarded in the presence of pyridine. Thus the isomerization was normally complete in 45 min at 50 °C in $CDCl_3$ solvent, but, if 1 drop of pyridine was added to the 0.5-cm^3 NMR solution of III, no isomerization to IV occurred in 1 day at 50 °C. Attempts to study the kinetics quantitatively by integration of NMR spectra for this system were unsuccessful since sufficient accuracy and reproducibility could not be obtained. The systems with R = 4-$MeOC_6H_4$ and 4-MeC_6H_4 were more suitable since the peak heights of the separate methyl signals for isomers III and IV could be used to obtain the relative concentrations accurately. When R = 4-$MeOC_6H_4$; L = C_5H_5N, the approach to equilibrium III ⇌ IV followed first-order kinetics in $CDCl_3$ at 35 °C with k_{obsd} = 8.7 × 10^{-4} s^{-1} but the methoxy signals due to the two isomers were too close together in the 60-MHz NMR spectrum for convenience and no further studies were undertaken. Fortunately, when R = 4-MeC_6H_4; L = C_5H_5N, the signals in the NMR spectra due to the methyl protons of isomers III and IV were resolved, as illustrated by the spectra shown in Figure 4, and reproducible kinetic data were obtained. The approach to equilibrium III ⇌ IV in $CDCl_3$ at 50 °C followed first-order kinetics as shown by the plots of Figure 5. The reaction was strongly retarded in the presence of free pyridine and a graph of $1/k_{obsd}$, where k_{obsd} were the observed first-order rate constants, vs. the concentration of pyridine gave a straight line as shown in Figure 6. The relationship

$$k_{obsd}\ (s^{-1}) = \frac{1}{4200 + 7 \times 10^5\ [C_5H_5N]}$$

was obtained. Pyridine must retard the isomerization III ⇌ IV by interaction with a reaction intermediate since no chemical reaction of pyridine with either III or IV occurred and the equilibrium constant for the reaction III ⇌ IV was, within experimental error, independent of pyridine concentration. It was shown that arylcyclopropanes fail to react with

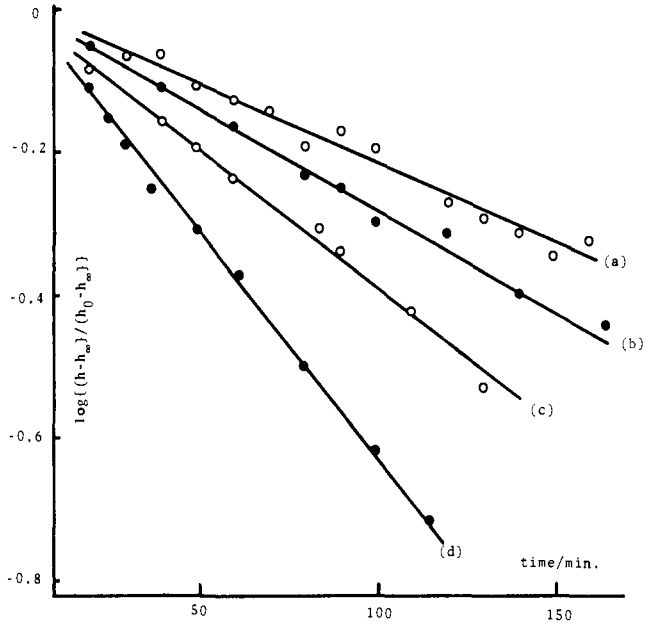


Figure 5. First-order plots for the isomerization III ⇌ IV, R = 4-tolyl; L = C_5H_5N, in $CDCl_3$ at 50 °C. Concentration of pyridine: (a) 1.59×10^{-2} M; (b) 8.0×10^{-3} M; (c) 1.09×10^{-3} M; (d) 0 (h_0, h, and h_∞ refer to the height of the ^1H NMR resonance due to the methyl protons of III at times 0, t, and ∞, respectively).

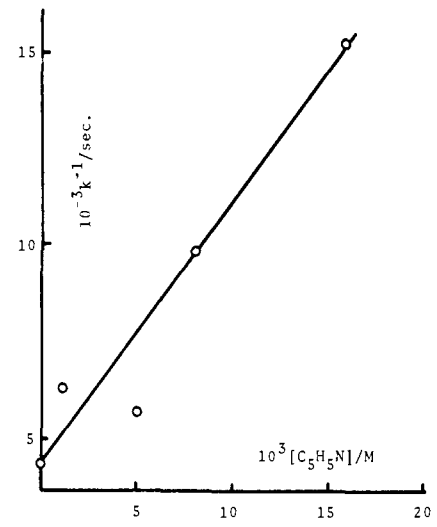


Figure 6. Relationship between the first-order rate constants for reaction III ⇌ IV, R = 4-tolyl; L = C_5H_5N, in $CDCl_3$ at 50 °C and the concentration of added pyridine.

cis- or *trans*-$PtCl_2(C_5H_5N)_2$ and hence that a mechanism of isomerization involving reversible dissociation of arylcyclopropane from III or IV is not possible.

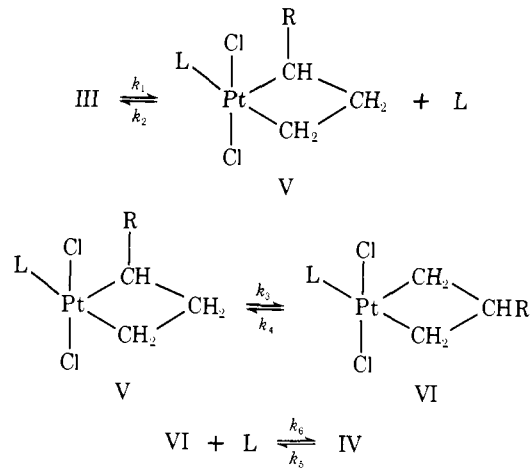
Discussion

There are several interesting questions raised by the above results. Platinum(II) appears to act like several other electrophiles in cleaving a C–C bond of arylcyclopropanes adjacent to the aryl group[14] and the mechanism of formation of the platinacyclobutane complexes has been discussed previously.[2] The factors which influence the equilibrium constants for reactions III ⇌ IV and the mechanism of isomerization will be discussed here.

The equilibrium constants for reactions III ⇌ IV are expected to be influenced by both electronic and steric effects. To evaluate reliably the importance of electronic effects it would be desirable to have a wider range of para substituents on the arylcyclopropane derivatives, but, within the limited range which we have been able to prepare, it seems that electron-releasing substituents lead to isomer IV being favored. With R = alkyl, only isomer IV has been observed, though it is not certain if this is the product of kinetic or thermodynamic control.[6,14,15] The conclusion that isomer III will be stabilized by electron-withdrawing substituents R is expected by analogy with the known stabilization of acyclic alkyl derivatives of transition metals by electronegative alkyl groups.[10]

Our results indicate strongly that steric effects are important in determining the equilibrium constants and rates of reactions III ⇌ IV. This is clearly seen by comparing the equilibrium constants for systems with R = C_6H_5 and L = pyridine or 2-methylpyridine and with L = pyridine and R = phenyl or 2-tolyl. In each case the ortho substituent favors isomer IV. Steric effects in III and IV with R = C_6H_5 and L = C_5H_5N were studied by making space-filling (CPK) models, using bond distances and angles from X-ray studies of similar molecules.[16] The models show clearly that for isomer III the phenyl group must adopt a locked-in conformation due to steric interactions with the chloride ligands and particularly with the adjacent pyridine ligand. In contrast, for isomer IV, particuarly if the phenyl group occupies an equatorial position of a puckered PtC_3 ring,[17] there are essentially no steric constraints to rotation about the phenyl–carbon bond. Thus entropy effects would be expected to favor isomer IV and this was confirmed experimentally when R = 4-methoxyphenyl and L = pyridine. Interactions between substituents on the MC_3 ring and other ligands on the metal have been largely ignored in discussions of steric effects in metallocyclobutane complexes (probably because in catalytic systems the nature of these ligands is generally not known), but they may well be important in influencing the steric course of olefin metathesis.[18]

Scheme III

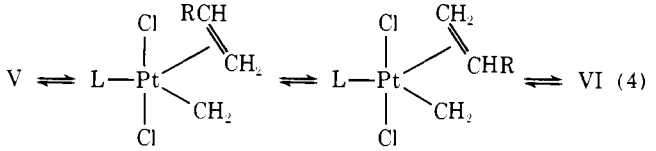


The mechanism by which the skeletal isomerization III ⇌ IV occurs is relevant to the mechanism of olefin metathesis, and so is of general interest. The observations that isomerization occurs readily with monodentate ligands L but is retarded in the presence of free ligand suggests that the reaction proceeds by preliminary reversible dissociation of a ligand L, followed by rearrangement of the five-coordinate intermediate (Scheme III). This would also be consistent with the observation that complexes with chelate ligands, for which ligand dissociation is not expected to occur readily, do not easily undergo the skeletal isomerization. If the steady-state approximation is made for the concentrations of intermediates V and VI in Scheme III, then the rate of reaction is expected to be given by the expression (see Appendix for derivation)

$$\frac{-d(III)}{dt} = \frac{(k_1k_3k_6 + k_2k_4k_5)\{[III] - [III]_e\}}{k_2k_4 + k_3k_6 + k_2k_6[py]}$$

where [III] and $[III]_e$ represent the concentration of isomer III at any time and the concentration at equilibrium, respectively. Thus, the approach to equilibrium is expected to follow first-order kinetics and to be retarded in the presence of excess pyridine as was found experimentally. Thus when R = 4-tolyl and L = pyridine, we can calculate $(k_2k_4 + k_3k_6)/(k_1k_3k_6 + k_2k_4k_5) = 4200$ s and $k_2k_6/(k_1k_3k_6 + k_2k_4k_5) = 7 \times 10^5$ L mol^{-1} s at 50 °C in $CDCl_3$ solution.

If the overall mechanism of Scheme III is accepted, the problem remains of exactly how the isomerization V ⇌ VI occurs. By analogy with the proposed mechanism of olefin metathesis, the obvious mechanism involves the intermediacy of a carebene-olefin-platinum(II) complex as shown in eq 4.



The intermediates are 18-electron species and could not be formed without prior ligand dissociation (20-electron complexes are unknown in organoplatinum chemistry). Despite these attractions, we believe that this mechanism is incorrect for the following reasons. Firstly, one would expect that thermal decomposition of the complexes would give $RCH{=}CH_2$, ethylene, and other hydrocarbons arising from C-C bond cleavage of the original cyclopropane, RC_3H_5.[17,19] However, when R = Ph and L = pyridine, thermal decomposition gave only phenylcyclopropane and isomers of propenylbenzene with no products of C-C bond cleavage. More convincing evidence arises from studies using complexes derived from *cis*- or *trans*-1,2-diarylcyclopropanes. The mechanism of eq 4 would naturally lead to cis-trans isomerization along with skeletal isomerization, whereas the experimental evidence indicates that skeletal isomerization occurs without cis-trans isomerism.[6,7] For example, *trans*-1,2-bis(4-tolyl)cyclopropane gave $[PtCl_2\{CH(4\text{-tolyl})CH_2CH(4\text{-tolyl})\}(4\text{-t-Bu}C_5H_4N)_2]$, which isomerized to $[PtCl_2\{CH(4\text{-tolyl})CH(4\text{-tolyl})CH_2\}(4\text{-t-Bu}C_5H_4N)_2]$. In each case the stereochemistry about the ring remained trans and the initial cyclopropane was recovered on treating the complex with triphenylphosphine.[20] We believe therefore that the isomerization V ⇌ VI occurs by a mechanism which does not involve C-C bond cleavage, but the precise mechanism is not yet understood and work is continuing. Since cis-trans isomerism occurs during metathesis of alkenes with most catalysts,[21] the mechanism of isomerization of the platinacyclobutane complexes is probably different from the mechanism for most catalytic systems, but such a mechanism could account for stereospecific metathesis reactions found with some catalysts.[22]

Experimental Section

^{1}H NMR spectra were obtained using a Perkin-Elmer R12b spectrometer operating at 60 MHz and ^{13}C NMR spectra using a Varian XL100 spectrometer operating at 25.2 MHz.

Phenylcyclopropane was a commercial sample. Other arylcyclopropanes were prepared using the Simmons-Smith reaction. As far as we are aware, the preparations described below are new, though other arylcyclopropanes have been prepared in a similar way.[23] A typical example is described.

2-Tolylcyclopropane. To a hot solution of copper(II) acetate monohydrate (0.25 g) in glacial acetic acid (50 cm^3) was added zinc granules (17 g) and the hot mixture was shaken for several minutes. The solvent was decanted and the zinc-copper couple was washed with acetic acid (50 cm^3) and then with ether (3 × 50 cm^3).

To the zinc-copper couple was added ether (40 cm^3) and the mixture was heated under nitrogen for 30 min. Diiodomethane (10.5 cm^3) was added dropwise over a period of 30 min and the mixture was left for a further 15 min. Next, 2-methylstyrene (10.5 cm^3) was added dropwise over a period of 90 min and the mixture was heated under reflux for 48 h. The mixture was hydrolyzed by pouring into ice-cold hydrochloric acid (50 cm^3, 1 M). The ether layer was separated and dried over magnesium sulfate and the ether was evaporated to give the product, which was purified by vacuum distillation: yield 45%; ^{1}H NMR in $CDCl_3$ δ (C_6H_4) 6.98 (m), δ(CH_3) 2.70 (s), δ(CH) 1.57 (m), δ(CH_2CH_2) 0.70 ppm (m). The purity was confirmed by GLC-MS, which showed the complete absence of 2-methylstyrene.

Similarly were prepared the following: 4-tolylcyclopropane [^{1}H NMR in $CDCl_3$ δ(C_6H_4) 7.21 (s), δ(MeC) 2.50 (s), δ(CH) 2.00 (m), δ(CH_2CH_2) 0.95 ppm (m)]; 4-methoxyphenylcyclopropane [^{1}H NMR in $CDCl_3$ δ(C_6H_4) 6.82 q, δ(CH_3O) 3.47 (s), δ(CH) 1.62 (m), δ(CH_2CH_2) 0.62 ppm (m)]; 4-ethoxyphenylcyclopropane [^{1}H NMR in $CDCl_3$ δ(C_6H_4) 6.79 (q), δ(CH_3) 1.21 (t), δ(CH_2O) 3.73 (q)[3], J(HH)-7 Hz, δ(CH_2CH_2) 0.60 (m), δ(CH) 1.72 ppm (m)].

1-Deuterio-1-phenylcyclopropane. This was prepared by the method of McQuillin and co-workers,[6] and was shown to be isotopically pure by NMR (absence of CHPh resonance) and MS.

Zeise's dimer, $Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2$, was prepared by the literature method.[22]

Dichloro(1-phenylpropane-1,3-diyl)platinum(IV). A mixture of $[Pt_2Cl_4(C_2H_4)_2]$ (0.2 g) and phenylcyclopropane (0.5 g) in diethyl ether (10 cm^3) was heated under reflux for 6 h. The insoluble yellow product was filtered off, washed with ether, and dried in vacuo, yield 63%, mp 137 °C dec. Anal. ($C_9H_{19}Cl_2Pt$), C, H, Cl.

Dichlorobis(pyridine)(1-phenylpropane-1,3-diyl)platinum(IV). The above product (0.1 g) was suspended in dichloromethane (2 cm^3) at 0 °C and solution of pyridine (0.1 g) in CH_2Cl_2 (1 cm^3) at 0 °C was added. A clear solution was obtained. The volume of solvent was reduced and methanol (3 cm^3) was added to precipitate the product as pale yellow crystals, yield 61%, mp 130 °C. Anal. ($C_{19}H_{20}Cl_2N_2Pt$)H, N, C: calcd, 42.1; found, 41.3. Similarly were prepared the following. $[PtCl_2(CHPhCH_2CH_2)(4\text{-}MeC_5H_4N)_2]$, yield 49%, mp 146 °C dec. Anal. ($C_{21}H_{24}Cl_2N_2Pt$) C, H, N. $[PtCl_2(CHPhCH_2CH_2)(bpy)]$, yield 59%, mp 229 °C dec. Anal. ($C_{19}H_{18}Cl_2N_2Pt$) H, N. C: Calcd, 42.3; found, 41.5. $[PtCl_2(CHPhCH_2CH_2)(Me_2NCH_2CH_2NMe_2)]$, yield 43%, mp 129 °C. Anal. ($C_{15}H_{26}Cl_2N_2Pt$) C, H, N.

Dichlorobis(pyridine)(phenylpropane-1,3-diyl)platinum(IV). The mixture of isomers III and IV, R = Ph; L = C_5H_5N, was prepared by warming a solution of isomer III (0.1 g) in $CDCl_3$ at 50 °C for 2 h, reducing the volume of solvent, and precipitating the product with methanol, yield 60%. Anal. C, H, N. Similarly was prepared $[PtCl_2(PhC_3H_5)(4\text{-}MeC_5H_4N)_2]$ as a mixture of isomers III and IV, yield 74%. Anal. C, H, N.

Dichloro(*N,N,N',N'*-tetramethylethylenediamine)(2-phenylpropane-1,3-diyl)platinum(IV) was prepared by reaction of tmed (0.04 g) with an equilibrium mixture of III and IV, R = Ph; L = C_5H_5N (0.2 g), in CH_2Cl_2 (2 cm^3). After 7 days, the solvent was evaporated and the product was recrystallized from methanol, yield 32%, mp 172 °C. Anal. ($C_{15}H_{26}Cl_2N_2Pt$) C, H, N.

Similarly was prepared $[PtCl_2(CH_2CHPhCH_2)(bpy)]$, yield 74%, mp 235 °C dec. Anal. ($C_{19}H_{18}Cl_2N_2Pt$) C, H, N.

Dichlorobis(2-methylpyridine)(2-phenylpropane-1,3-diyl)platinum(IV). To a suspension of $[PtCl_2(CHPhCH_2CH_2)]$ (0.2 g) in CH_2Cl_2 (3 cm^3) was added 2-methylpyridine (6 drops) until a clear solution was obtained. The solvent was evaporated and the residual oil was washed repeatedly with pentane until a pale yellow solid was obtained, yield 55%. Anal. ($C_{21}H_{24}Cl_2N_2Pt$)H, N, Cl. C: calcd, 44.2; found, 41.6.

Dichloro(1-(4-tolyl)propane-1,3-diyl)platinum(IV). This was prepared by heating a mixture of $[Pt_2Cl_4(C_2H_4)_2]$ (0.1 g) with 4-tolylcyclopropane (0.2 g) in ether (6 cm^3) under reflux for 3.5 h. The yellow precipitate was filtered off, washed with ether, and dried under vacuum. Anal. ($C_{10}H_{12}Cl_2Pt$) C, H.

Dichlorobis(pyridine)[1-(4-tolyl)propane-1,3-diyl]platinum(IV) was prepared by treating a suspension of $[PtCl_2\{CH(4\text{-tolyl})CH_2CH_2\}]$ (0.05 g) in dichloromethane (3 cm^3) with pyridine (4 drops). The solvent was evaporated and the product was washed thoroughly with pentane, mp 128 °C. Anal. ($C_{20}H_{22}cl_2N_2Pt$) C, H, N.

By similar methods were prepared the following: $[PtCl_2\{CH_2CH(2\text{-tolyl})CH_2\}]$, $[PtCl_2\{CH(4\text{-}MeOC_6H_4)CH_2CH_2\}]$, $[PtCl_2\{CH(4\text{-}EtOC_6H_4)CH_2CH_2\}]$, $[PtCl_2\{CH_2CH(2\text{-tolyl})CH_2\}(C_5H_5N)_2]$ [yield 27%, mp 128 °C. Anal. ($C_{20}H_{22}Cl_2N_2Pt$), C, H, N], $[PtCl_2\{CH(4\text{-}MeOC_6H_4)CH_2CH_2\}(C_5H_5N)_2]$ [yield 30%, mp 135

°C. Anal. ($C_{20}H_{22}Cl_2N_2OPt$)H, N. C: calcd, 41.9; found, 41.0], [$PtCl_2$\{$CH(4\text{-}EtOC_6H_4)CH_2CH_2$\}$(C_5H_5N)_2$] [Anal. ($C_{21}H_{24}Cl_2N_2OPt$) C, H, N], [$PtCl_2$\{$C^1H(4\text{-tolyl})C^2H_2C^1H(4\text{-tolyl})$\}$(4\text{-}t\text{-}BuC_5H_4N)_2$] [Anal. ($C_{35}H_{44}Cl_2N_2Pt$) C, H, N. ^{13}C NMR in $CDCl_3$ $\delta(C^1)$ 6.3 ppm, $^1J(PtC)$ = 338 Hz, $\delta(C^2)$ 14.6, $^2J(PtC)$ = 125 Hz], [$PtCl_2$\{$C^1H(4\text{-tolyl})C^2H(4\text{-tolyl})C^3H_2$\}$(4\text{-}t\text{-}BuC_5H_4N)_2$] [$^{13}C$ NMR in $CDCl_3$ $\delta(C^1)$ 15.7, $^1J(PtC)$ = 341 Hz, $\delta(C^2)$ 50.5, $^2J(PtC)$ = 105 Hz, $\delta(C^3)$ −1.6, $^1J(PtC)$ = 383 Hz].

Kinetic Studies. The platinum complex III, R = 4-tolyl; L = C_5H_5N (ca. 0.03 g), was dissolved in a standard solution of pyridine in $CDCl_3$ (0.5 cm^3) and the resulting solution transferred to an NMR tube. The tube was placed in the probe of the spectrometer held at 50 °C, and spectra were recorded at suitable time intervals. The height of the resonance due to the methyl protons of isomer III was taken as a measure of the concentration of III.

$[PtCl_2(C_5H_5N)_2]$[24b] with Phenylcyclopropane. Phenylcyclopropane (0.20 g) was added to *trans*-$[PtCl_2(C_5H_5N)_2]$(0.15 g) in $CHCl_3$ (10 cm^3) and the mixture was stirred at 50 °C for 24 h. No reaction occurred. Similar experiments with *cis*-$[PtCl_2(C_5H_5N)_2]$ and phenylcyclopropane and in the solvents ether and tetrahydrofuran gave the same result. Cyclopropane and phenylcyclopropane failed to react with $[PtCl_2(CH_3CN)_2]$ in similar experiments.

Appendix

Since the kinetic analysis for systems similar to Scheme III is not given in standard texts, a summary is given here.

Assuming stationary-state approximations for V and VI,

$$\frac{d[V]}{dt} = k_1[III] - k_2[V][L] - k_3[V] + k_4[VI] = 0$$

$$\frac{d[VI]}{dt} = k_3[V] - k_4[VI] + k_5[IV] - k_6[VI][L] = 0$$

Putting [III] + [IV] = C, the total concentration, and solving for [V] we obtain

$$[V] = \frac{\{k_1k_4 - k_4k_5 + k_1k_6[L]\}[III] + k_4k_5C}{\{k_2k_4 + k_3k_6 + k_2k_6[L]\}[L]} \quad (i)$$

Now, the rate of reaction is given by

$$\frac{-d[III]}{dt} = k_1[III] - k_2[V][L]$$

Substituting for [V] from eq i

$$-d[III]/dt = \frac{(k_1k_3k_6 + k_2k_4k_5)[III] - k_2k_4k_5C}{k_2k_4 + k_3k_6 + k_2k_6[L]} \quad (ii)$$

Now, at equilibrium we have

$$[III]_e + [IV]_e = C \text{ and } [IV]_e/[III]_e = K,$$

the equilibrium constant for reaction III ⇌ IV.

$$C = [III]_e + K[III]_e$$

At equilibrium, $-d[III]/dt = 0$ and substituting for C in eq ii we obtain

$$k_1k_3k_6[III]_e - Kk_2k_4k_5[III]_e = 0$$

and hence $K = k_1k_3k_6/k_2k_4k_5$, from which

$$C = [III]_e\,(1 + k_1k_3k_6/k_2k_4k_5)$$

Substitution of this expression for C into eq ii gives

$$-d[III]/dt = \frac{(k_1k_3k_6 + k_2k_4k_5)\{[III] - [III]_e\}}{k_2k_4 + k_3k_6 + k_2k_6[L]}$$

References and Notes

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