and tRNA but also can provide a means of elucidating transient intermediates and elementary steps in the pathway to aminoacyl-tRNA formation. Studies of this nature have been hampered thus far by the difficulties of obtaining substantial amounts of purified enzyme and of maintaining the enzyme activity.

Finally it will be of interest to identify groups on the enzyme which are involved in binding and catalysis. Although some work has been aimed at defining the role of the highly reactive sulfhydryl group,[61,62] little else has been done to unravel the chemical nature of the active site(s). This kind of work generally requires significant amounts of pure, stable enzyme, so it may yet be some time before definitive research in this area is carried out.

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(61) M. Iaccarino and P. Berg, *J. Mol. Biol.*, 42, 151 (1969).

(62) T. Kuo and M. DeLuca, *Biochemistry*, 8, 4762 (1969).

Rapid Intramolecular Rearrangements in Pentacoordinate Transition Metal Compounds

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Pentacoordination is now found throughout the Periodic Table, but it occurs predominantly within two areas—in the compounds of group V (such as phosphorus(V)) and of the transition metals in a formal d^8 electronic configuration (*e.g.*, zerovalent iron).[1]

In group V, the ground-state geometry is almost exclusively trigonal bipyramidal (TBP) rather than square pyramidal (SP), and the relative energies of positional TBP isomers are determined by preference rules based on ligand electronegativity. Further, stereochemical nonrigidity is a characteristic and chemically important feature for which a general rearrangement mechanism has been established.[2]

In contrast, although many pentacoordinate transition metal complexes have been synthesized, and X-ray diffraction studies have established several solid-state structures, the factors determining the stability of geometric and positional isomers are not readily apparent. For d^8 complexes, most of the structures correspond closely to either TBP or, less commonly, SP geometry, although a few structures show quite large distortions from these idealized forms. In view of the close stability of SP and TBP forms in transition metal complexes, intramolecular rearrangement might be expected to occur readily. Indeed, at the outset of this work there were indications in the literature that this may well be so (*vide infra*), although no unambiguous example of such behavior had been reported.

In this Account we present the results of studies on a series of related complexes of d^8 electronic configuration, whose stereochemistries, dynamic behavior, and mechanism of rearrangement in solution have been investigated by nmr spectroscopy. From these studies some tentative generalizations have been drawn. However, pentacoordinate intermediates have also been invoked in ligand exchange reactions and catalytic processes involving d^8 metal complexes. Little consideration has been given to the detailed stereochemistry of such intermediates or to the implications of dynamic behavior occurring during their lifetime. Preliminary results involving such intermediates are also presented.

Background Observations.

Early ^{13}C nmr studies on iron pentacarbonyl found only one resonance line,[3] even though two signals (3:2 ratio) would be expected for the TBP ground-state geometry,[3] implying a rapid exchange of carbonyl ligands between nonequivalent sites. The first unambiguous evidence for a rapid intramolecular rearrangement in a d^8 pentacoordinate transition metal complex was reported in 1969 by Udovich and

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(1) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem., Soc.*, 20, 245 (1966).

(2) *e.g.*, (a) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, 91, 5384 (1969); (b) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968); (c) R. R. Holmes, *ibid.*, 5, 296 (1972).

(3) (a) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, 29, 1427 (1958); (b) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 58, 1893 (1962).

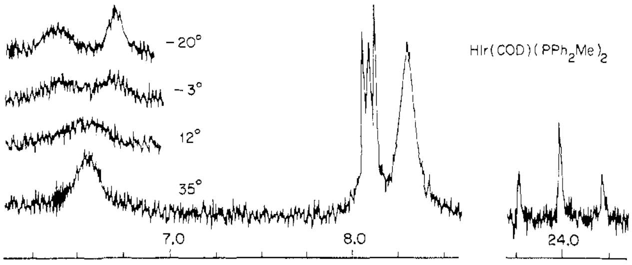

Figure 1.

Clark,[4] the variable low-temperature ^{19}F nmr spectrum of the compound $CF_3Co(CO)_3PF_3$ indicating two equilibrating isomers which exchange ligands between axial and equatorial sites. Contemporaneous studies on the compound[5] $HIr(CO)_2(P(C_6H_5)_3)_2$ and more recently on several $HM(PF_3)_4$ and related species[6] have provided further evidence that rapid isomer equilibration is a general phenomenon in such pentacoordinate complexes.

Diene Complexes of Pentacoordinate Ir(I) and Rh(I). Some Mechanistic Distinctions.

Concurrent with these latter reports,[7] we synthesized compounds of the type $RM(diene)L_2$ (M = Ir, Rh; R = H, CH_3, C_6H_5; L = tertiary phosphine or arsine; diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD)) and studied their ^1H nmr spectra over a wide temperature range. In each case, a low-temperature limiting spectrum was obtained which displayed features requiring the corresponding static structure to have the L ligands in symmetric positions, but the vinyl protons on the diene to be in two nonequivalent sites. The limiting spectrum measured at −20° for $HIr(COD)(PCH_3(C_6H_5)_2)_2$ in CH_2Cl_2 is shown in Figure 1; two separate vinyl resonances are observed for the 1,5-cyclooctadiene ligand (at τ 6.30 and 6.71), the hydride group attached to Ir appears as a triplet (τ 24.0) resulting from equal coupling to the two phosphorus nuclei, and only one methyl resonance (τ 8.08 virtually coupled) is observed for the two $PCH_3(C_6H_5)_2$ ligands. Moreover, only one ^{31}P resonance is observed for all compounds. The analogous NBD complexes of Rh(I) have equivalent methine protons which, by virtue of the symmetry of the NBD molecule, indicates that the nonequivalent vinyl protons are on the *different* double bonds. A TBP ground-state geometry is, therefore, indicated with the R group in one axial position, the phosphine ligands occupying two equatorial sites, and the diene spanning the remaining axial and equatorial sites (C_s symmetry). This is confirmed (Figure 2) by a single-crystal X-ray structural determination[7c] of $CH_3Ir(COD)(P(CH_3)_2C_6H_5)_2$. The only significant deviation from an idealized TBP structure is in the P–Ir–P angle which is 101.5° instead of the idealized 120°, undoubtedly because of interactions between the equatorial olefin and the phosphine ligands.

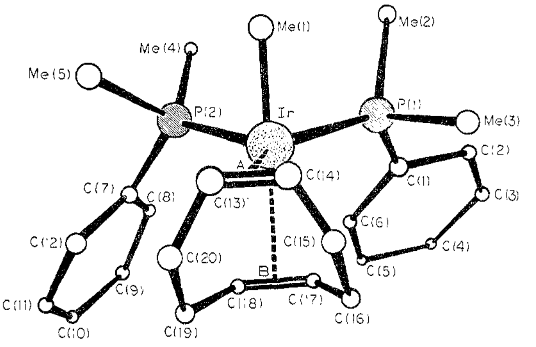

Figure 2.

Variable-temperature nmr studies of these complexes show that two independent dynamic processes occur, the relative rates of which depend quite differently upon the composition of the complex. One process is that of ligand dissociation from the five-coordinate species, as evidenced by the collapse of coupling to the R group in the complexes involving phosphines and/or loss of the structure of the ligand methyl resonances. This process often occurs at distinctly higher temperatures (see Figure 3, +117° spectrum) which enables it to be observed separately from the second process; we defer discussion of such intermolecular processes until later. The second process causes substantial changes only in the diene resonances, most importantly, causing the coalescence of the separate vinyl signals which were observed in the limiting spectrum (*e.g.*, at 35° in Figure 1). This process is an intramolecular rearrangement which leads to interchange of the axial and equatorial double bonds found in the instantaneous structure.

The variable temperature nmr spectrum of $CH_3Ir(COD)(P(CH_3)_2C_6H_5)_2$ (as shown in Figure 3) provides the most information with regard to the mechanism of the rearrangement. In the limiting spectrum at −3° the appropriate signals for all the groups are observed. However, two distinct phosphine methyl resonances are observed as well as the separate vinyl proton signals. The two methyls on *each* dimethylphenylphosphine reside in different environments (*i.e.*, are diastereotopic) (Figure 2) and give rise to separate nmr signals. This is true even with rapid rotation around all bonds. However, should the two phosphine ligands interchange sites, coalescence of the separate methyl signals will occur. Inspection of Figure 3 (up to 87°), however, indicates that, when the temperature is raised into the range where coalescence of the vinyl proton signals occurs, the two phosphine methyl patterns remain distinct. Therefore, the intramolecular rearrangement we observe for this complex *interchanges only the nonequivalent double bonds and not the two phosphine ligands.* Similar behavior is observed for the other $P(CH_3)_2Ph$ complexes, and by analogy this conclusion is extended to the entire set of complexes.

What mechanistic information can be derived from these experimental observations? If we view the mechanism in a permutational (or topological) context,[8] we can see that several permutational pro-

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(4) C. A. Udovich and R. J. Clark, *J. Amer. Chem. Soc.*, 91, 526 (1969).

(5) G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 725 (1969).

(6) (a) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 94, 5271 (1972); (b) D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *Chem. Commun.*, 322 (1971).

(7) (a) J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 92, 6976 (1970); (b) D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, 30, C84 (1971); (c) M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 11, 2243 (1972).

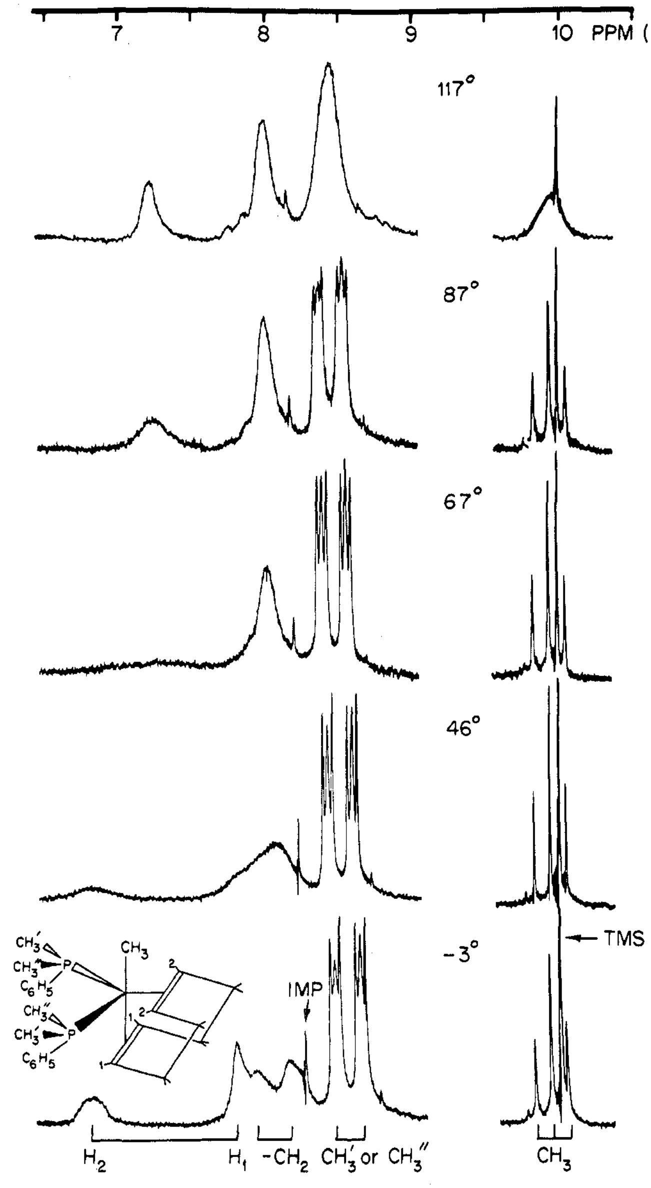

Figure 3. Temperature dependence of 100-MHz ^{1}H spectrum of $CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2$ in chlorobenzene. IMP refers to acetone present from recrystallization.

cesses can lead to the interchange of axial and equatorial olefin sites. The *four* most reasonable schemes are depicted in Figure 4. Also indicated on each scheme is the most probable physical process which would produce the appropriate olefin site exchange.

Scheme B involves the interchange ligands between two sites within the trigonal-bipyramidal structure, one axial and one equatorial, without affecting remaining ligands. The actual physical motion depicted is a twist of the diene about a pseudotwofold axis perpendicular to the plane containing the double bonds. The intervening structure III might be either a transition state in which the relative disposition of R, P_1, and P_2 remain unchanged or an intermediate in which the ligands have relaxed somewhat to approximately SP geometry.

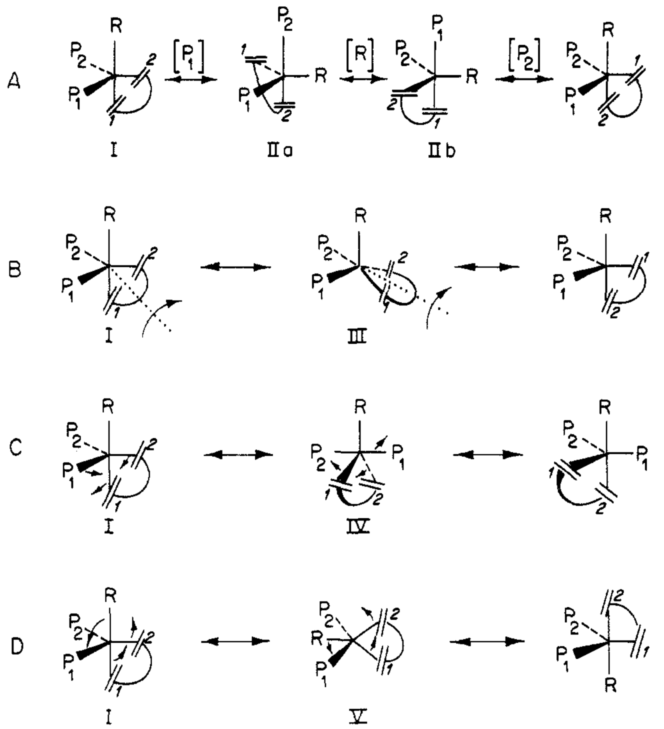

Figure 4. Mechanistic schemes to account for axial–equatorial equilibration of COD vinyl protons in the complexes $RIr(COD)P_2$.

Each of the schemes C and D involves a permutation of three sites within the trigonal TBP structure. In C one axial and two equatorial ligands can be interchanged by a rotation about a pseudo-threefold axis, *via* IV as a transition state. Scheme D, on the other hand, couples both axial ligands with one equatorial ligand in a motion of the R group from one face to another of the pseudotetrahedral configuration of the remaining ligands.

Scheme A proceeds through two TBP intermediate structures, each of which is generated by permutation of four ligands within the structure preceding it. The specific mechanism for each step is the Berry or pseudorotation mechanism. Olefin site interchange can be accomplished by three reversible and sequential pseudorotations, with $[P_1]$, [R], and $[P_2]$ stepwise as pivots. This may seem a somewhat convoluted scheme at first, but two points may be noted: (i) the third pseudorotation about $[P_2]$ is the reverse of the first about $[P_1]$; (ii) IIa and IIb are enantiomers and their interconversion might be expected to be facile. Olefin equilibration could also be achieved by a different Berry process, *e.g.*, configuration IV in C could be reached by a pseudorotation from I by using the equatorial olefin as a pivot. This scheme would involve the diene spanning equatorial sites in IV which would seem to be unfavorable energetically and, indeed, for reasons discussed below with respect to path C, this alternative Berry process cannot be operative here.

If these schemes are examined carefully, C and D, but *not* A and B, lead to interchange of the two ligands P_1 and P_2 while olefin site exchange takes place. The alternate Berry process involving IV as intermediate also causes P_1,P_2 interchange. Hence, only schemes A and B are in accord with the conclusions drawn from the spectral behavior of the PMe_2Ph compounds, providing, therefore, the first

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(8) See, *e.g.*, (a) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968); (b) M. Gielen and N. Vanlautem, *Bull. Soc. Chim. Belg.*, **79**, 679 (1970); (c) J. R. Shapley, Ph.D. Thesis, Harvard University, 1971; (d) W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).

Table I

$RIr(COD)P_2$	ΔG_c^*, kcal/mol $^{-1\,a}$ R = CH_3	R = H
$P(CH_3)_2C_6H_5$	16.3	13.3
$P(CH_3)(C_6H_5)_2$	$>16.9^a$	14.1
$P(C_6H_5)_3$	$\gg 14.0^a$	17.7
$P(C_2H_5)(C_6H_5)_2$		17.6
$P(C_3H_7)(C_6H_5)_2{}^c$		$>20.6^b$
$P(C_6H_{11})(C_6H_5)_2{}^c$		$>20.1^b$

[a] ΔG_c^* value at coalescence temperature of vinyl resonances. [b] Lower limit since intermolecular exchange intervenes. [c] C_3H_7 = isopropyl; C_6H_{11} = cyclohexyl.

experimental evidence which conclusively eliminates some of the theoretically possible rearrangement mechanisms for pentacoordinate transition metal complexes. These results, however, do not permit a rigorous distinction between A and B.

Free energies of activation calculated from the nmr data obtained for the compounds $RIr(COD)L_2$ are presented in Table I. These numbers illustrate the dependence of a barrier to intramolecular rearrangements upon the composition of the complex and lead to several conclusions: (a) the barriers are medium-to-high within the range generally accessible by nmr techniques (*ca.* 5-20 kcal/mol); (b) the barrier is strongly dependent on the steric bulk of the phosphine ligands, *i.e.*, $P(C_6H_5)_2C_6H_{11} \sim P(C_6H_5)_2C_3H_7 > P(C_6H_5)_3 \sim P(C_6H_5)_2C_2H_5 > P(C_6H_6)_2CH_3 > P(C_6H_5)(CH_3)_2$; (c) the barrier is somewhat higher for R = CH_3 than H. Similar trends are observed in the analogous Rh(I) complexes involving norbornadiene as ligand.[7b]

The dependence of the rearrangement barrier on the steric bulk of the ligands is readily interpreted in terms of scheme A. The conversion of I to IIa involves a greater amount of reorganization of the electronic and steric balance of the complex than does IIa to IIb. Hence it would be expected that I to IIa would be the rate-determining step of this sequence and, assuming the Hammond postulate, the transition state for this step will resemble the high-energy intermediate IIa. Proceeding from I to IIa leads to a compression of the angle P–Ir–P from the idealized 120 to 90°. This change should be more disadvantageous for large ligands, thus causing an increase in the barrier to rearrangement.

A similar explanation can also be advanced for B, where III might be expected to have a small (~90°) P–Ir–P angle.

Studies on Chelated Phosphine Complexes: Effect of Ring Strain.

In the complex $CH_3Ir(COD)(diphos)$ (diphos = 1,2-bis(diphenylphosphino)ethane), in which the phosphine ligands are linked, a sharp triplet pattern was observed for the methyl group, but no indication of vinyl proton nonequivalence was seen down to ~ −90°. The X-ray structure of this complex[9] showed the stereochemistry to be essentially that shown in Figure 2, the only significant difference being the *very small P–Ir–P angle of 84.9°*, presumably resulting from the geometric constraints produced by the chelating diphos ligand. This large compression of the P–Ir–P angle when compared to a nonchelating analog (*ca.* 17°) implies a high degree of strain within the five-membered chelate ring in the ground-state structure.

This observation, in conjunction with scheme A or B, provides an interpretation of our inability to achieve limiting spectra for the diphos complex. In A structures IIa and IIb would be expected to have a nearly ideal P–Ir–P angle of 90° which would mean the five-membered ring would be essentially *unstrained in these intermediates.*[10] Hence I is destabilized relative to IIa in the chelated molecules and the relief of ring strain afforded in IIa lowers the energy barrier for this rate-determining interconversion as compared to unstrained systems. Similarly, in B, III is expected to be less strained than I.

Study of the corresponding 1,3-bis(diphenylphosphino)propane complex, where the resulting six-membered ring would be less strained, lends credence to this interpretation. The limiting low-temperature spectrum is obtained at −45°, and the barrier to rearrangement is *ca.* 13.4 kcal/mol, a value greater than that estimated for the diphos complex but less than that for the unchelated analog. Further, the X-ray structure[11] of the 1,3-bis(diphenylphosphino)propane complex shows the P–Ir–P angle to be 93.4°, a value intermediate between those of the diphos and $P(CH_3)_2C_6H_5$ complexes. In the 1,4-(diphenylphosphino)butane complex the barrier is even higher (>16.5 kcal/mol), in agreement with the proposed mechanism.

If the chemical shift separation of the vinyl resonances in the diphos complex is assumed to be similar to that for the other chelating phosphines, an upper limit to the barrier for this complex can be estimated as <*ca.* 9 kcal/mol. Furthermore, as shown in Table II, ΔG_c^* for each of the chelating ligand complexes can be compared with that of an unchelated analog. These results establish that the chelated compounds have significantly lower barriers than their unchelated counterparts, the decrease amounting to as much as 7 kcal/mol.

Studies on Complexes with Tin Ligands: Effects of π Bonding

In view of the high degree of strain found for the ground-state isomer of $CH_3Ir(diphos)(COD)$, why is this positional isomer more stable than that with the methyl group equatorial and the chelating phosphine ligand comfortably spanning axial–equatorial sites (*e.g.*, IIa in Figure 4)? Might this not be illustrative of a site preference effect either of the strongly σ-bonding methyl group for the axial site or the more π-bonding phosphine ligand for the equatorial sites? If this were so, then the structure with the R group equatorial might be stabilized if the R group had *strong* π-bonding ability. Previous studies on $SnCl_3^-$ as a ligand had indicated it to be a very strong π-

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(9) M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 12, 260 (1973).

(10) The unstrained "bite" angle of diphos appears to be *ca.* 84°. For example, see J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 91, 6301 (1969).

(11) S. A. Bezman and M. R. Churchill, *Inorg. Chem.*, 12, 531 (1973).

Table II

$CH_3Ir(COD)L_2$	ΔG_c*, kcal/mol^{-1}	∠P-Ir-P, deg
L_2 = 1,2-bis(diphenylphosphino)ethane	<9.0[a]	84.9
L_2 = 1,2-bis(diphenylphosphino)propane	13.4	93.4
L_2 = 1,2-bis(diphenylphosphino)butane	>16.5	
L = $P(CH_3)(C_6H_5)_2$	>16.9	(101.5)[b]
L_2 = 1,2-bis(dimethylarsino)benzene	11.9	
L = $As(CH_3)_2C_6H_5$	>15.5	

[a] Estimated on basis that vinyl group separation is 120 Hz. [b] Value for $P(CH_3)_2C_6H_5$ complex.

acid ligand, and we noted that compounds of the type $Ir(diene)_2SnCl_3$ (diene = COD, NBD) had been isolated.[12,13] Moreover, the X-ray crystal structure[13] shows $Ir(COD)_2SnCl_3$ to be TBP, with $SnCl_3^-$ occupying an equatorial site and the diene ligands each spanning axial-equatorial positions. By displacement of one diene by two phosphine ligands, $Ir(diene)P_2SnCl_3$ complexes can be isolated which are analogous to the previously described iridium-alkyl complexes except that the σ-bonding alkyl has been replaced by the π-bonding $SnCl_3^-$ ligand.

The parent compound, $Ir(COD)_2SnCl_3$, shows only one vinyl resonance at 33°, instead of the four expected if the solid-state structure were retained and static in solution. Similarly eight compounds of the type $Ir(COD)L_2SnCl_3$ (L = phosphine, phosphonite, arsine) show ^1H nmr spectra much less complex than that expected for any individual static structure, but variable-temperature studies have failed as yet to achieve limiting spectra.

The corresponding NBD complexes, however, are more informative, since NBD will not span equatorial-equatorial sites readily and offers the methine resonances as a further structural probe. The ^1H nmr of $Ir(NBD)_2SnCl_3$ (33°) shows two vinyl and two methine resonances, consistent with a SP structure with $SnCl_3^-$ apical, but we prefer to assign this complex a TBP ground-state configuration as found for the corresponding COD complex. Rapid enantiomeric equilibration (I $\rightleftharpoons$ II, Figure 5) using $SnCl_3^-$ as pivot in a Berry process would result in the observed spectrum, *i.e.*, equilibration of the vinyl protons 1 with 3, and 2 with 4, but *not* of the methine protons 5 and 6. In contrast, ten substituted derivatives of the type $Ir(NBD)L_2SnR_3$ (L = phosphine, phosphinite, or arsine; R = Cl or CH_3) display only *one* vinyl and *one* methine resonance at 33°. At −90°, however, the complexes $Ir(NBD)P_2SnCl_3$ (P = $P(CH_3)_2C_6H_5$, $P(CH_3)(C_6H_5)_2$, $P(C_6H_5)_3$, $P(C_4H_9)_3$) each show the *two* vinyl, *two* methine pattern. Further, the ^{31}P spectrum of the tri(*n*-butyl)phosphine species, $Ir(NBD)(P(C_4H_9)_3)_2SnCl_3$, at −80° is a sharp singlet. Hence, as before, $Ir(NBD)L_2SnCl_3$ are assigned as TBP[14] but undergo rapid equilibration between I and II (Figure 6) at −90°. At ambient temperatures these compounds must undergo a further rearrangement *via* a structure which causes coalescence of the pairs of vinyl and methine resonances. In the PMe_2Ph complex the diastereotopic methyl groups on the phosphine remain distinct during this process. The only intermediate consistent with these observations is III (Figure 6), with $SnCl_3$ axial and the two phosphine ligands in equatorial sites. The dynamic behavior observed for the system depicted in Figure 6 is therefore closely related to A in Figure 4 except *replacement of the alkyl (or hydride) ligand by $SnCl_3$ has altered the relative energies of the positional isomers.*

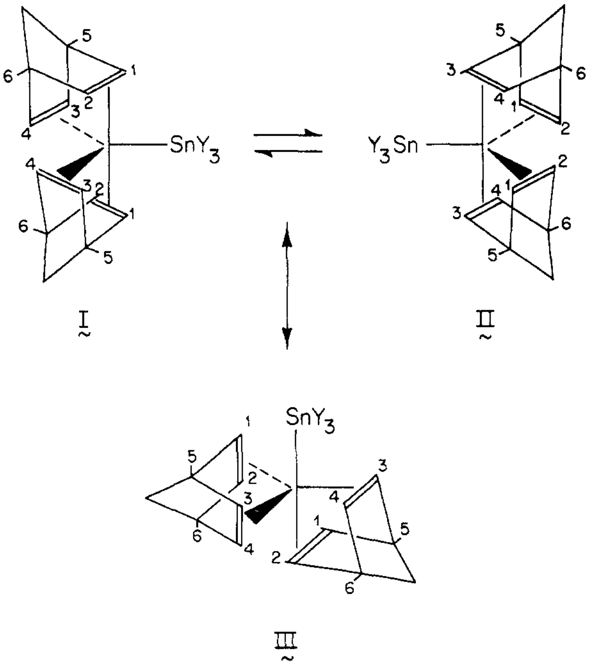

Figure 5.

The calculated barriers (I + II → III) for the $Ir(NBD)P_2SnCl_3$ compounds are not greatly dependent on the steric bulk of the phosphine ligands, the spread of values (*ca.* 1 kcal/mol) being of the order of experimental error.[14] Interestingly, however, replacement of the monodentate phosphine ligands by the chelating diphos ligand causes an *increase* in the barrier by *ca.* 3 kcal/mol. This is precisely the reverse of that observed in the corresponding alkyl derivatives. However, inspection of path A (Figure 4) and Figure 6 shows that, whereas *with the chelating phosphine strain destabilization occurs in the ground state of the alkyl derivatives, it occurs in the transition state of these $SnCl_3^-$ complexes, i.e.*, the chelate spans the idealized 90° in the ground state of the $SnCl_3^-$ complexes, but on passing to the high-energy intermediate *III* the chelate must open to formally 120°. Strain thus develops in the *transition state*, thereby raising the barrier to intramolecular rearrangement. These observations can therefore be convincingly interpreted in terms of path A (the Berry mechanism). Similar arguments can be presented for path B, but they are intuitively much less satisfying.

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(12) J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

(13) P. Porta, H. M. Powell, R. J. Mawby, and L. M. Venanzi, *J. Chem. Soc. A*, 455 (1967).

(14) The X-ray crystal structure determined by Professor M. R. Churchill shows $Ir(NBD)(P(CH_3)_2Ph)_2SnCl_3$ to be a distorted TBP with $SnCl_3$ equatorial as depicted in idealized form in Figure 6. The distortion is toward the SP with $SnCl_3$ apical, which is the intermediate or transition state configuration for the interconversion I ↔ II. The low barrier observed for I ↔ II and the insensitivity of this barrier to steric factors can be seen to arise from this ground-state distortion.

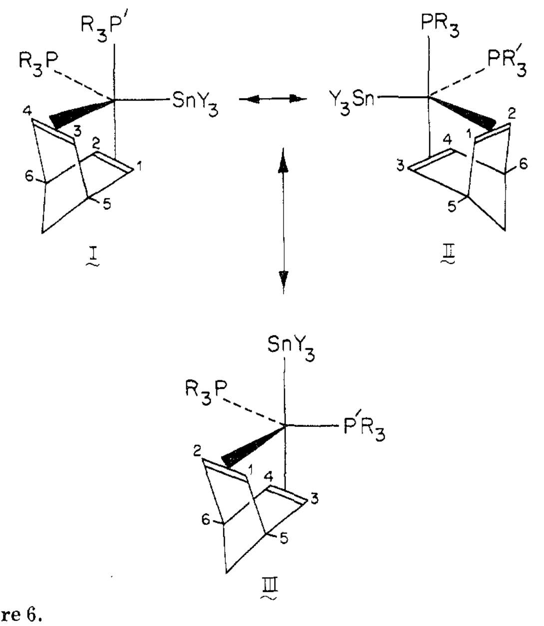

Figure 6.

On the assumption that these interpretations are correct, what predictions can be made? What if $SnCl_3^-$ were replaced by $Sn(CH_3)_3^-$ or PPh_3 in these complexes? Both these ligands are weaker π acceptors than $SnCl_3^-$, and thus isomers III (Figures 5 and 6) should be stabilized and isomers I and II destabilized by this substitution, and consequently the process I + II → III should be more facile. In accord with this prediction, in $Ir(NBD)_2Sn(CH_3)_3$ coalescence to the *one* vinyl, *one* methine pattern (I + II ↔ III) occurs at *ca.* 0°, whereas in the corresponding $SnCl_3^-$ complex the *two* vinyl, *two* methine pattern shows no sign of coalescence below +60°. Also, the compounds $Ir(NBD)_2P^+$ ($P = P(C_6H_5)_3$ or $P(CH_3)_2C_6H_5$) show closely similar behavior to the $Sn(CH_3)_3^-$ species, indicating that $Sn(CH_3)_3^-$ and these phosphine ligands have similar site preferences. Hence the analogous COD complexes would seem to display only one vinyl resonance even at low temperatures because isomer III (Figures 5, 6) is more readily accessible than for the NBD complexes, presumably because of the larger "bite angle" of COD.

Studies on $Ir(NBD)(COD)SnR_3$ ($R = CH_3$, Cl) are consistent with this viewpoint. The low-temperature spectrum (0°) ($R = CH_3$) shows two vinyl and two methine resonances of the NBD ligand, as well as two vinyl COD signals, consistent with a rapid equilibration of the type I ↔ II shown in Figure 5. At 90°, however, *both sets* of NBD resonances coalesce, but the COD vinyl sets *remain distinct*. Therefore, this process involves an isomer analogous to III (Figure 5), but with COD spanning the equatorial sites. The alternate isomer with NBD bridging two equatorial sites which would cause equilibration of the COD vinyl sets is clearly not readily accessible under these conditions.

Some Conclusions and Tentative Generalizations

Although to generalize on this restricted set of complexes may be premature, the following tentative proposals are offered as a basis for prediction and hence as a stimulus to further work.

1. **Site Preferences.** This property can be broadly related to the bonding properties of the ligands, those ligands which are strong π acceptors (*e.g.*, $SnCl_3^-$, CO) preferring equatorial sites in a TBP geometry, or, conversely, those which are strong σ donors (*e.g.*, H^-, CH_3^-) preferring axial sites. Ligands without starkly differentiated bonding properties may not exhibit strong positional preferences (*e.g.*, PR_3, $SnMe_3^-$). This observation is not unexpected since in TBP d^8 solid-state structures where steric effects are not significant the strongest π-bonding ligand is found in an equatorial site, *e.g.*, $Mn(CO)_4NO$. This qualification with regard to steric effects, however, is an important one, as we discuss next.

2. **Ligand–Ligand Interactions.** Steric interactions are not only dependent upon the steric bulk of the ligands involved but also on the relative positions within the coordination sphere, *i.e.*, for the TBP geometry the interactions decrease in the sequence equatorial–axial > equatorial–equatorial > axial–axial. Large ligand–ligand interactions may cause the stabilization of a positional isomer different from that predicted as the most stable by the site preference rule; *e.g.*, $RhH(CO)(PPh_3)_3$ is TBP with the hydride but also the carbonyl group axial. Site preference would direct the hydride axial and the carbonyl ligand equatorial. However, minimization of steric repulsion between the bulky phosphine ligands finally determines the most stable ground-state isomer, overriding the equatorial preference of the carbonyl ligand. In the analogous iridium(I) complex replacement of one triphenylphosphine by a carbonyl ligand to form $IrH(PPh_3)_2(CO)_2$ causes competition between site preference and steric effects, resulting in two isomers[5,6a] being populated in solution. However, in both isomers the positional preference of hydride for the axial site is evident, overriding purely steric considerations which would place the two phosphines in axial sites.

3. **Ring Strain in Chelated Ligands** It is clear that chelates which form four-, five-, or six-membered rings with the metal atom will generally prefer to bridge axial–equatorial sites rather than equatorial–equatorial. The diequatorial isomer therefore will be expected to be destabilized relative to the axial–equatorial isomer.

4. **The Berry or Pseudorotation Mechanism** The Berry mechanism appears to offer a consistent and intuitively appealing interpretation of the dynamic behavior observed for this series of complexes. However, let us examine in more detail what we imply by this statement.

For an intramolecular rearrangement it is important to maintain the distinction between the abstract (permutational) process defined by the initial and final configurations and any physical motion which relate the reactant and product states. The Berry mechanism as originally conceived was concerned with the internal rearrangement of pentacoordinate molecules of high symmetry (*e.g.*, D_{3h}, C_{2v}) in which a symmetric angular deformation of the ligands was proposed to cause axial–equatorial site interchange. Is the Berry mechanism applicable therefore to molecules of lower symmetry as are described here? Certainly when the axial (and/or equatorial) ligands differ greatly in properties (*e.g.*, bonding character), the bending motion transferring the axial pair of ligands to equatorial sites will not be symmetrical, and the physical motion that will connect such isomers is thus less well defined.

However, in all cases where discriminating experimental evidence is available,[2,7] the permutation process observed is that predicted by the Berry mechanism. It would appear justifiable, therefore, at this juncture to choose the Berry mechanism as a description for the stepwise connectivity of TBP isomers without the implication that the detailed physical motions involved need correspond *precisely* to the idealized model.

A permutationally equivalent description such as the turnstile mechanism[15] will also offer an adequate interpretation of the present data. Distinction between the Berry and turnstile mechanisms in pentacoordinate rearrangements rests on differences in the physical motions of the ligands and the nature (stereochemistry, energy) of the transition states. A compelling choice between the two mechanisms can only be based on an unambiguous experimental distinction (which has yet to be achieved) or on a sound theoretical basis. Nevertheless, we prefer to describe the rearrangement in terms of the Berry mechanism rather than the turnstile, since the former is more evident to manipulate conceptually and easier to illustrate in practice. Hence, if the Berry mechanism is used in this manner, and the relative stabilities of TBP configurations are related by the positional, steric, and strain rules mentioned above, an attractive and useful rationale of these (and other) experimental results is evident.

Some Applications of these Results

Other Fluxional Pentacoordinate TBP Molecules. Studies on $Fe(CO)_x(PF_3)_{5-x}$ (x = 0–5)[16] and $M(PF_3)_5$ (M = Fe, Rh, Os)[6a] show the barrier to rearrangement to be lower than in $RCo(PF_3)_{4-x}(CO)_x$ (R = H, CF_3)[4,17] where limiting spectra have been obtained. These observations can be explained qualitatively by the above proposals. Rearrangement of the molecules $RCoL_4$ of ground-state C_{3v} symmetry (R axial) must, if the Berry process is operative, proceed *via* an intermediate with the strongly σ-bonding R group at an unfavorable equatorial site. For ML_5 molecules no such unfavorable transition state or intermediate develops. In this context, it has been proposed from a study of pseudotetrahedral ML_4H molecules[6a] that hydrides may have access to a unique mechanism in which the hydride ligand may "hop" from one face to another of the pseudotetrahedral arrangement of the L ligands. For the complexes $IrH(diene)P_2$, however, *no single step nor any combination of single-step processes of the hop type* can account for our experimental observations, and application of the hop mechanism must be regarded with caution in TBP systems.

Exchange Reactions of Square d^8 Complexes. The accepted mechanism for ligand substitution in a four-coordinate square-planar complex is an associative process proceeding through a TBP intermediate, in which the entering ligand occupies an equatorial site.[18] Since substitutions nearly always take place with retention of configuration (at least for Pt(II) complexes), the lifetime appears to be shorter than the time necessary for an intramolecular rearrangement. However, retention of configuration is not observed for the trialkylphosphine-catalyzed cis to trans isomerization of bis(trialkylphosphine)platinum dihalides. A mechanism involving intramolecular rearrangement of the five-coordinate intermediate can be proposed,[19] but an alternate process involving halide ionization may be operative.

We have investigated[20] the exchange of tertiary phosphine with the square complexes $[RPtP_3]^+$ (R = H, CH_3; P = tertiary phosphine) by nmr methods. The exchange process would be expected to involve the intermediate $[RPtP_4]^+$, stable hydride analogs of which undergo rapid internal rearrangement. However, in each case substitution at the phosphine cis to the hydride occurs faster than at the trans site and, furthermore, by a ratio which increases with increasing steric bulk of P. The five-coordinate intermediate of C_{3v} symmetry (R axial) which would be predicted as the most stable from the preference rules would lead directly to cis substitution. Trans substitution may arise either by intramolecular rearrangement of this intermediate *via* the less favorable isomer of C_{2v} symmetry (R equatorial) *or* by intermolecular exchange involving the direct formation of this latter isomer. In either case, this model would predict the energy of the C_{2v} structure to be increased (relative to the C_{3v} species) by increased steric interactions between the bulkier phosphine ligands resulting in the observed cis to trans relative rates of substitution. Hence, if intramolecular rearrangement is occurring the rate is considerably slower than intermolecular exchange.

However, in square complexes of the type M(diene)LCl (M = Rh, Ir; diene = COD, NBD; L = phosphine or arsine) the two distinct vinyl resonances coalesce into one signal on addition of free L.[21] This dynamic process is effectively a cis–trans isomerization, and, since ionization processes can be discounted, must occur *via* intramolecular rearrangement of the intermediate $M(diene)L_2Cl$.

The complexes $M(diene)L_2R$ (R = H, CH_3) show the effects of dissociation and exchange of L under certain conditions. When intramolecular rearrangement is slower than the intermolecular process, it is observed that the nonequivalent double bonds present in the stable five-coordinate complex are preserved in the four-coordinate intermediate.[7b] This intermediate must thus be square (and *not* tetrahedral), indicating that in the general equilibrium $M(diene)L_2X \rightleftharpoons M(diene)LX + L$ the idealized geometries involved are TBP and square, the relative energies of which are dependent on the nature of the ligands. Thus we have observed in this equilibrium

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(15) I. Ugi, D. Marquarding, H. Klusacek, P. Gillepsie, and F. Ramirez, *Accounts Chem. Res.*, 4, 288 (1971).

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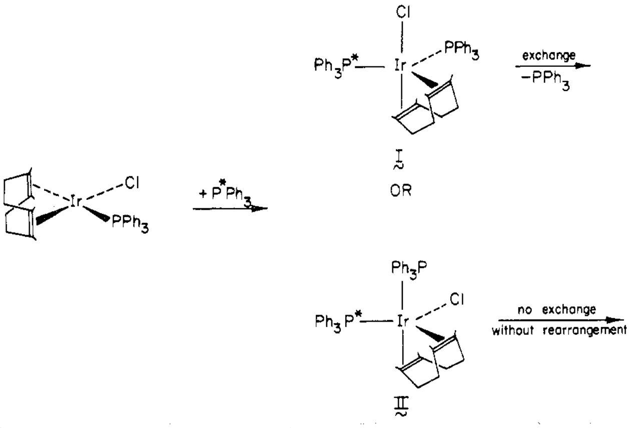

Figure 7. Intermediate TBP structures for the system Ir(COD)(PPh_3)Cl + PPh_3.

the pentacoordinate species is favored H > $SnCl_3$ > CH_3, and $P(CH_3)_2C_6H_5$ > $P(CH_3)(C_6H_5)_2$ > $P(C_3H_7)(C_6H_5)_2$ ~ $P(C_6H_{11})(C_6H_5)_2$ > $P(C_6H_5)_3$. We therefore formulate the structure of the intermediate M(diene)L_2Cl in Figure 7 as TBP with either chloride at an axial (I) or equatorial site (II). If structure I were formed, exchange of L can proceed without axial-equatorial vinyl proton interchange, and the intramolecular and intermolecular processes are entirely separate. This is the case for M(diene)L_2R (R = H, CH_3). If *only* intermediate II were formed, *intermolecular exchange cannot take place without the occurrence of intramolecular rearrangement.* Indeed, under certain conditions, the intermolecular exchange rate may be determined by the intramolecular process. In this case the intra- and intermolecular rates are related, which is apparently the case for M(diene)L_2Cl where the rate of vinyl coalescence was taken as equal to the rate of intermolecular ligand exchange.[21] In general, however, the intra- and intermolecular exchange reaction must be regarded as totally separate processes.

Catalytic Processes. In several homogeneous catalytic reactions involving d^8 metal complexes, five-coordinate intermediates play a key role. For example, in the hydroformylation[22] of olefins with Co(I) complexes, at least four of the proposed intermediates are pentacoordinate, *e.g.*, for ethylene as substrate, $HCo(CO)_4$, $HCo(CO)_3(C_2H_4)$, $C_2H_5Co(CO)_4$, and $C_2H_5COCo(CO)_4$. Clearly a complete understanding of the catalytic process requires details of the stereochemistry of such species and their configurational stability. In this connection, we have recently synthesized[23] the complexes $HRu(NO)P_3$ (P = tertiary phosphine) and examined their catalytic properties. The structure of $HRu(NO)(P(C_6H_5)_3)_3$ has been determined to be TBP both in solution and solid state,[24] with hydride and nitrosyl ligands occupying axial sites. This complex in solution is found to catalyze very efficiently the isomerization of olefins; the complex with $P(CH_3)(C_6H_5)_2$ as ligand, however, is an ineffective catalyst. ^1H and ^{31}P nmr data reveal that this complex has a different configuration in solution, as might be expected from a competition of site preference and steric factors. The corresponding $P(C_3H_7)(C_6H_5)_2$ complex (C_3H_7 = isopropyl) in which both configurations are populated in solution is again catalytically active. It is thus tempting to associate catalytic activity with the presence of a *particular* configuration in solution.

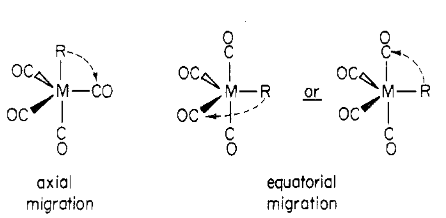

Figure 8.

A key step of several catalytic and stoichiometric reactions involving carbon monoxide is the migration of a bound alkyl group R to a carbonyl ligand, forming a transient four-coordinate d^8 acyl derivative, *i.e.*, $RM(CO)_4 \rightarrow RCOM(CO)_3$. Such steps occur in the catalyzed hydroformylation of olefins[22] and in the aldehyde and ketone syntheses using $Fe(CO)_4{}^{2-}$ developed by Collman[25] and coworkers. Infrared evidence indicates that the pentacoordinate $RM(CO)_4$ species are TBP (C_{3v} symmetry, R axial), but we would expect rapid axial–equatorial carbonyl exchange *via* a TBP intermediate with R equatorial (C_{2v}). Hence the question of stereochemistry at the metal during the alkyl migration step may be posed. As is evident from Figure 8, migration of the alkyl from an axial site to an equatorial carbonyl produces approximately a tetrahedral ligand arrangement—which, in the spirit of a correlation diagram, is the excited state of the stable d^8 square-planar species. This latter, however, is readily generated by an alkyl migration from an equatorial site to an equatorial or axial carbonyl ligand in the C_{2v} species.[26] Hence a rapid intramolecular rearrangement of the ground-state C_{3v} structure to the reactive C_{2v} may be necessary for the migration reaction to occur readily and hence for the catalytic cycle to proceed.

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[26] It is clear that a square-planar species is *directly* produced by an equatorial–equatorial migration if *both* the R group and the reacting carbonyl are allowed to migrate toward each other.