states of aliphatic ketones may also have a somewhat nonplanar geometry. Since factors which may restrain the out-of-plane bending of α-C–C bond of an aliphatic ketone, such as α methylation or confining the carbonyl group in a cage-like system, increase the lifetime of $^1n,\pi^*$ and reduce the rate of intersystem crossing, the total Franck–Condon factor may well be a product of several terms, and the decrease in the k_{isc} may be due at least in part to the modification in the Franck–Condon factor involving the out-of-plane bending of α-C–C bonds in the various states of aliphatic ketones.

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Rapid Intramolecular Rearrangements in Pentacoordinate Transition Metal Compounds. On the Rearrangement Mechanism of Some Fluxional Iridium(I) Complexes[1]

Sir:

Stereochemical nonrigidity is a characteristic and chemically important feature of pentacoordinate phosphorus(V) compounds,[2] and several elegant studies have recently established a detailed and apparently general molecular rearrangement mechanism.[3] In contrast, although pentacoordination is now well known for transition metal complexes,[4] only a few observations of rapid intramolecular rearrangement in such complexes have been reported.[5] And in no case has information been presented which would distinguish between the theoretically possible polytopal mechanisms for the rearrangement process.[6] We wish to describe a series of iridium(I) complexes, which provide the first such evidence regarding the mechanism of site interchange for a fluxional pentacoordinate transition metal compound.

We have prepared compounds of the type RIr(COD)P_2 (see Table I) by standard methods,[7] and have measured their ^{1}H nmr spectra over a wide temperature range. The numerical results of this study are summarized in Table I, and the spectra we observe for $CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2$ (from -3 to $+117°$) are presented in Figure 1.

For each compound the low-temperature limiting spectrum shows for the COD ligand two vinylic resonances and two broad methylenic resonances[10] (*e.g.*, $CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2$ at $-3°$ in Figure 1). In addition, the resonance of R appears as a (1:2:1) triplet, indicating equal coupling to the two phosphorus atoms. Furthermore, the phosphine methyl resonances appear as multiplets with pseudotriplet structure, resulting from virtually coupled $X_3AA'X'_3$ spin systems.[11] For the $P(C_6H_5)(CH_3)_2$ compounds the diastereotopic[12] methyl groups on each phosphine give rise to a *pair* of multiplets (Figure 1, $-3°$). On the basis of these and other observations[13] the compounds RIr(COD)P_2 are assigned the (idealized) trigonal bipyramidal (TBP) structure I (see Figure 2).

As the temperature is raised the separate vinylic resonances seen in the limiting spectrum gradually coalesce to a single resonance at the mean. Concomitant averaging of the COD methylene signals also takes place. However, the triplet pattern for R and the pseudotriplet phosphine methyl patterns are maintained throughout, and furthermore, there is *no equilibration of the resonances of the two diastereotopic methyl groups* in the $RIr(COD)(P(C_6H_5)(CH_3)_2)_2$ compounds (Figure 1, -3 to $+87°$). Phosphine dissociation, implied by collapse of the structure of the R and phosphine methyl resonances, occurs only at higher temperatures (*e.g.*, 117° for CH_3Ir(COD)-

(1) Work supported in part by the Petroleum Research Fund.
(2) (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966); (b) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).
(3) G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc*, **89**, 6801 (1967); G. M. Whitesides and H. L. Mitchell, *ibid.*, **91**, 5384 (1969); D. Gorenstein and F. H. Westheimer, *ibid.*, **92**, 634 (1970).
(4) See ref 2a; also see J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084 (1969); K. N. Raymond, D. W. Meek, and J. A. Ibers, *ibid.*, **7**, 1111 (1968), and references contained therein.
(5) (a) $Fe(CO)_5$, F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); (b) $Fe(PF_3)_x(CO)_{5-x}$, C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969); $(C_4H_6)Fe(PF_3)_2(CO)$, J. D. Warren and R. J. Clark, *ibid.*, **9**, 373 (1970); $CF_3Co(PF_3)(CO)_3$, C. A. Udovich and R. J. Clark, *J. Amer. Chem. Soc.*, **91**, 526 (1969); (c) $HIr(CO)_2(P(C_6H_5)_3)_2$, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 725 (1969).
(6) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969).
(7) These compounds were prepared by treating $(Ir(COD)Cl)_2$ in benzene with the required amount of phosphine ligand (P) and methyllithium or isopropylmagnesium bromide. Satisfactory elemental analyses have been obtained for each compound. The preparation of $HIr(COD)(P(C_6H_5)_3)_2$ has been reported,[8] but the nmr behavior communicated here has not received prior mention. We had independently prepared this hydride by treating $Ir(COD)(P(C_6H_5)_3)_2^{+}$ [9] with hydrazine.
(8) (a) H. Yamazaki, M. Takesada, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **42**, 275 (1969); (b) M. Lavecchia, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **4**, 29 (1970).
(9) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).
(10) In some solvents the methylenic resonances are not clearly resolved (*e.g.*, dichloromethane).
(11) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(12) For terminology, see K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).
(13) (a) The separate vinylic resonances have quite different line widths. Since coupling to R is small, this difference must arise from differential coupling to the phosphorus atoms, more in keeping with the TBP structure than with the alternative tetragonal pyramid structure.[8b] We tentatively assign the lower field (broader) signal to the equatorial vinyl protons. (b) The phosphorus–hydride coupling constants (*ca.* 22 Hz) are consonant with those found for similar iridium species with hydride cis to phosphorus (see ref 5c); the phosphine–methyl patterns indicate rather strong P–P coupling, a situation not found for iridium complexes with *cis*-phosphines. (c) We have also prepared the analogous 1,2-diphenylphosphinoethane–hydride complex, and its nmr spectrum is consistent only with a TBP structure. A forthcoming paper will describe other compounds of this type more fully. (d) The compound $Ir(COD)_2SnCl_3$ has been shown to have a TBP structure, with COD spanning axial–equatorial sites: P. Porta, H. M. Powell, R. J. Mawby, and L. M. Venanzi, *J. Chem. Soc. A*, 455 (1967). (e) An X-ray structure determination is presently in progress to verify this assignment.

Table I. ^{1}H Nmr Data for RIr(COD)P_2[a]

Compound[b]	Chemical shifts, τ: Methylene	Vinyl	Phosphine methyl	R	Coupling constants, Hz: J_{P-H_R}	N[c]	Temp, °C: T_L[d]	T_C[e]
$CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2$	8.2	6.77, 8.05	8.32, 8.46	10.16	11.1	6.5	0	67[f]
$CH_3Ir(COD)(P(C_6H_5)_2(CH_3))_2$	8.2	6.53, 7.85	8.19	10.21	10.8	6.1	30	>80[g]
$HIr(COD)(P(C_6H_5)(CH_3)_2)_2$	8.1	6.57, 6.98	8.18, 8.32	24.11	23.8	7.2	−40	−2
$HIr(COD)(P(C_6H_5)_2(CH_3))_2$	8.26, 8.35	6.39, 6.71	8.08	23.99	22.5	6.6	−20	10
$HIr(COD)(P(C_6H_5)_3)_2$	8.22, 8.45	6.20, 6.55		23.79	22.0		30	70[f]

[a] Values for dichloromethane solutions, except noted. [b] COD = 1,5-cyclooctadiene. [c] $N = |^2J_{P-H} + {}^4J_{P-H}|$ for methylated phosphine $H_3PP'H'_3$ spin systems. [d] Temperature at which limiting low-temperature spectrum is recorded. [e] Temperature at which vinylic resonances coalesce. [f] Chlorobenzene solution. [g] Onset of phosphine dissociation occurs before coalescence is complete (benzene solution).

$(P(C_6H_5)(CH_3)_2)_2$, Figure 1[14]). Clearly the process causing coalescence of the diene resonances must be intramolecular[15] and involves exchange of axial and equatorial sites in the fluxional TBP structure. The rate at which this process occurs depends on the ligands as H > CH_3 and $P(C_6H_5)(CH_3)_2$ > $P(C_6H_5)_2(CH_3)$ > $P(C_6H_5)_3$.[16]

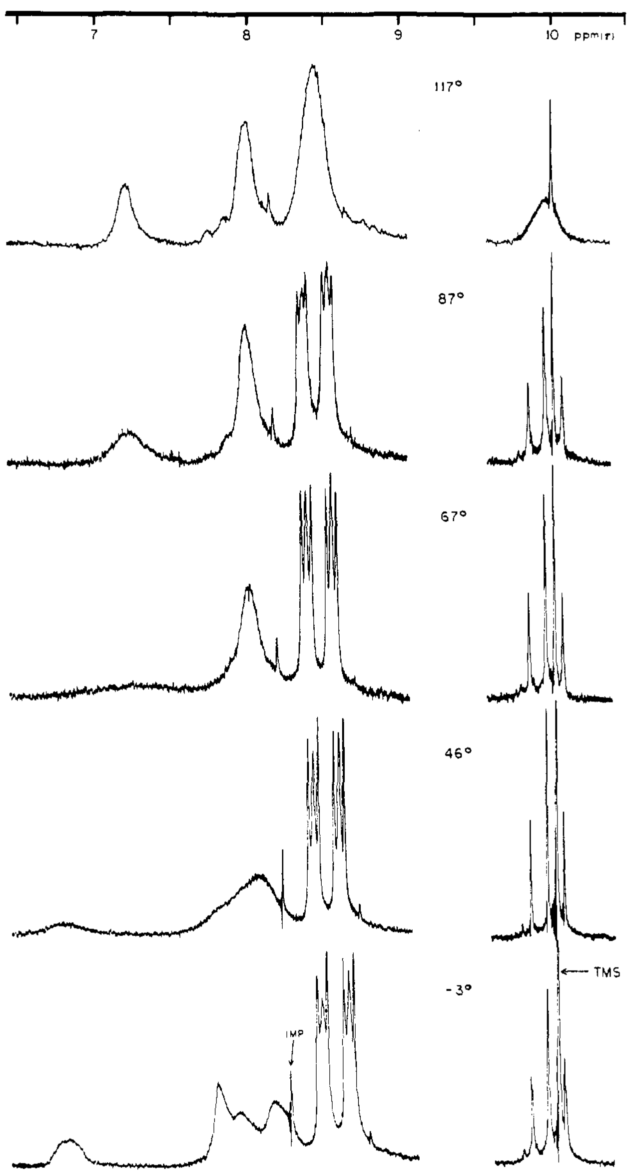

Figure 1. Temperature dependence of the 100-MHz ^{1}H spectrum of $CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2$ in chlorobenzene. IMP refers to acetone, present from recrystallization.

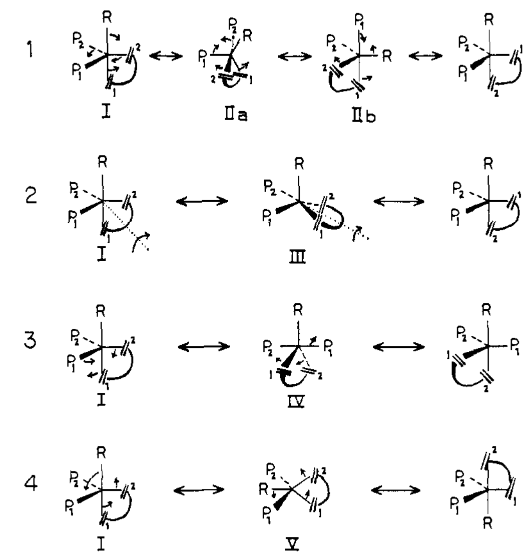

Figure 2. Mechanistic schemes to account for axial–equatorial equilibration of COD vinyl protons in I.

Several possible mechanisms, derived from general topological considerations, can account for axial–equatorial site exchange.[6] The four most reasonable schemes for this system are depicted in Figure 2.[17] Scheme 1 involves the Berry or pseudorotation process,[18] which requires simultaneous interchange within two axial–equatorial pairs, using the remaining equatorial ligand as a "pivot." This process appears general for phosphorus(V) compounds,[3] and is in complete accord with our observations presented here. Each of schemes 3 and 4[19] permutes three sites within the TBP structure, but causes interchange of the enantiotopic phosphorus atoms. This would lead to equilibration of the pair of diastereotopic methyl

(14) All spectral changes are reversible with temperature.

(15) Intramolecular dissociation and recombination of one end of the diene *via* a *planar* intermediate would equilibrate the diastereotopic methyl groups. A tetrahedral intermediate is highly unlikely on energetic grounds. This point will be amplified in a full paper.

(16) Activation parameters derived from a compete line-shape analysis will be reported subsequently.

(17) TBP configurations in which the diene spans two equatorial (or two axial) sites are unlikely to be intermediates in these processes (see ref 13d), and schemes which involved such species were not included in Figure 2. In any case, such schemes are disallowed as they too would lead to equilibration of the diastereotopic methyl resonances.

(18) R. S. Berry, *J. Chem. Phys.*, **32**, 923 (1960).

(19) Mechanism 4, in which R tunnels through the pseudotetrahedral intermediate configuration V, would have been more attractive for R = H than for R = CH_3; *cf.* E. L. Muetterties, *et al.*, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).

resonances, contrary to observation. Scheme 2 involves a twist of the diene about an axis normal to the plane containing the double bonds. However, these nmr results cannot distinguish this twist process from the pseudorotation mechanism, because the intermediate configuration III has the same (C_s) symmetry as that found in the process IIa → IIb.[20] Experiments designed to distinguish unambiguously between these two mechanisms are currently in progress.

Finally, it was suggested[21] that the equilibration of the diene resonances observed during the intermolecular exchange of $P(C_6H_5)_3$ with $Ir(COD)P(C_6H_5)_3Cl$ resulted from an angular twist of the diene in the proposed intermediate, $Ir(COD)P(C_6H_5)_3)_2Cl$. Our observations on the closely related but stable pentacoordinate complexes afford a more detailed description of the intramolecular rearrangement occurring during the lifetime of such an intermediate. Studies underway are aimed at integrating a mechanistic picture of this type into a more general understanding of exchange reactions of planar four-coordinate d[8] metal complexes.[22]

(20) The observed dependence on phosphine ($P(C_6H_5)(CH_3)_2$ > $P(C_6H_5)_2CH_3$ > $P(C_6H_5)_3$) suggests steric compression and/or metal–phosphine bonding changes in the rate limiting transition state. This favors scheme 1 over scheme 2.

(21) K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 109 (1969), and references therein.

(22) *Cf.* P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).

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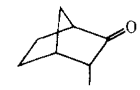
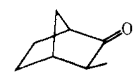
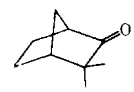
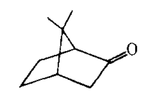
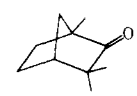
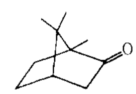
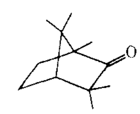
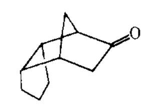
Table I. Quenching of Ketone Fluorescence

Ketone[a]	No.	$k_q^f\tau_f$[b] t-DCE	$k_q^f\tau_f$[b] c-DEE	k_q^f(DCE)/k_q^f(DEE)
	**1**	29	7.1	4.1
	**2**	21	2.6	8.1
	**3**	14	5.1	2.8
	**4**	14	2.7	5.2
	**5**	4.7	0.6	7.9
	**6**	5.0	7.3	0.69
	**7**	5.2	0.4	13.0
	**8**	5.6	2.6	2.1
	**9**	1.5	<0.1	>15
	**10**	34	8.1	4.2

[a] 0.1 *M* in acetonitrile. [b] Slopes of Stern–Volmer plots of t-DCE and c-DEE quenching of ketone fluorescence. Error limits ±10%.

Quenching of the Fluorescence of Norcamphor and Its Derivatives by *trans*-1,2-Dicyanoethylene and *cis*-1,2-Diethoxyethylene. Evidence for Two Distinct Quenching Mechanisms[1]

Sir:

Available evidence[2] indicates that the n,π* states of alkyl ketones possess an excited carbonyl function which is simultaneously an electrophilic reagent (specifically reactive in the volume of space near the carbonyl plane and close to the oxygen atom) and a nucleophilic reagent (specifically reactive in the volume of space above and below the carbonyl plane). We report here that the utility of this simple model is nicely demonstrated in the fluorescence quenching of norcamphor, and a series of its methylated derivatives, by *trans*-1,2-dicyanoethylene (t-DCE) and *cis*-1,2-diethoxyethylene[3] (c-DEE).

Slopes of the Stern–Volmer plots for fluorescence quenching by t-DCE and c-DEE are given in Table I. Linear slopes were observed in all cases, which indicates that eq 1 (ϕ_f^0 = ketone fluorescence in the absence of quencher, ϕ_f = ketone fluorescence in the presence of quencher, k_q^f = the bimolecular rate constant for ketone fluorescence quenching, τ_f = the ketone singlet lifetime, and (Q) is the concentration of quencher) is valid for the systems studied. The measured fluores-

$$\frac{\phi_f^0}{\phi_f} = 1 + k_q^f\tau_f(Q) \quad (1)$$

cence lifetimes of **1**, **4**, and **8** were found to be 5.2, 4.4, and 4.1 nsec, respectively. The relative fluorescence quantum yields of **1–8** were found to vary ±20% from an average value (ϕ_f^{rel} of **8** = 1.00)[4] with the sole exception of **5** which was about 50% lower than the average value. Thus, it seems safe to conclude that the trends in $k_q^f\tau_f$ will reflect trends in k_q^f for the compounds listed in the table. Furthermore, the ratio k_q^f(DCE)/k_q^f(DEE), which removes the problems of knowledge of τ_f, shows a wide variation, thus providing further evidence for a dichotomy of mechanism.

From the data listed in the table it can be seen that the response of k_q^f to ketone structure, while quite different for t-DCE relative to c-DEE, is easily understandable on the basis of the expected reactivity pattern of a

(1) Molecular Photochemistry. XXV. Paper XXXIV: N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, 92, 5727 (1970). The authors thank the Air Force Office of Scientific Research for their generous support of this research.

(2) (a) For example, see J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 138 (1970), and references therein; (b) M. Kasha, "Light and Life," W. N. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 31; H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(3) W. M. McElvain and C. H. Stammer, *J. Amer. Chem. Soc.*, 73, 915 (1951).

(4) Ketone solutions were approximately 0.1 *M* in acetonitrile. Measurements made on an Aminco-Bowman spectrophotofluorimeter.