Table II. Activation Parameters for Reactions of Ligand-Bridged Diiron Carbonyl Complexes with $P(C_6H_5)_3$

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2{}^{a,b}$	37 (2)	+10 (4)
$Fe_2(CO)_6(\mu\text{-}N_2C_{12}H_8)^{c,d}$	10.2 (5)	−34 (2)
$Fe_2(CO)_6(\mu\text{-}OC(NC_6H_4OCH_3)_2)^{c,d}$	15.0 (5)	−20 (2)
$Fe_2(CO)_6(\mu\text{-}OC(NC_6H_5)_2)^{c,d}$	12.7 (5)	−26 (2)
$Fe_2(CO)_6(\mu\text{-}S_2C_6H_3CH_3)^{c,e}$	12.5 (5)	−31 (2)
$Fe_2(CO)_6(\mu\text{-}SC_6H_5)_2{}^{c,f}$	21.6 (5)	−4 (2)
$Fe_2(CO)_5(\mu\text{-}SC_6H_5)_2P(C_6H_5)_3{}^{b,f}$	35.5 (7)	+16 (2)

[a] This work. Values in parentheses are estimated standard deviations in the least significant digits. [b] First-order pathway. [c] Second-order pathway. [d] Reference 3; toluene solution. [e] Reference 2; toluene solution. [f] Reference 20; decalin solution.

constants are given in Table I for the reactions of Fe_2-$(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ with triphenylphosphine, triphenyl phosphite, and tri-*n*-butylphosphine to give the corresponding monosubstituted products, $(CO)_3Fe(\mu\text{-}P(C_6H_5)_2)_2Fe(CO)_2L$. These rate constants are independent of the nature and concentration of the attacking nucleophile. This result contrasts markedly with those for the organosulfur- and organonitrogen-bridged systems.

Both activation parameters for substitution on the phosphido-bridged complex are also distinctly different from those for the corresponding organosulfur- and organonitrogen-bridged systems. Activation parameters for the reactions of triphenylphosphine with the variously bridged diiron hexacarbonyl complexes are given in Table II. For $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$, $\Delta H^{\ddagger}$ is more than 15 kcal/mol and $\Delta S^{\ddagger}$ more than 14 eu greater than for the corresponding substitution reactions of the sulfur- and nitrogen-bridged diiron hexacarbonyl complexes.

The rate law, large activation enthalpy, positive activation entropy, and insensitivity to the nature of the entering group imply that the rate-limiting step for the substitution reaction of the phosphido-bridged complex is the dissociative loss of a carbonyl ligand to give $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2$. This reactive intermediate is then rapidly trapped by the entering group (an S_N1 or D mechanism). However, a slightly more complex alternative cannot be eliminated: an intramolecular iron–phosphorus bond rupture (bridge opening) could be the rate-limiting step. This would be followed by entering group capture, loss of carbon monoxide, and reclosure of the bridge.

Evidently, the S_N2 or I_a mechanism which is found for organosulfur- and organonitrogen-bridged diiron hexacarbonyl complexes is inaccessible to the diphenylphosphido-bridged complex. To some extent, this mechanistic difference may represent an effect of the bridging substituent on the iron–carbon bond strength; however, this is unlikely to be the major factor. Infrared[2,3,16,18] and Mössbauer[19] spectra suggest similar electronic environments for iron and carbon monoxide in the phosphorus-, nitrogen-, and sulfur-bridged complexes.

The substitution rates of sulfur- and nitrogen-bridged diiron hexacarbonyl complexes are sensitive to the steric characteristics of the bridging ligands. Bulky bridging groups which project over the carbonyl ligand trans to the iron–iron bond inhibit the bimolecular substitution reaction. This observation has been interpreted as a reflection of steric destabilization of the seven-coordinate activated complex.[2,3] For Fe_2-$(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$, molecular models indicate that the phenyl groups effectively block the iron octahedral face defined by the bridging ligands and the apical carbonyl. Accordingly, the kinetic observations reported here can be given a simple interpretation: the bimolecular mechanism observed for other substrates is not observed for $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ because steric destabilization of the seven-coordinate activated complex increases the activation energy of this process to a value greater than that necessary for carbonyl dissociation.

This interpretation is supported by a recent study[20] of the second step in the reaction of triphenylphosphine with $(OC)_3Fe(\mu\text{-}SC_6H_5)_2Fe(CO)_3$. In this complex, both of the carbonyl ligands trans to the iron–iron bond can be displaced by triphenylphosphine. Whereas displacement of the first carbonyl to give $(OC)_3Fe(\mu\text{-}SC_6H_5)_2Fe(CO)_2P(C_6H_5)_3$ follows a second-order rate law and an S_N2 mechanism,[2,20] Basato has shown that displacement of the second carbonyl to give $[Fe(\mu\text{-}SC_6H_5)(CO)_2P(C_6H_5)_3]_2$ follows a first-order rate law and an S_N1 mechanism. This change of mechanism is attributed to steric inhibition of the second substitution step by the triphenylphosphine ligand.[20] The activation parameters for carbon monoxide dissociation from this substituted, organosulfur-bridged complex and from $Fe_2(CO)_6(\mu\text{-}P$-$(C_6H_5)_2)_2$ are very similar (see Table II).

Registry No. $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$, 19599-68-9; $P(C_6H_5)_3$, 603-35-0; $P(OC_6H_5)_3$, 101-02-0; $P(n\text{-}C_4H_9)_3$, 998-40-3; Fe_2-$(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(C_6H_5)_3$, 58409-41-9; $Fe_2(CO)_5(\mu\text{-}P$-$(C_6H_5)_2)_2P(OC_6H_5)_3$, 58409-42-0; $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(n$-$C_4H_9)_3$, 58409-43-1; $Fe_2(CO)_4(\mu\text{-}P(C_6H_5)_2)_2(P(n\text{-}C_4H_9)_3)_2$, 58409-44-2.

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Ligand Dissociation and Intramolecular Rearrangement in ML₅ Complexes. Evidence for Closely Related Transition States

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There have been many studies of substitution reactions in planar d^8 transition metal complexes.[1-3] However, information about the nature of the transition states and the role of possible intramolecular processes has been difficult to obtain. We have

Table I. Free Energies of Activation for Ligand Dissociation and Intramolecular Exchange in ML_5 Complexes

Complex	$\Delta G^{\ddagger}$-(inter), kcal mol^{-1}	T, °K	$\Delta G^{\ddagger}$-(intra), kcal mol^{-1}	$\Delta\Delta G^{\ddagger}$, kcal mol^{-1}
$Co[P(OC_2H_5)_3]_5^+$	17.9	390	12^a	6
$Ir[P(OC_2H_5)_3]_5^+$	>14.5	410	10.4	≥4
$Ni[P(OC_2H_5)_3]_5^{2+}$	14.5	350	10.3^a	4
$Rh[P(OC_2H_5)_3]_5^+$	13.8	333	9.9	3.9
$Pt[P(OC_2H_5)_3]_5^{2+}$	10.5	300	9.2	1.3
$Pd[P(OC_2H_5)_3]_5^{2+}$	8.5	200	8.0	0.5
$Rh[P(OCH_3)_3]_5^+$	14	333	7.5	6.5
$Rh[P(OC_2H_5)_3]_5^+$	13.8	333	9.9	3.9
$Rh[P(O\text{-}n\text{-}C_3H_7)_3]_5^+$	13.9	333	10.7^b	3.2
$Rh[P(O\text{-}n\text{-}C_4H_9)_3]_5^+$	14.3	333	11.1	3.2
$Rh[P(OCH_2)_3CCH_3]_5^+$	16.8	333	7.5	9.3

^{a} Not measured directly; estimated from the corresponding $P(OCH_2)_3CCH_3$ complex.[4] ^{b} Estimated from other n-alkyl values.[4]

obtained such information for the reaction coordinate involved in ligand substitution reactions of square-planar systems by examining the dissociative behavior of stable five-coordinate intermediates using NMR spectroscopy. This viewpoint for obtaining kinetic and mechanistic data has been previously pointed out.[3b]

Using the nomenclature of Langford and Gray,[3b] we have attempted to examine the *intimate* mechanism of ligand association in square-planar systems. Previous work in the area[2,3] has concerned itself with distinguishing the relative strength of the bonds to the entering and leaving ligands as the reaction coordinate is traversed. Here we examine the stereochemistry of the complex as it passes from five- to four-coordination in a system which has maximum symmetry for the reaction coordinate. An important question is whether the two trans ligands in the square planar complex, which become axial in the trigonal-bipyramidal complex, remain collinear with the metal atom during the associative process. It is concluded that they do not.

Planar four-coordinate and trigonal-bipyramidal five-coordinate forms can be isolated for the same metal–ligand combination, allowing the starting material (ML_5) to be studied spectroscopically; all ligands are the same, leading to maximum skeletal symmetry in reactants, in products, and along the reaction coordinate. NMR spectroscopy can be used to establish stereochemistry, study intramolecular rearrangements, and measure kinetic and thermodynamic parameters for ligand association–dissociation processes at equilibrium with identical entering and leaving groups. Evidence for a relationship between the reaction coordinate for planar ML_4 ligand association reactions and for ML_5 intramolecular rearrangements is presented.

Free energies of activation, $\Delta G^{\ddagger}$(inter), for the equilibrium

$$ML_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_4 + L \tag{1}$$

(where M = Co, Rh, Ir, Ni, Pd, or Pt, L = $P(OC_2H_5)_3$; where M = Rh, L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}n\text{-}C_3H_7)_3$, $P\text{-}(O\text{-}n\text{-}C_4H_7)_3$, or $P(OCH_2)_3CCH_3$) have been obtained from ^{31}P {^1H} spectra, using NMR line shape methods (Table I).

The $\Delta G^{\ddagger}$(inter) data are all consistent with process 1 with k_1 independent of solvent or added ligand concentration. The same ordering, for constant ligand is found as was previously established for $\Delta G^{\ddagger}$(intra)[4]

$$\begin{array}{ccc} Co & > & Ni \\ \vee & & \vee \\ Rh & > & Pd \\ \wedge & & \wedge \\ Ir & > & Pt \end{array}$$
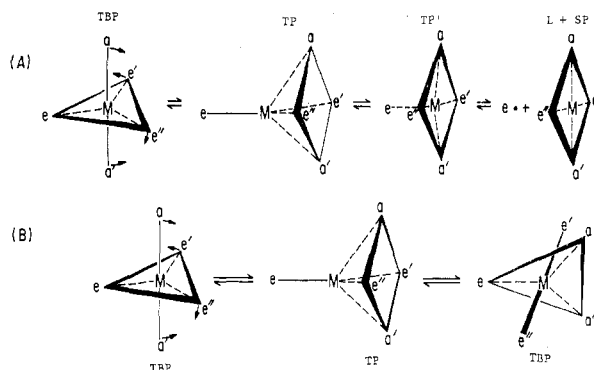
Figure 1. Reaction paths for ligand dissocation (A) for intramolecular rearrangement (B). The labeling of the various stereochemistries is the same in Figures 1 and 2: TBP, trigonal bipyramid; TP, tetragonal pyramid; TP′, tetragonal pyramid with elongated axial bond; SP, square plane; L, free ligand.

Figure 1(A) shows an intimate model for intermolecular ligand exchange involving a planar four-coordinate species, a series of tetragonal-pyramidal five-coordinate stereochemistries along the reaction coordinate, and a trigonal-bipyramidal five-coordinate species. The entering group attacks perpendicular to the plane of the four-coordinate complex ending in the equatorial plane of the five-coordinate compound along with two trans ligands of the planar molecule. Intramolecular exchange in the five-coordinate species [Figure 1(B)] involves trigonal-bipyramidal ground states and tetragonal-pyramidal transition states.

The evidence for these models may be summarized as follows.

(i) The ML_5 Ground State. $^{31}P\{^1H\}$ NMR studies of over 20 ML_5 complexes show that the ground states are trigonal bipyramidal.[4]

(ii) The Reaction Coordinate for Intramolecular Rearrangement. Rearrangement has been shown to involve simultaneous exchange of two axial with two equatorial ligands.[4] The tetragonal pyramid is the simplest intermediate for effecting this change[5] and many of the geometries required by the reaction coordinate have been found in crystal structure studies.[6] Barriers are commonly less than 4 kcal mol^{-1}, comparable to crystal packing forces, as shown by the simultaneous presence of tetragonal-pyramidal and trigonal-bipyramidal $Ni(CN)_5^{3-}$ within the same crystal.[7] Deformations will occur most easily in the direction requiring the smallest free energy change in the isolated molecule, i.e., along the reaction coordinate for intramolecular rearrangement.

(iii) The ML_4 Ground State. Crystallographic evidence for planar or near-planar geometries in four-coordinate Pt^{2+}, Pd^{2+}, Ir^+, and Rh^+ chemistry is abundant. Ni^{2+} complexes are either planar diamagnetic or tetrahedral paramagnetic; in the present series, they are diamagnetic. The ML_4 complexes considered here (many of which can be isolated) are planar, possibly with distortions in some cases due to steric crowding.

(iv) The Reaction Coordinate for Ligand Association. The evidence for attack of L along the pseudo-C_4 axis of planar HML_3^+ cations, leaving the ligand trans to hydride unique, shows unambiguously that the dissociating group in HML_4^+ complexes comes from an "equatorial" site.[8] Extrapolation of this conclusion to the ML_4–ML_5 case is reasonable. C_4 attack and equatorial dissociation have been incorporated in Figure 1(A).

The identical trends in barriers for inter- and intramolecular exchange, as M is varied (Table I), *suggest* that similar or identical geometries occur along the two reaction coordinates. Tetragonal-pyramidal geometries have been incorporated in both reaction coordinates in Figure 1. This implies that the axial ligands in the trigonal-bipyramidal complex do not

Notes
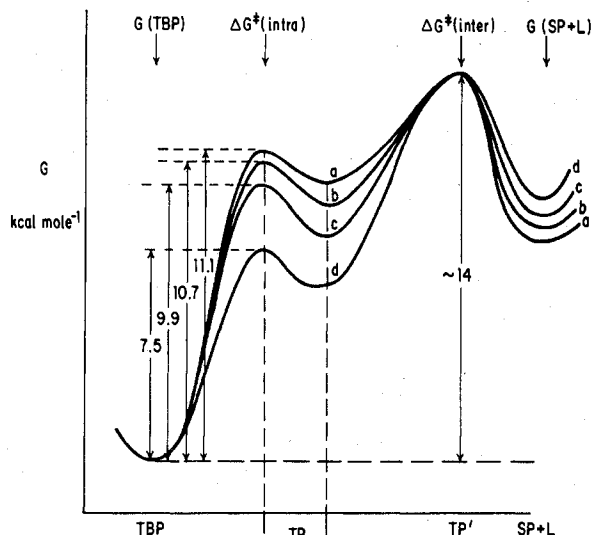
Figure 2. Schematic reaction coordinate for ligand dissociation in ML$_5$ complexes. (The curves do not necessarily have to have minima in the middle, particularly if the coordinate for intramolecular exchange alone has no minimum.) A family of curves is shown which semiquantitatively represent the situation for RhL$_5$ complexes: a, L = P(O-n-C$_4$H$_9$)$_3$; b, L = P(O-n-C$_3$H$_7$)$_3$; c, L = P(OC$_2$H$_5$)$_3$; d, L = P(OCH$_3$)$_3$.

remain collinear throughout the dissociative reaction. A family of schematic free energy changes is shown in Figure 2, assuming the intermediate (or transition state) for intramolecular exchange also occurs on the reaction coordinate for ligand dissociation. This tetragonal-pyramidal geometry occurs near one vertical dotted line in the figure—to the left if there is no minimum in the reaction coordinate for intramolecular exchange, to the right if there is. Intramolecular exchange can be effected by population of the tetragonal-pyramidal state followed by return to a rearranged trigonal bipyramid. Both $\Delta G^{\ddagger}$(intra) and $\Delta G^{\ddagger}$(inter) are well-defined maxima in the ligand dissociation reaction coordinate (Figure 2). The geometrical correspondence between Figures 1 and 2 is shown by the symbols TBP, TP, TP', SP, and L.

Table I shows that while $\Delta G^{\ddagger}$(intra) increases with increasing steric bulk of the ligand for RhL$_5^+$ compounds due to steric crowding of the tetragonal pyramid relative to the trigonal bipyramid,[4] the corresponding $\Delta G^{\ddagger}$(inter) values are almost constant. The invariance of $\Delta G^{\ddagger}$(inter) to alkyl phosphite size may be interpreted as the cancelation of two steric effects: one, the sterically unfavorable effect of crowding of the basal ligands in the TP intermediate; two, the steric assistance to axial bond breaking in TP'. These two steric effects nearly cancel and the resulting invariance of $\Delta G^{\ddagger}$(inter) reflects the very similar electronic properties of the ligands. $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}$(inter) $- \Delta G^{\ddagger}$(intra) and is a rough measure of the free energy necessary to break the axial bond in TP. Figure 2 shows a set of semiquantitative reaction coordinates for the RhL$_5^+$ complexes. Curves are normalized to coincide at the TBP point. The SP + L section, unlike the rest of the curve, is likely to be quite sensitive to solvent; the equilibrium constant for dissociation [a function of G(P + L) $- G$(TBP)] increases as the steric bulk of L increases, making curve (a) the lowest at the SP + L position.

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Photoelectron Spectra of Group 5 Compounds. II.[1] Conformational Analysis of Diphosphine (P$_2$H$_4$)

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The photoelectron spectra of certain hydrazines,[2-4] disulfides,[5] peroxides,[6] and aminophosphines[7,8] have been assigned to a unique conformer, being present under normal PE spectroscopic conditions. In contrast, different rotamers could be detected in the PE spectra of hexahydropyridazines[3b] and tetrasubstituted diphosphines and diarsines[9] and were assumed for polysilanes.[10] The composition of the rotameric mixture (trans:gauche) obtained for tetramethyldiphosphine from the relative PE peak areas[9] had to be revised.[11]

For the simplest diphosphine P$_2$H$_4$ structural data[12,13] and the results from ab initio[14] and semiempirical[15] methods are available which are consistent with preponderant gauche conformation. However, some discrepancies remain in the reported equilibrium dihedral angles, barrier magnitudes, or the amount of trans isomers. Therefore, it was of interest to elucidate the structure of P$_2$H$_4$ by PE spectroscopy.[16] To gain some insight into its conformational composition we tried to simulate the experimental PE spectrum of P$_2$H$_4$ with EHMO, CNDO, and the reported ab initio orbital energies.[14,17a]

Experimental Section and Computational Details

The He I (584-Å) PE spectra were recorded with a Perkin-Elmer PS 16 spectrometer and calibrated with argon (resolution 35–40 meV).

Diphosphine was prepared as described by Baudler and Schmidt,[18] by treating calcium phosphide (Riedel de Haen AG, Seelze) with water in a high-vacuum line, followed by purification by trap to trap distillation.

To retard decomposition, giving PH$_3$ and solid polymers P$_n$H$_n$ catalyzed by traces of acids, a continuous flow of ammonia was passed through the PE spectrometer and the inlet equipment over a period of 24 h before the actual measurements. To maintain a constant

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