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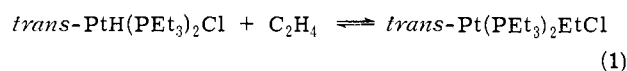
Kinetics and Mechanism of the Reaction of Methyl Acrylate with *trans*-Bis(triethylphosphine)hydridoplatinum(II) Nitrate

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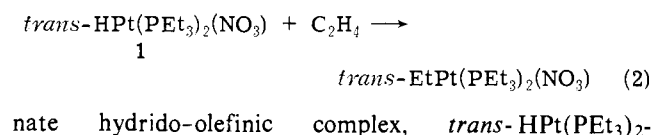
Abstract: The kinetics of the reaction of HPt(PET₃)₂(NO₃) with methyl acrylate (OI) have been examined. The kinetic features have been interpreted in terms of the mechanism HPt(PET₃)₂NO₃ + OI = HPt(PET₃)₂(OI)⁺ + NO₃⁻ (K₁), HPt(PET₃)₂(MeOH)⁺ + OI = HPt(PET₃)₂(OI)⁺ + MeOH (K₂), HPt(PET₃)₂(OI)⁺ → RPt(PET₃)₂⁺ (k₃), RPt(PET₃)₂⁺ + NO₃⁻ = RPt(PET₃)₂NO₃, which yields a rate law $d[\text{RPt}(\text{PET}_3)_2(\text{NO}_3)]/dt = k_3 K_1 K_2 [\text{OI}][\text{Pt}]_T / (K_2 [\text{NO}_3^-] + K_1 [\text{MeOH}] + K_1 K_2 [\text{OI}])$. Values of k_3 , K_1 , and K_2 have been determined to be $(5.4 \pm 0.6) \times 10^{-2} \text{ sec}^{-1}$, $(8.2 \pm 0.9) \times 10^{-2}$, and 90 ± 17 , respectively. A kinetic isotopic effect of 1.34 ± 0.06 was observed for $k_3(\text{H})/k_3(\text{D})$. Evidence for a four-coordinate cationic intermediate, HPt(PET₃)₂(OI)⁺, is presented.

The catalytic hydrogenation and isomerization of olefins by metal complexes have been extensively studied.¹ It is generally believed² that one of the key steps in such processes is the insertion of the unsaturated molecule into the metal-hydrogen bond. Platinum(II) hydrides are particularly suitable for the studying of these types of insertion reactions, primarily because of the stabilities of the hydride and the resulting alkyl complexes. Thus far two general trends, pertinent to a consideration of the ease of the insertion reaction, have emerged. (i) The presence of catalytic amounts of a strong π -acceptor such as SnCl₂ effectively catalyzes the formation of the alkyl complex. Thus, in the absence of any catalyst, eq 1 is established under rather vigorous

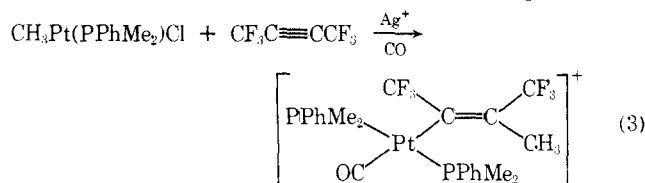


conditions (95° and 80 atm),³ whereas in the presence of 1 mol % of tin(II) chloride, the equilibrium is established within 30 min at 25° and 1 atm.⁴ It has been proposed^{5,6} that the π -acceptor strength and the considerable trans influence of the SnCl₃⁻ ligand promote the formation

of a five-coordinate intermediate and the weakening of the Pt-H bond, thus enhancing the insertion reaction. Such five-coordinate intermediates (e.g., Pt(PPh₃)₂H(SnCl₃)-(C₈H₁₆)) have actually been isolated.⁷ Spectroscopic measurements indicate that both a Pt-H bond and a π bonded octene ligand are present in this compound. Kinetic measurements⁸ on reaction 1 in the presence of SnCl₂ as catalyst also support a mechanism involving a five-coordinate species, HPt(PET₃)₂(SnCl₃)(C₂H₄), as the insertion intermediate. (ii) The presence in the hydrido complex of a ligand labile to substitution greatly facilitates the insertion reaction. Thus, in the presence of Ag⁺, *trans*-HPt(PR₃)₂X (X = Cl or Br; PR₃ = PPh₃, PPh₂Me, PPhMe₂, or PET₃) reacts rapidly with olefins forming the corresponding alkyl complexes.⁹ Facile insertion also occurs when X is a good leaving group such as NO₃⁻ (eq 2).^{9,10} A four-coordi-

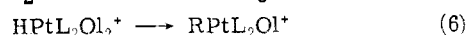
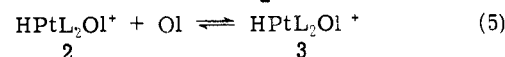
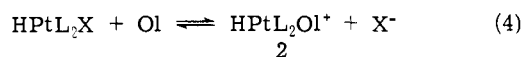


$(C_2H_4)^+BPh_4^-$ has been isolated.¹⁰ Even the more stable alkyl complex, $CH_3Pt(PPhMe_2)_2Cl$, undergoes insertion with acetylenes in the presence of Ag^+ (eq 3).¹¹ On

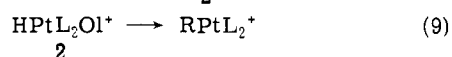
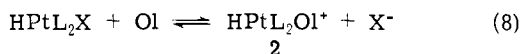


the other hand the five-coordinate $CH_3Pt(HBpz_3)(CH_3C\equiv CCF_3)$, which contains the strongly bonded tridentate ligand $HBpz_3$ ($pz = \text{pyrazolyl}$, $C_3H_3N_2$), is extremely stable and no insertion is observed.¹² These observations lead to two different mechanistic proposals¹³ for the uncatalyzed insertion reactions (Schemes I and II). In

Scheme I



Scheme II



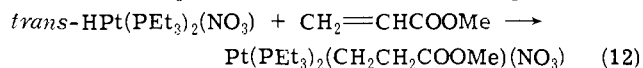
Scheme I, a five-coordinate intermediate involving two olefins, **3**, is proposed, *via* which insertion occurs. In Scheme II, a four-coordinate hydrido-olefinic complex, **2**, is thought to be the actual reacting intermediate.

In the study of the reaction of ethylene with $HPt(PEt_3)_2(\text{acetone})^+$,¹⁴ **4**, kinetic measurements in acetone yield the rate law

$$-\frac{d[PtH]_{\text{total}}}{dt} = \frac{k[C_2H_4][PtH]_{\text{total}}}{1 + k'[C_2H_4]} \quad (11)$$

where $[PtH]_{\text{total}} = [HPtL_2(\text{acetone})^+] + [HPtL_2(C_2H_4)^+]$. Unfortunately, this result fails to discriminate between the two alternative mechanisms conclusively. While it is perfectly compatible with Scheme II, it is also explainable in terms of Scheme I provided that (a) eq 4 is extremely rapid and lies completely to the right such that the observed olefin dependence is due to eq 5, or (b) **2** contains a coordinated solvent (*i.e.*, $H^+PtL_2Ol(S)$) which reacts with another olefin by a dissociative mechanism involving loss of S as the rate determining step.¹³

This uncertainty might, however, be removed by using **1** instead of the solvent complex **4**. The additional information obtained from the NO_3^- dependence of the reaction may provide a distinction between the two schemes. In this paper the kinetics of reaction 12 are described, and its mechanistic implications are discussed. Liquid olefin,



namely methyl acrylate, is used instead of ethylene to ensure the more accurate determination of olefin concentration.

Experimental Section

Materials. *trans*- $HPt(PEt_3)_2(NO_3)$ was prepared by the method of Chatt and Shaw³ and recrystallized from hexane. Methyl acrylate ($CH_2=CHCOOMe$, Eastman Kodak Co.) was purified by distillation under partial vacuum immediately before use. Sodium

nitrate (B.D.H.) was recrystallized from methanol and vacuum dried. Sodium perchlorate (Fisher Scientific Co.) was recrystallized from ethanol and vacuum dried at 70° for at least 12 hr. Spectroscopic grade methanol (Anachemia Chemical Co.) was dried over magnesium and distilled under nitrogen before use.

Preparation of $Pt(PEt_3)_2(CH_2CH_2COOCH_3)(NO_3)$. Methyl acrylate was added to a hexane solution of *trans*- $HPt(PEt_3)_2(NO_3)$ and $Pt(PEt_3)_2(CH_2CH_2COOMe)(NO_3)$ was precipitated out on standing. The crude product was filtered off and recrystallized from methanol-ether containing a few drops of methyl acrylate. Alternatively, the compound can be prepared by the addition of methyl acrylate to a methanolic solution of $HPt(PEt_3)_2(NO_3)$ followed by the addition of ether (mp 81–83°).

Anal. Calcd for $PtC_{16}H_{37}O_5P_2$: C, 33.10; H, 6.38; N, 2.41. Found: C, 33.25; H, 6.20; N, 2.34.

Infrared analysis in Nujol shows a strong absorption at 1693 cm^{-1} due to an uncoordinated $-COOMe$ group but no absorption in the 1500–1650- cm^{-1} region nor *ca.* 2200 cm^{-1} . Its 1H nmr spectrum (in CD_3OD and in the presence of methyl acrylate) shows the $-COOCH_3$ signal at -3.98 ppm from TMS as a singlet. The methylene protons of the alkyl group are masked by the phosphine protons. The methyl signals of the ethyl group in PEt_3 center at $\delta -1.2$ ppm and exhibit a quintet structure with relative intensities close to a 1:2:2:2:1 pattern, indicative of a *cis* configuration.¹⁵ However, we were unable to obtain a satisfactory ^{31}P nmr spectrum to confirm this point.

Preparation of *trans*- $DPt(PEt_3)_2Cl$. The compound was prepared according to the method of Uguagliati and Baddley,¹⁶ although a longer reaction time (3 hr at 60°, then stirring at room temperature overnight) was allowed, and a nitrogen atmosphere was used during deuteration. No infrared absorptions at 2231 cm^{-1} were observed, and a strong band at 1598 cm^{-1} $\nu(Pt-D)$ appeared.

Preparation of *trans*- $DPt(PEt_3)_2(NO_3)$. To a solution of 0.234 g of $DPt(PEt_3)_2Cl$ in 15 ml of CH_3OD was added dropwise a solution of 0.085 g of $AgNO_3$ in 0.5 ml of D_2O and 4 ml of CH_3OD . The reaction mixture was allowed to stand under nitrogen for 0.5 hr and then passed through a short Florisil column. The solution was then evaporated to dryness and the residue was extracted with benzene, passed through a Florisil column, and evaporated again to dryness. The resulting colorless oil was dissolved in 2 ml of ether and 5 ml of hexane and then evaporated to about 5 ml. On cooling this solution to -78° , *trans*- $DPt(PEt_3)_2(NO_3)$ was formed as a white microcrystalline solid, yield 190 mg, mp 50–51°. The infrared spectrum was transparent in the region 2200–2300 cm^{-1} , and $\nu(Pt-D)$ appeared at 1633 and 1590 cm^{-1} .

Kinetic Measurements. The kinetics of the reaction were followed spectrophotometrically, using a Cary 14 spectrophotometer equipped with a thermostated cell compartment. All kinetic measurements were performed in anhydrous methanol at $25.0 \pm 0.2^\circ$. The reaction was initiated by a rapid injection of a measured volume of methyl acrylate to a methanolic solution of $HPt(PEt_3)_2(NO_3)$ containing predetermined quantities of $NaNO_3$ and $NaClO_4$. The spectral changes accompanying the reaction were monitored at 295 nm. Generally, the ionic strengths of the reaction mixtures were maintained at 0.2 *M* using $NaClO_4$. The initial concentration of *trans*- $HPt(PEt_3)_2(NO_3)$ was generally of the order of 1×10^{-3} *M*, while the concentration of $NaNO_3$ varied over the range of 1×10^{-2} to 2×10^{-1} *M*, and the concentration of olefin from 5×10^{-2} to 4×10^{-1} *M*. Thus, a pseudo-first-order condition in olefin was attained. The pseudo-first-order rate constants, k_{obsd} , were determined either from standard first-order plots ($\log(A_t - A_\infty)$ vs. time, where A_∞ is the absorbance at six to eight half-lives) or from Guggenheim plots ($\log(A_t - A_\Delta)$ vs. time, where Δ is a time interval greater than two half-lives). The two methods agreed with each other to within 5% and the plots were linear for more than two half-lives.

Results and Discussion

Stoichiometry and Product. Pure samples of the reaction product $Pt(PEt_3)_2(CH_2CH_2COOCH_3)(NO_3)$ were isolated from the reaction mixture thus providing qualitative support for the proposed stoichiometry (eq 12). The stoichiometry is further confirmed by comparing the spectrum of the reaction solution, following completion of the reaction with

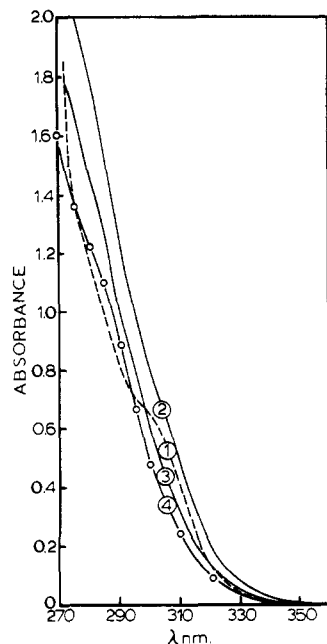


Figure 1. Spectral change accompanying the reaction of *trans*-HPt(PEt₃)₂(NO₃) with CH₂=CHCOOMe in MeOH: 1, spectrum of 7.6×10^{-4} M *trans*-HPt(PEt₃)₂(NO₃), optical path 1 cm; 2, immediately after the addition of 20 μ l CH₂=CHCOOMe (0.0734 M); 3, 5 min after addition; 4, 60 min (infinity spectrum); O-O-O spectrum of 7.6×10^{-4} M Pt(PEt₃)₂(CH₂CH₂COOMe)(NO₃) in the same solvent mixture.

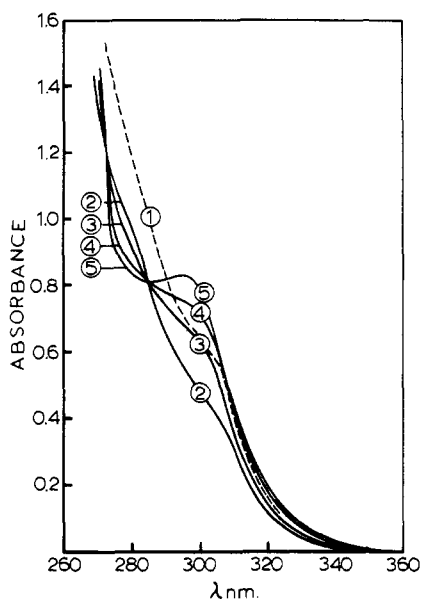


Figure 2. Spectral change accompanying the reaction of *trans*-HPt(PEt₃)₂(NO₃) with CH₂=CH₂ in MeOH: 1, spectrum of *trans*-HPt(PEt₃)₂(NO₃), optical path 1 cm; 2, immediately after the addition of 4 ml of CH₂=CH₂ gas; 3, 8 min; 4, 17 min; 5, 100 min (infinity spectrum).

that of a solution containing the same concentration of an authentic sample of the product in the same solvent mixture (Figure 1). The matching of the two spectra shows that the reaction is quantitative. Also depicted in the figure are the spectral changes accompanying the reaction. The formation of an intermediate during the course of reaction is evidenced by an initial increase in absorbance in the region 270–350 nm immediately after the addition of methyl acrylate (1 to 2 in Figure 1), followed by a much slower decrease in absorbance (2–4). Similarly, in the corresponding reaction of **1** with ethylene in methanol (Figure 2), a rapid

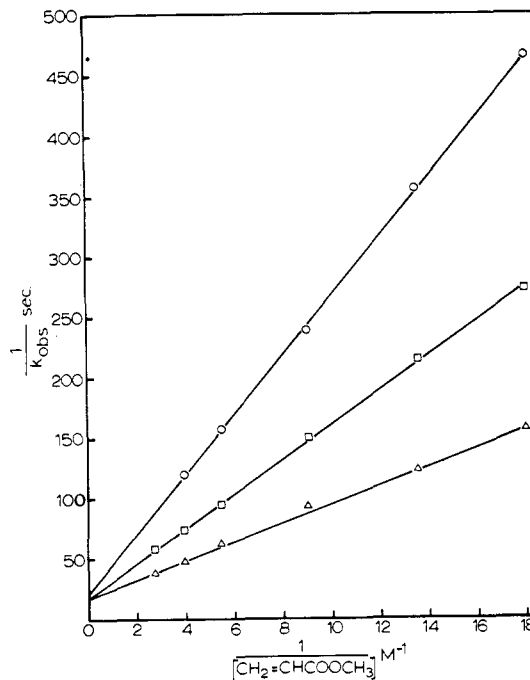


Figure 3. The plot of $1/k_{\text{obsd}}$ vs. $1/[\text{CH}_2=\text{CHCOOMe}]$ for the reaction of *trans*-HPt(PEt₃)₂(NO₃) with CH₂=CHCOOMe in MeOH at 25°, $\mu = 0.2$ M: Δ , [NO₃⁻] = 0.01 M; \square , [NO₃⁻] = 0.05 M; \circ , [NO₃⁻] = 0.10 M.

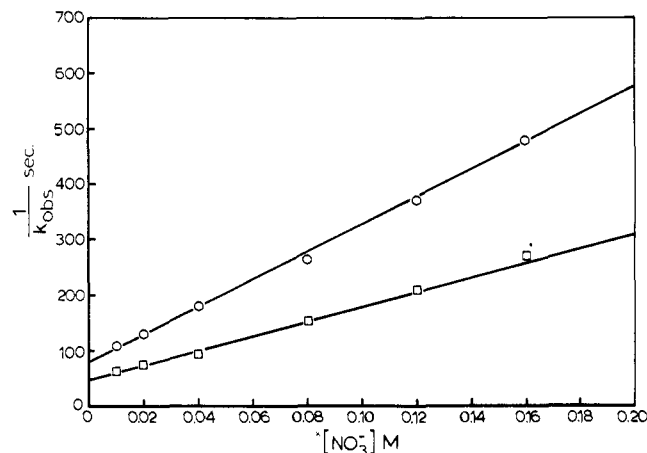


Figure 4. The plot of $1/k_{\text{obsd}}$ vs. [NO₃⁻] for the reaction of *trans*-HPt(PEt₃)₂(NO₃) with CH₂=CHCOOMe in MeOH at 25°, $\mu = 0.2$ M: \circ , [CH₂=CHCOOMe] = 0.089 M; \square , [CH₂=CHCOOMe] = 0.176 M.

initial reaction is observed (1 to 2) followed by a slower second reaction (2–5). Isosbestic points at 285 and 273 nm develop during the second reaction. Since *trans*-HPt(PEt₃)₂(C₂H₄)⁺BPh₄⁻ has actually been isolated¹⁰ for the reaction of **1** with ethylene in methanol, it is reasonable to identify the intermediates for both the ethylene and methyl acrylate reactions as hydrido-olefinic platinum complexes, **2**. This interpretation will be used as a basis to explain the kinetic results.

Kinetics. The results of the kinetic measurements are summarized in Table I. Under the experimental conditions employed, that is when the olefin concentration greatly exceeds that of the platinum complex, pseudo-first-order behavior is observed according to eq 13, where $k_{\text{obsd}} =$

$$\frac{d[\text{Product}]}{dt} = k_{\text{obsd}}[\text{Pt}]_T \quad (13)$$

Table I. Kinetic Data of the Reaction of *trans*-HPt(PEt₃)₂(NO₃) with Methyl Acrylate in Methanol at 25°

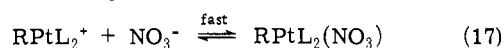
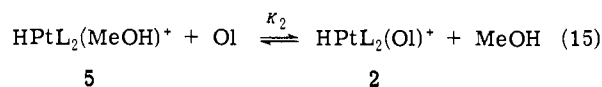
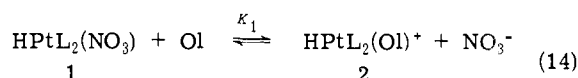
Ionic strength, <i>M</i>	[NO ₃], <i>M</i>	[PtH(D)], <i>M</i>	[Ol], <i>M</i>	<i>k</i> _{obsd} , sec ⁻¹	1/[Ol], <i>M</i> ⁻¹	1/ <i>k</i> _{obsd} , sec		
0.2	0.01	1.18 × 10 ⁻³	0.369	2.69 × 10 ⁻²	2.71	37.2		
			0.258	2.18 × 10 ⁻²	3.88	45.9		
			0.185	1.64 × 10 ⁻²	5.40	61.0		
			0.111	1.09 × 10 ⁻²	9.00	91.7		
			0.0739	8.11 × 10 ⁻³	13.5	123		
			0.0554	6.42 × 10 ⁻³	18.0	156		
	0.05	1.32 × 10 ⁻³	0.369	1.75 × 10 ⁻²	2.71	57.2		
			0.258	1.38 × 10 ⁻²	3.88	73.5		
			0.185	1.08 × 10 ⁻²	5.40	93.0		
			0.111	6.66 × 10 ⁻³	9.00	150		
			0.0739	4.68 × 10 ⁻³	13.5	214		
			0.0554	3.68 × 10 ⁻³	18.0	272		
	0.10	1.15 × 10 ⁻³	0.258	8.37 × 10 ⁻³	3.88	119		
			0.185	6.35 × 10 ⁻³	5.40	157		
			0.111	4.21 × 10 ⁻³	9.00	238		
			0.0739	2.79 × 10 ⁻³	13.5	358		
			0.0554	2.14 × 10 ⁻³	18.0	467		
			0.0887	9.06 × 10 ⁻³		110		
	0.01	1.40 × 10 ⁻³	0.0887	9.06 × 10 ⁻³		110		
			0.02	7.53 × 10 ⁻³		133		
			0.04	5.64 × 10 ⁻³		177		
			0.08	3.81 × 10 ⁻³		262		
			0.12	2.69 × 10 ⁻³		372		
			0.16	2.09 × 10 ⁻³		478		
			0.01	1.33 × 10 ⁻³	0.176	1.55 × 10 ⁻²		64.4
					0.02	1.35 × 10 ⁻²		74.0
					0.04	1.06 × 10 ⁻²		94.4
					0.08	6.65 × 10 ⁻³		150
					0.12	4.82 × 10 ⁻³		208
					0.16	3.73 × 10 ⁻³		268
	0.5	0.01	1.17 × 10 ⁻³	0.367	8.85 × 10 ⁻³	2.72	113	
				0.252	6.74 × 10 ⁻³	3.97	147	
				0.182	5.70 × 10 ⁻³	5.50	175	
0.110				3.90 × 10 ⁻³	9.10	256		
0.0734				2.58 × 10 ⁻³	13.6	388		
0.176				1.21 × 10 ⁻²		82.6		
0.2	0.01	1.34 × 10 ⁻³ (PtD)	0.176	1.21 × 10 ⁻²		82.6		
			0.02	9.90 × 10 ⁻³		101		
			0.04	7.35 × 10 ⁻³		136		
			0.08	4.73 × 10 ⁻³		212		
			0.12	3.48 × 10 ⁻³		287		
			0.16	2.85 × 10 ⁻³		351		
	0.01	1.42 × 10 ⁻³ (PtD)	0.369	2.09 × 10 ⁻²	2.71	47.8		
			0.258	1.59 × 10 ⁻²	3.88	63.0		
			0.185	1.23 × 10 ⁻²	5.40	81.3		
			0.111	8.37 × 10 ⁻³	9.00	119		
			0.739	5.93 × 10 ⁻³	13.5	168		
			0.0554	4.73 × 10 ⁻³	18.0	211		

pseudo-first-order rate constant and [Pt]_T = total concentrations of Pt-hydrides in solution.

The effect of olefin on the reaction is similar to that observed in the reaction of **4** with ethylene, namely the olefin dependence is less than first order, so that *k*_{obsd} approaches a limiting value as the concentration of olefin increases (eq 11). At constant nitrate concentration, the plots of 1/*k*_{obsd} vs. 1/[Ol] are linear with positive intercepts which are constant under different NO₃⁻ concentrations (Figure 3).

The concentration of NO₃⁻ and the ionic strength of the reaction solution also have marked influences on the rate of the reaction. Increase of NO₃⁻ concentration or decrease in ionic strength inhibits the reaction (Table I). The plots of 1/*k*_{obsd} vs. [NO₃⁻] at constant olefin concentration are linear with positive intercepts (Figure 4), the magnitudes of which depend inversely on the olefin concentrations used.

Mechanism. The spectral changes accompanying the reaction, together with the observed kinetic behavior, are consistent with the following mechanistic scheme



Employing rapid preequilibrium assumptions¹⁷ for eq 14 and 15, and denoting

$$[\text{Pt}]_T = [\text{HPtL}_2(\text{NO}_3)] + [\text{HPtL}_2(\text{MeOH})^+] + [\text{HPtL}_2(\text{Ol})^+] \quad (18)$$

then the rate of reaction is

$$\frac{d[\text{RPtL}_2(\text{NO}_3)]}{dt} = k_3[\text{HPtL}_2(\text{Ol})^+] \quad (19)$$

$$\frac{d[\text{RPtL}_2(\text{NO}_3)]}{dt} = \frac{k_3 K_1 K_2 [\text{Ol}][\text{Pt}]_T}{(K_2[\text{NO}_3^-] + K_1[\text{MeOH}] + K_1 K_2 [\text{Ol}])} \quad (20)$$

$$\frac{d[\text{RPtL}_2(\text{NO}_3)]}{dt} = k_{\text{obsd}}[\text{Pt}]_T \quad (21)$$

Table II. Summary of the Determined Values of the Rate Constants and Equilibrium Constants for the Reaction of HPt(PET₃)₂(NO₃) with Methyl Acrylate in Methanol at 25° and Ionic Strength 0.2 M

Variable held constant	Intercept ^a	Slope ^a	Calcd value
[NO ₃ ⁻] = 0.01 M	I ₁ = 18 ± 2 sec	S ₁ = 7.8 ± 0.2 sec M	k ₃ = (5.6 ± 0.7) × 10 ⁻² sec ⁻¹ S ₁ = 7.3 sec M ^e
[NO ₃ ⁻] = 0.05 M	I ₁ = 19 ± 2 sec	S ₁ = 14.2 ± 0.2 sec M	k ₃ = (5.3 ± 0.6) × 10 ⁻² sec ⁻¹ S ₁ = 16.2 sec M ^e
[NO ₃ ⁻] = 0.1 M	I ₁ = 22 ± 4 sec	S ₁ = 24.6 ± 0.3 sec M ⁻¹	k ₃ = (4.6 ± 0.9) × 10 ⁻² sec ⁻¹ ^b S ₁ = 25.8 sec M ⁻¹ ^e
[Ol] = 0.0887 M	I ₂ = 80 ± 6 sec	S ₂ = 2440 ± 60 sec M ⁻¹	K ₂ = 84 ± 15 ^d K ₁ = (8.5 ± 0.9) × 10 ⁻² ^c
[Ol] = 0.176 M	I ₂ = 45 ± 3 sec	S ₂ = 1370 ± 40 sec M ⁻¹	K ₂ = 97 ± 18 ^d K ₁ = (7.7 ± 0.9) × 10 ⁻² ^c

^a The error is the standard deviation of least-square plot. ^b Not included in the calculation of the average value of k₃. ^c K₁ calculated using k₃ = (5.4 ± 0.6) × 10⁻² sec⁻¹ and eq 26. ^d K₂ calculated using k₃ = (5.4 ± 0.6) × 10⁻² sec⁻¹ and eq 27. ^e S₁ calculated using k₃ = (5.4 ± 0.6) × 10⁻² sec, K₁ = (8.2 ± 0.9) × 10⁻², K₂ = (90 ± 17), and eq 24.

where

$$k_{\text{obsd}} = \frac{k_3 K_1 K_2 [\text{Ol}]}{K_2 [\text{NO}_3^-] + K_1 [\text{MeOH}] + K_1 K_2 [\text{Ol}]} \quad (22)$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{K_2 [\text{NO}_3^-] + K_1 [\text{MeOH}] + K_1 K_2 [\text{Ol}]}{k_3 K_1 K_2 [\text{Ol}]} \quad (23)$$

Thus, at constant NO₃⁻ concentration, 1/k_{obsd} is linear in 1/[Ol] with

$$\text{slope} = S_1 = \frac{K_2 [\text{NO}_3^-] + K_1 [\text{MeOH}]}{k_3 K_1 K_2} \quad (24)$$

$$\text{intercept} = I_1 = \frac{1}{k_3} \quad (25)$$

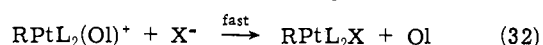
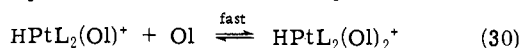
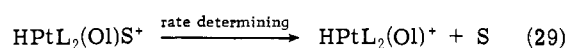
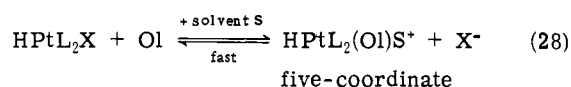
and at constant olefin concentration, 1/k_{obsd} is linear in [NO₃⁻] with

$$\text{slope} = S_2 = \frac{1}{k_3 K_1 [\text{Ol}]} \quad (26)$$

$$\text{intercept} = I_2 = \frac{[\text{MeOH}] + K_2 [\text{Ol}]}{k_3 K_2 [\text{Ol}]} \quad (27)$$

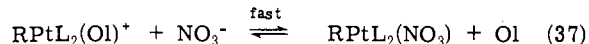
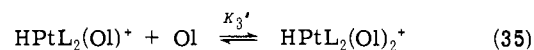
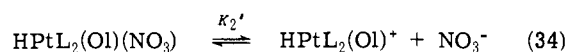
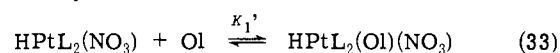
Treatment of the kinetic data according to expressions 25, 26, and 27 yields the values for k₃, K₁, and K₂, respectively. These calculated values are summarized in Table II. The quantitative nature of the proposed mechanism is strongly supported by the internal consistency of the determined values of k₃, K₁, and K₂, and also by the calculated value of S₁ using eq 24 (Table II).

It is highly doubtful that there is participation of solvent in the insertion step (eq 16), since the coordinating abilities of the various ligands in the reaction solution are in the order of NO₃⁻ > Ol > MeOH (K₁ = (8.2 ± 0.9) × 10⁻² and K₂ = 90 ± 17). The value of k₃ is invariant with respect to the concentration of NO₃⁻, the strongest coordinating ligand in the system, through the concentration range 0.01–0.1 M. The participation of a second olefin is difficult to reconcile with the observed olefin and NO₃⁻ dependence. In order to account for the less than first-order dependence in olefin using Scheme I, it is necessary to impose a mechanism of the type



The rate determining step involves the formation of a four-coordinate species from a five-coordinate one. Since there is a strengthening of the Pt–H bond in going to the transition state, an inverse secondary kinetic isotopic effect $k_{\text{H}}/k_{\text{D}} < 1$ would therefore be expected, contrary to our observations. A large secondary kinetic isotopic effect has been observed in the substitution reaction of *trans*-HPt(PET₃)₂Cl with pyridine, $k_{\text{H}}/k_{\text{D}} = 1.44$, and has been taken as evidence for the formation of five-coordinate intermediate in a SN2 type of mechanism.¹⁸ The present observed isotopic effect, $k_{\text{H}}/k_{\text{D}} = 1.34$, is inconsistent with this scheme (see below).

Alternatively, Scheme I has to be modified as



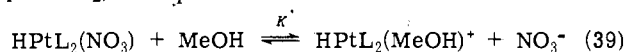
This mechanism yields a rate law

Rate =

$$\frac{k_4' K_1' K_2' K_3' [\text{Pt}]_{\text{T}} [\text{Ol}]^2}{\{1 + K_1' [\text{Ol}]\} [\text{NO}_3^-] + K_1' K_2' [\text{Ol}] + K_1' K_2' K_3' [\text{Ol}]^2} \quad (38)$$

which can be simplified to eq 20 provided that eq 33 lies essentially to the right, *i.e.*, $K_1' [\text{Ol}] \gg 1$. This is, however, ruled out on the basis of low temperature nmr studies. The ¹H nmr spectrum at –50° of a solution containing 0.29 M HPt(PET₃)₂NO₃ and 0.14 M CH₂=CHCOOCH₃ in CD₃OD shows that the chemical shifts for most of the olefin protons are identically those of the free olefin (>80%). Even after the temperature of the reaction mixture is raised until the product peaks start appearing ($T \sim -10^\circ$), the chemical shifts of the olefinic peaks remain unchanged. This indicates that coordination of the olefin does not occur extensively, hence the assumption $K_1' [\text{Ol}] \gg 1$ is invalid. On the other hand this observation is consistent with our proposed mechanism which predicts a less than 10% formation of **2** under the above experimental conditions.

Further, from the experimentally determined values of K₁ and K₂, the equilibrium constant K for the reaction



can be calculated to be 9 × 10⁻⁴. Hence a 1 × 10⁻³ M methanolic solution of HPtL₂(NO₃) is expected to exist almost entirely as HPtL₂(MeOH)⁺. Conductivity measurement of a 1.2 × 10⁻³ M solution yields an equivalent con-

Table III. The Kinetic Isotopic Effect in the Reaction of HPt(PET₃)₂(NO₃) with Methyl Acrylate in Methanol

Pt complex	Variable held constant	Intercept	Slope	$k_3(\text{H})/k_3(\text{D})$	
Pt-H	[NO ₃ ⁻] = 0.01 M	$I_1 = 18 \pm 2$ sec	$S_1 = 7.8 \pm 0.2$ sec M $S_1 = 10.6 \pm 0.2$ sec M	1.23 ± 0.24 ^a	
Pt-D		$I_1 = 22 \pm 2$ sec			
Pt-H	[O] = 0.176	$I_2 = 45 \pm 3$ sec		$S_2 = 1370 \pm 40$ $S_2 = 1810 \pm 25$	1.36 ± 0.06
Pt-D					
Pt-H		1.43 ± 0.14 ^a			
Pt-D			1.32 ± 0.05		
Pt-H	Av 1.34 ± 0.06				
Pt-D					

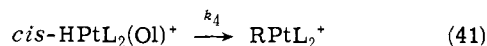
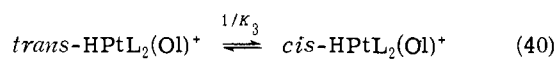
^a In calculating the average, the value is ignored because of the large error involved in determining the magnitude of the intercept.

ductance of 72 ohm⁻¹ cm² (94 ohm⁻¹ cm² for NaNO₃) showing that ionization is indeed extensive.

Although accurate determination of the equilibrium constants K_1 and K_2 from the rapid initial spectral changes prior to kinetic changes is precluded because of the subsequent insertion process, yet it is possible to estimate an approximate value of K_2 . By determining the initial increase in absorbance at 295 nm of a 1×10^{-3} M solution of HPtL₂(NO₃) in MeOH (under this condition, the complex is essentially in the form of HPtL₂(MeOH)⁺) as a function of various concentrations of methyl acrylate, an equilibrium constant of about 130 is obtained for K_2 which agrees well with the kinetically determined value (90 ± 17).

Infrared analysis of the product Pt(PET₃)₂(CH₂CH₂-COOCH₃)(NO₃) in Nujol shows that the ester group is not coordinating as is evidenced by the high frequency of 1693 cm⁻¹ for $\nu(\text{C}=\text{O})$. In the reaction of **1** with ethylene, a similar reaction pattern was observed (Figure 2), and the reaction is also inhibited by the presence of added NO₃⁻ ion.¹⁹ It has already been shown that the reaction of ethylene with the solvento complex, **4**, exhibits the same olefin dependence.¹⁴ It therefore appears that the presence of the ester group in the olefin is irrelevant to the mechanistic scheme.

From geometrical considerations, it is generally believed that insertion requires a cis disposition of the hydride and olefin ligands.²⁰ Such a requirement can be incorporated in our mechanism by imposing a rapid cis-trans isomerization before the rate determining step.



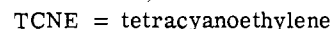
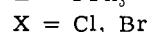
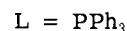
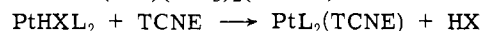
With this modification rate law 20 becomes

$$\text{Rate} = \frac{k_4 K_1 K_2 [\text{Ol}][\text{Pt}]_T}{(1 + K_3)(K_2[\text{NO}_3^-] + K_1[\text{MeOH}] + K_1 K_2 [\text{Ol}])} \quad (42)^{21}$$

which is of the same form, except k_3 becomes $k_4(1 + K_3)^{-1}$. Catalyzed^{22,23} and uncatalyzed²⁴ cis-trans isomerizations of square planar Pt(II) complexes have been observed and appropriate mechanisms discussed. In the uncatalyzed isomerization of Pt(PET₃)₂(*o*-tolyl)Cl in methanol,²⁴ evidence is presented for a dissociative mechanism in which the rate determining step is the breaking of the metal-chloride bond to yield a three-coordinate intermediate. The replacement of the chloride ligand by the more weakly coordinating nitrate ligand is expected to allow a more facile isomerization. Indeed, when AgNO₃ is added to *cis*-Pt(PET₃)₂(*o*-tolyl)Cl, the *trans* complex, *trans*-Pt(PET₃)₂(*o*-tolyl)(NO₃), is produced immediately.²⁵ Although we have proposed a catalyzed cis-trans isomerization in a previous paper,¹³ essentially on the basis of analogy rather than direct evidence, it seems reasonable to antic-

ipate that complexes **1**, **2**, and **5** may isomerize rapidly compared with the insertion step, *via* an uncatalyzed pathway, if indeed such an isomerization is required.

A kinetic isotopic effect $k_3(\text{H})/k_3(\text{D})$ is found to be 1.34 ± 0.06 by comparing the corresponding slopes and intercepts (eq 24-27) of the deuteride and hydride insertion reactions, under identical conditions (Table III). This value is consistent with a simultaneous breaking (Pt-H) and making (C-H) of bonds in the proposed mechanism and is inconsistent with the involvement of a diolefin intermediate, **3**. The small kinetic isotopic effect ($k_{\text{H}}/k_{\text{D}} = 0.9$) in reaction 43¹⁶ compared with that obtained in this study suggests, not unexpectedly, that the two mechanisms are quite different. In reaction 43, when X = CN and L = PET₃, *trans*-PtH(CN)(PET₃)₂(TCNE) has been isolated.¹⁶



(43)

The occurrence of insertion *via* this mechanism, namely one involving a four-coordinate species, probably depends on (i) the substitution lability of the *trans* ligand, *e.g.*, NO₃⁻, acetone, and (ii) the use of a polar medium which stabilizes the cationic intermediate. Under other conditions, particularly when the ligand *trans* to the hydride is a strong π -acceptor such as CO or CN⁻, or presumably SnCl₃⁻ (but see ref 26), which favor five-coordination about Pt(II), insertion may proceed *via* a five-coordinate intermediate.

Finally, it should be noted that, while Scheme I and the results of Halpern, *et al.*, are consistent with Tolman's 16-18 electron "rule,"²⁷ the above interpretation of our kinetic data for this present system in terms of Scheme II adds another example to the growing list of exceptions to this "rule."

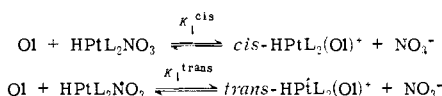
Acknowledgments. We thank the National Research Council of Canada for continued financial support of this work.

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 (17) Conceivably, the formation of **2** might not be fast compared with the insertion. The rapid pre-equilibrium assumption would then break down.
 (18) C. D. Falk and J. Halpern, *J. Amer. Chem. Soc.*, **87**, 3003 (1965).
 (19) In the reaction of **1** with $\text{CH}_2=\text{CH}_2$, preliminary kinetic runs showed that in a methanolic solution saturated with $\text{CH}_2=\text{CH}_2$, at ionic strength of 0.01 M, increasing the concentration of NO_3^- from 0.007 to 0.1 M decreases the K_{obsd} value from 2.5×10^{-4} to $1 \times 10^{-4} \text{ sec}^{-1}$.
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$$K_1 = K_1^{\text{cis}} + K_1^{\text{trans}} \text{ where}$$



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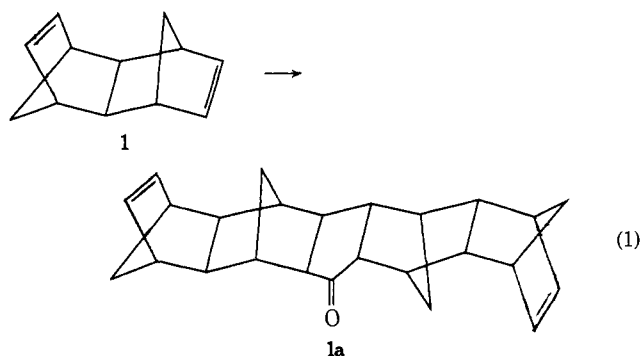
Resolution and Chiroptic Properties of a Dissymmetric Cyclopentanone with Exceptional Rotatory Power

Edward Weissberger

Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. Received May 14, 1974

Abstract: The resolution and chiroptic properties of an extremely rigid cyclopentanone showing unusually high rotatory power are presented. The high observed molecular ellipticity is thought to be due to an unprecedented number of perturbing atoms all lying in octants of the same sign augmented by five-membered ring nonplanarity. Because the carbonyl chromophore is isolated, the ketone must be regarded as inherently achiral in spite of a normal $n \rightarrow \pi^*$ transition.

Recently, the efficient cyclic coupling of olefins to carbon monoxide induced by iron carbonyls has been reported^{1,2} and the mechanism³ of this novel reaction discussed. One example of the process is illustrated by reaction 1. In the absence of metal complexing substituents^{2b} at the bridge position of the active norbornyl ring, the isolated ketones belong to the C_2 point group having the exo-trans-exo stereochemistry illustrated in reaction 1. Although diene **1** belongs to the C_s point group, ketone **1a** is dissymmetric, being formed as a racemic mixture. Each enantiomer has all four chiral centers of the cyclopentanone ring of the same designated absolute configuration; for example, that illustrated in reaction 1 has the *S* configuration.⁴



A striking feature of ketone **1a** and related materials^{1,2,5} is the extreme rigidity imposed upon the cyclopentanone ring by the presence of the two fused norbornyl systems. Consequently, at room temperature in cyclohexane, the $n \rightarrow \pi^*$ transition shows a well-resolved vibrational progression with level spacing of approximately 1260 cm^{-1} corresponding to the pseudo carbon-oxygen single bond of the π^* state. This progression is as well resolved as those of

many ketones in low-temperature glasses. Indeed, even in ethanol the $n \rightarrow \pi^*$ transition of **1a** is resolved into its vibrational components, although compared with cyclohexane as solvent the resolution is greatly reduced. A detailed discussion of the nature of this unusual electronic excitation will be presented separately.

In the following presentation, we wish to discuss the resolution and chiroptic properties observed for ketone **1a**, an inherently achiral system with exceptional rotatory power. Inherent achirality of unstrained cyclopentanones exemplified by $n \rightarrow \pi^*$ transitions of normal intensity and normal rotational strength is illustrated by 2-phenylcyclopentanone^{6,7} and 2-methyl-2-phenylcyclopentanone⁸ whose molecular rotations are 253 and 166°, respectively. Thomas and Mislow⁷ have discussed the chiroptic properties of the 3-phenyl-2-norbornanones in comparison with 2-norbornanone and have noted that neither the extinction coefficients nor the molar ellipticities are abnormally high. The octant rule⁹ has proved itself to be an effective semiempirical tool for predicting the sign of Cotton effects as a function of absolute configuration when applied to the $n \rightarrow \pi^*$ transition of inherently achiral carbonyl chromophores;^{9,10} conversely, one is often able to determine the absolute configuration of an enantiomer by measuring the sign of the Cotton effect. The octant rule has been extended to inherently chiral ketones, when the carbonyl $n \rightarrow \pi^*$ transition is coupled to a remote π system¹¹ or pseudo- π system.¹² For example, the $n \rightarrow \pi^*$ transition of β,γ -unsaturated ketones shows enhanced absorption and rotatory power.^{12,13} Nevertheless, this treatment relies upon the availability of a nearby π system and does not apply to ketones having normal molar absorptions for the $n \rightarrow \pi^*$ transition in the range of 20–80.^{11,14} Relative orientations of the carbonyl and cyclopropyl chromophores in β,γ -cyclopropylnorbornanones determine whether the carbonyl chromophore appears to be inherently chiral or