change. We conclude that the effect of phase change is small in comparison with other complications.

Summary

The rates and products of reactions of free radicals result from competition among several alternative reactions. The commonly large differences in concentration between liquid-phase and gas-phase reactions produce obvious differences in gross rates of reaction. When the most important competing reactions are of different (first and second) order, yields and products are affected as well. Two other aspects of concentration effects can be experimentally important: the cage effect in solution, and the slowing of unimolecular reactions at low pressures. The former can be observed, and the second eliminated, at higher pressures in the gas phase. All of these effects are expected and largely predictable.

The most important contribution of this paper is to emphasize the importance of solvation in reactions of radicals in solution; perhaps there are no really free radicals in solution in the gas-phase sense.[44] Chemists have been slow to recognize this situation because nearly all of our information comes from ratios of rate constants for competing reactions where solvation has similar effects on both. However, in the cleavage and abstraction reactions of alkoxy radicals[42] there is a large and clear effect of solvent and phase change. Even in two reactions as similar as the reaction of a chlorine atom with a primary and a secondary hydrogen atom, an effect has now been detected.[16a] Other examples of solvation were the association of nitrogen dioxide and (in nonradical reactions) the dimerization of cyclopentadiene and the chlorination of isobutylene. It now appears that solvents interact to some extent with all radicals as well as ions and that gas-phase studies are essential to establish the effects of zero solvation in liquid-phase reactions.

Since studies of competing reactions do not tell us whether these reactions are individually accelerated or retarded by solvation, it is important to measure the absolute rate constants for the same reaction at the same temperature in the gas phase and in solution. In further studies of competing reactions, a few more of the most and least polar reactions should be compared in the two phases to see if the distinction between chlorine atoms and alkyl radicals is as sharp as it now seems. The effects of remote substituents[16b,32] seem to be a sensitive tool. Because of the importance of reactions of aryl radicals with aromatic hydrocarbons, further work on the competition of addition and transfer reactions of alkylbenzenes[27,31-35] also seems desirable.

In choosing experimental conditions for practical synthesis through free radicals, the following factors deserve consideration. Liquid-phase reactions require small volumes and favor bimolecular reactions and cage products. Gas-phase reactions usually employ low concentrations which can moderate fast reactions, permit use of high temperatures without high pressures, favor unimolecular reactions, and eliminate cage reactions. High-pressure gas reactions resemble those in the liquid phase. However, the choice of phase depends mostly on consideration of the competing reactions in Table III and how the competition will be affected by phase or concentration changes.

Finally, wall effects are much more important in gas-phase reactions, where diffusion is faster, than in liquid-phase reactions. However, in reactions on walls or in heterogeneous catalysis we are not concerned with free radicals but with bound or complexed radicals which are beyond the scope of this paper.

Acknowledgment. The author appreciates careful readings of this paper and/or numerous useful suggestions by Drs. S. W. Benson, David M. Golden, William A. Pryor, and Cheves Walling.

(44) For earlier speculation on this point, see F. R. Mayo, *Discussions Faraday Soc.*, 14, 250 (1953).

Rotation of Styrene and *t*-Butylethylene in Platinum(II) Complexes with 2,4,6-Trimethylpyridine

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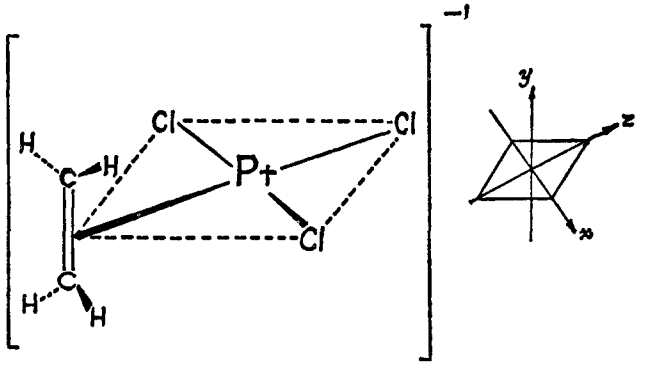
Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. *Received January 13, 1967*

Abstract: Several 1,3-dichloro-2-olefin-4-(2,4,6-trimethylpyridine)platinum(II) complexes, **2**, have been prepared and their nmr spectra determined. Although at room temperature there is a single signal for the 2,6-methyl groups, at about −50° the signal splits. This behavior is interpreted to indicate rapid (on the nmr time scale) rotation of the olefinic species about its coordination axis and a "freezing out" at the lower temperature.

In Zeise's anion, **1**, ethylene is known to be oriented at right angles to the square plane in the crystal state.[1] In connection with some other work[2] in this laboratory, we prepared 1,3-dichloro-2-ethylene-4-(2,4,6-trimethylpyridine)platinum(II), **2**, R = H. Although the compound is almost certainly *trans*, the exact spatial arrangement of the ligands with respect to each other is of interest.

(1) J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, 7, 130 (1954).
(2) A. R. Brause and M. Orchin, submitted for publication.



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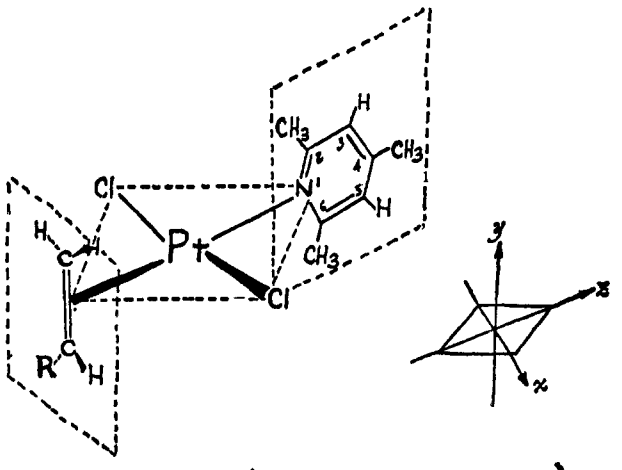


2 (R ≡ H, CH_3, Ph, t-C_4H_9)

The exceptional stability of *ortho*-substituted aryl nickel complexes, *e.g.*, *trans*-[$(PPhEt_2)_2Ni(mesityl)_2$], has been ascribed[3] to the interference of the *ortho* substituents with the bulky tertiary phosphine ligands on each side of the nickel atom which prevents rotation of the aryl group about the Ni–C bond. Although there may be some question as to the validity of the interpretation, it is quite clear that substantial steric hindrance to free rotation exists. In **2**, rotation round the Pt–N coordination bond as an axis is possible, but molecular models show that 2,6-methyl substitution would favor a geometry in which the pyridine ligand lies perpendicular to the square plane as shown. Although the ethylene group also might be perpendicular to the square plane as in **2**, the possibility of ethylenic rotation in solutions of the complex needs to be considered. If we involve the d_{z^2} orbital in the dsp^2 hybrid bonding orbitals,[4] then the availability of the d_{yz} orbital for d–π^* bonding should facilitate such rotation. Indeed, Cramer has shown[5] that the ethylene coordinated to rhodium(I) in the compound π-$C_5H_5Rh(C_2H_4)_2$ rotates freely at room temperature.

In the complex **2** (R = H), the *o*-methyl groups are in magnetically equivalent environments with respect to ethylene. If, however, an unsymmetrical olefin were complexed in place of ethylene and the pyridine moiety were "fixed," the *o*-methyls would become nonequivalent and such nonequivalence should be discernible by nmr techniques. Accordingly, the complexes **2** (R = CH_3, $C(CH_3)_3$, Ph) were prepared. A single nmr reasonance for the *o*-methyls would be presumptive evidence for free rotation of the olefin; splitting of the singlet at low temperature would be consistent with slowing down such rotation.

Experimental Section

1,3-Dichloro-2-ethylene-4-(2,4,6-trimethylpyridine)platinum(II), **2** (R = H), was prepared by addition of 2,4,6-trimethylpyridine to Zeise's salt[2] in 97% yield as a yellowish green powder, mp 155–157° dec (2-mmole scale). *Anal.* Calcd for $PtCl_2C_{10}H_{15}N$: C, 28.91; H, 3.64; Pt, 46.99. Found:[6] C, 29.12; H, 3.85; residue (Pt), 46.60.

Compound **2**, (R = CH_3) was synthesized *via* the propylene platinous chloride dimer. Simple displacement of ethylene by propylene from the ethylenic complex gave incomplete conversion. The ethylene platinous chloride dimer (500 mg, 0.85 mmole) was placed in a small vial and immersed in a Dry Ice–acetone bath. Propylene was bubbled in until about 5–7 ml had accumulated, and then the mixture was stirred magnetically at this temperature for 15 min. The Dry Ice bath was removed, and the mixture was stirred at room temperature until all the excess propylene had evaporated. Saturated potassium chloride solution was added, and the solution was stirred until no more solid material remained and a yellowish green solution resulted. Then 0.30 ml of 2,4,6-trimethylpyridine (1.95 mmoles, 15% excess) was slowly added, giving a yellow-green cloud and then a precipitate on standing. This was filtered and air dried, yielding 657 mg (90%) of a yellow powder, mp 103–105° dec. *Anal.* Calcd for $PtCl_2C_{11}H_{17}N$: C, 30.76; H, 3.99; Pt, 45.46. Found:[6] C, 30.05; H, 3.94; residue (Pt), 46.90.

Compound **2** [R = $(CH_3)_3C$] was made by the same dimeric route, except in this case no ice bath was necessary as the boiling point of *t*-butylethylene is 76°. From 1146 mg of impure dimer, which was first dissolved in acetone and filtered to remove impurities, there was obtained 1004 mg (55%) of a yellow-green powder, mp 129–133° dec. *Anal.* Calcd for $PtCl_2C_{14}H_{23}N$: C, 35.65; H, 4.92; Pt, 41.40. Found:[6] C, 34.80; H, 4.83; residue (Pt), 36.60.

Compound **2** R = Ph) was efficiently prepared by simple displacement. The ethylenic complex (958 mg, 2.30 mmoles) was dissolved in 25 ml of chloroform and 0.25 ml (2.2 mmoles) of styrene was added. The mixture was stirred magnetically for 30 min, then filtered, giving a clear yellow solution. The volume of solution was reduced with a nitrogen stream and pentane was added, giving a yellow-orange oil which on scratching and refrigeration overnight gave a highly crystalline orange-yellow material, mp 133–135° dec, yield 769 mg (68%). *Anal.* Calcd for $PtCl_2C_{16}H_{19}N$: C, 39.09; H, 3.90; Pt, 39.72. Found:[6] C, 38.45, H, 4.08; residue (Pt), 40.70.

Attempts to prepare 1,3-dichloro-2(α,α-diphenylethylene)-4-(2,4,6-trimethylpyridine)platinum(II) by either simple displacement or *via* the dimer were unsuccessful. A previous attempt to prepare the α,α-diphenylethylene dimer[7] was also unsuccessful.

Results and Discussions

The nmr spectral data are given in Table I. Our discussion shall concern itself only with the signals for the *o*-methyl groups. When the propylene complex **2** (R = CH_3) was examined only a single triplet (Figure 1) was observed for the *o*-methyls and there was no significant change at −46°. Owing to instrumental limitations, the temperature could not be much further lowered. We then decided to increase the

(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960). These authors suggest that the perpendicular orientation of the aryl ring forces interaction beteeen a π orbital of the aryl group and the dπ orbital in the plane of the molecule. Since both of the orbitals to be combined are occupied, this should lead to a raising of the highest occupied (dπ) orbital and hence a lowering of the energy difference between the highest occupied and lowest empty orbitals.

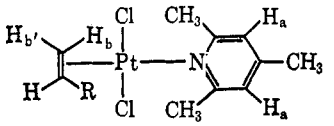
(4) We are using essentially the coordinate system employed by J. W. Moore, *Acta Chem. Scand.*, 20, 1155 (1966), in his complete treatment of the electronic absorption spectrum of Zeise's salt. The anion, **1**, and compound **2** (R = H) have C_{2v} symmetry and hence the necessity of using the symmetry axis in the square plane as the *z* axis. In $PtCl_4^{-2}$, the *z* axis is the fourfold symmetry axis perpendicular to the plane.

(5) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(6) Analyses by Galbraith Laboratories, Inc.

(7) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

Table I. Nmr Data[a] for the Complexes



	R′						
	H	CH_3		Ph		t-C_4H_9	
	Amb[b]	Amb	−46°	Amb	−60°	Amb	−46°
δ_{H_a}	7.05	6.99	7.02	6.95	7.00	7.00	7.03
J_{Pt-H_a}	9	9	9	10	10	10	10
$\delta_{H_b,H_{b'}}$	4.80	Multiplet centered at 4.65	...[c]	Multiplets centered at 4.65, 5.44	...[c]	Multiplet centered at 4.80	...[c]
$J_{Pt-H_b,H_{b'}}$	62	...[d]	...[c]	...[d]	...[c]	...[c]	...[c]
$\delta_{o\text{-}CH_3}$	3.17	2.90	3.03	2.97	2.93, 2.80	3.17	3.03, 3.00
$J_{Pt-o-CH_3}$	12	13	13	13	~13	12	~12
$\delta_{p\text{-}CH_3}$	2.37	2.20	2.20	2.18	2.12	2.32	2.20
δ_R	None	1.57 doublet	1.57 doublet	7.80, 7.48 multiplet	...[e]	1.32	1.15

[a] All chemical shifts are in parts per million (δ) and coupling constants in cycles per second. The resonance peak of $CHCl_3$ (δ 7.27) was used as an internal standard. [b] Ambient machine temperature. [c] Not examined in detail. [d] P. Kaplan and M. Orchin, *Inorg. Chem.*, in press, discuss platinum–olefin coupling in vinyl complexes.

bulk of the R group and prepared the compound **2** where R = Ph. The single triplet observed in the nmr at room temperature was split into two overlapping triplets at −60°; the chemical shifts of the two triplets were δ 2.93 ($J_{Pt-CH_3} \sim 12$ cps) and δ 2.80 ($J_{Pt-CH_3} \sim 12$ cps), a chemical shift difference of 7.8 cps at 60 Mc. The same effect was observed with compound **2** (R = *t*-butyl) although it was not as pronounced, and a difference of only 2 cps in the chemical shift was observed

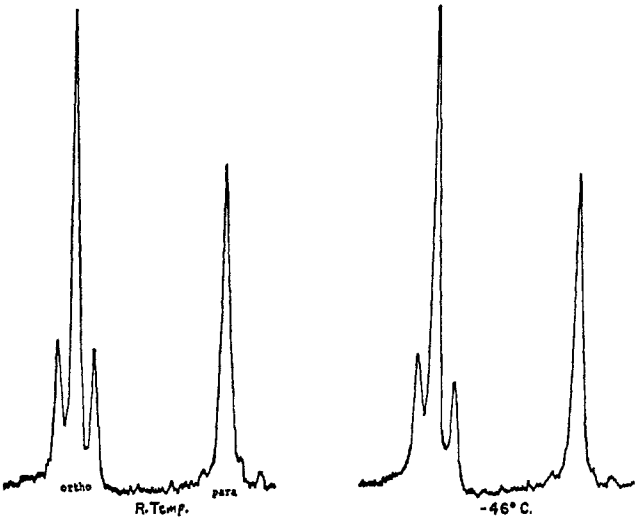


Figure 1. Nmr spectra of *o*- and *p*-methyls in the propylene complex.

(Figure 2). Since we assume that the pyridine is relatively fixed in these complexes, a single signal for the *o*-methyls in the styrene and *t*-butylethylene complexes implies a rotation of the vinyl compound around the coordination axis. Lowering the temperature "freezes" out the rotation and permits observation of the more stable conformer in the nmr spectra. Alternately, we could have considered that the olefin is fixed and the pyridine rotating at room temperature and frozen out at low temperature. Or, we may have considered both moieties free to rotate at room temperature and both frozen out at low temperatures. We do not consider either of these as likely as the "fixed" pyridine and the rotating ethylene. Rapid intermolecular exchange of free and complexed olefin would also account for the observation of a single absorption for the *o*-methyls. However, the spectrum of **2** (R = Ph) shows platinum–olefin coupling at room temperature and thus this explanation is excluded.

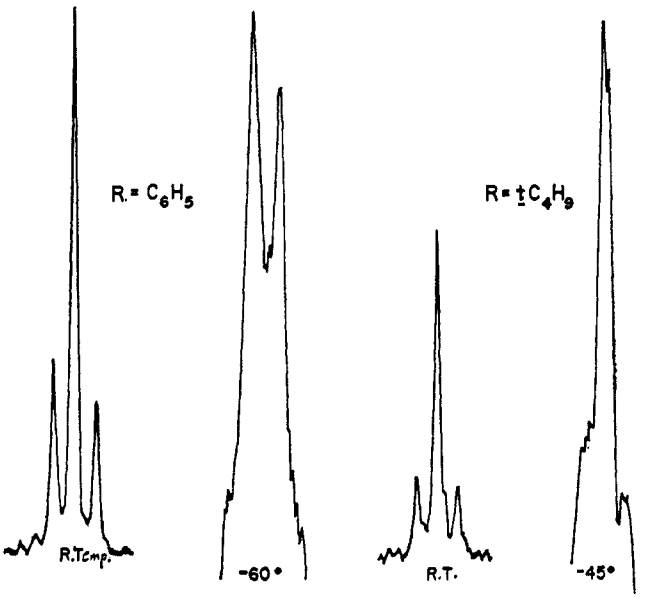


Figure 2. Nmr spectra of *o*-methyls for R-substituted complexes.

Failure to observe splitting with the propylene complex **2** (R = CH_3) may mean a smaller rotational barrier requiring temperatures lower than −60° or it may mean that the magnetic effect of the propylene on the *o*-methyl groups is too small to be observed across the square plane.

A decision as to whether the ethylenic moiety is frozen out parallel to or perpendicular to the square plane

could presumably be made by using α,α-diphenylethylene in place of ethylene in **2**. If both phenyls were either above or below the square plane, two signals for the *o*-methyls should be observed. However, if the diphenylethylene were frozen out so that one phenyl was above and one phenyl below the plane, the *o*-methyls would again be magnetically equivalent and only one signal should result. Unfortunately, the compound of interest could not be prepared, but the investigation is being pursued.

Acknowledgment. The authors wish to thank Dr. P. Kaplan, Dr. W. W. Bannister, and Mr. Paul Schmidt for their valuable comments, and Mr. Frank Stary for some assistance with the Varian A-60. This research was partially supported by the Sohio Corp. through a fellowship to Mr. Brause. Further, we should like to thank Engelhard Industries for donating our platinum supplies. The nmr spectrometer used in this work was purchased with the aid of a grant from the National Science Foundation.

Catalysis of α-Hydrogen Exchange. IV. Deuterium Exchange of Methoxyacetone[1,1a]

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Abstract: The kinetics of loss of deuterium from methoxyacetone containing deuterium α to the carbonyl group have been studied in aqueous solution. Catalytic constants have been determined for hydrogen ions, hydroxide ions, water, phenoxide ions, *p*-nitrophenoxide ions, trimethylamine, triethylamine, N-methylpyrrolidine, and N-methylmorpholine. In the presence of N-methylmorpholine buffers the reaction is slightly subject to catalysis by methylammonium chloride, presumably because of the intermediate formation of an enamine. Exchange at the methyl position is faster (by up to sixfold) than at the methylene position for all the catalysts studied except hydroxide ions, which brought about slightly more rapid exchange at the methylene position.

Many physiologically important reactions, such as aldol condensations, epimerizations, etc., involve deprotonation of an organic molecule (*e.g.*, a sugar) at a position that is α to a carbonyl group and to a hydroxy group. As a first step in studying the mechanisms of such reactions we have investigated the deuterium exchange of methoxyacetone. The methoxy substituent should have an influence on the acidity of hydrogen atoms attached to the same carbon atom that is quite similar to that of a hydroxy substituent, but the greater difficulty of oxidizing and deprotonating the methoxy substituent should decrease the probability of complicating side reactions.

Results

The proton magnetic resonance (pmr) spectrum of methoxyacetone consists of three singlets, at τ 5.97, 6.59, and 7.87, attributed to the methylene hydrogen atoms, the methoxy hydrogen atoms, and the carbon-bound methyl (referred to hereafter simply as methyl) hydrogen atoms, respectively, on the basis of their relative intensities and chemical shifts. When solutions of the compound in deuterium oxide are heated with sodium carbonate, the absorption due to the methylene and methyl hydrogen atoms decreases in intensity. We have studied the catalytic action of hydrogen ions and various bases on the dedeuteration of the deuterated methoxyacetone prepared in this way. The reaction was followed by extracting the aqueous reaction solutions with chloroform and integrating the pmr spectra of the chloroform extracts. The methoxy group of the ketone provides an internal standard for comparison with the increasing intensities of the other two absorption peaks. First-order rate constants were determined using the equation

$$k_p t = 2.303 \log \frac{(M/R)_\infty - (M/R)_0}{(M/R)_\infty - (M/R)_t} \qquad (1)$$

where R is the integrated intensity of the reference (methoxy) peak, M is the integrated intensity of the methyl or methylene peak, and the subscripts refer to the reaction time. For $(M/R)_\infty$ the theoretical values, 1 for methyl and $^2/_3$ for methylene, were used. For each run two rate constants may be calculated, one for loss of deuterium from the methylene group ($k_p^{CH_2}$) and one for loss of deuterium from the methyl group ($k_p^{CH_3}$).

It is assumed that the reaction is subject to catalysis by all the acids and bases present in the solution, so that in the presence of the B–BH$^+$ buffer the first-order rate constant k_p may be expressed

$$k_p = k_H[H^+] + k_h[OH^-] + k_w[H_2O] + k_B[B] + k_{BH}[BH^+] \qquad (2)$$

where the k's are catalytic constants for the various possible catalysts. Superscripts will be used to show

(1) This investigation was supported in part by Public Health Service Grant AM-10378 from the National Institute of Arthritis and Metabolic Diseases. For the preceding paper in this series see J. Hine, F. C. Kokesh, K. G. Hampton, and J. Mulders, *J. Am. Chem. Soc.*, 89, 1205 (1967).

(1a) NOTE ADDED IN PROOF. Since this paper was submitted, a a study of the deuterium exchange of methoxyacetone in the presence of sodium acetate and potassium bisulfate has been published by A. A. Bothner-By and C. Sun [*J. Org. Chem.*, 32, 492 (1967)].

(2) U. S. Public Health Service Postdoctoral Fellow, 1965–1966.