

# Intramolecular Rearrangements of M(bidentate phosphine)<sub>2</sub>XY Species

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**Abstract:** Intramolecular rearrangement barriers are shown to decrease with decreasing ring size for trigonal bipyramidal complexes of type  $\text{Ir}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2\text{CO}^+$ . Although some of these complexes dissociate carbon monoxide to some degree, this process is slow compared to the intramolecular process observed.  $\text{Ir}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2\text{HCl}^+$  is nonrigid and exists as the *cis* isomer. Rearrangement energetics are determined and physical pathways which accomplish the observed permutations are detailed. The closely related species *cis*- $\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}_2^+$  is stereochemically rigid. The barrier to intramolecular rearrangement of  $\text{ML}_4$  ( $\pi$ -acid) species is proposed as a criterion for quantitatively assessing metal-to-ligand bonding. In this way, the strong  $\pi$ -acidity of  $\text{O}_2$  and  $\text{S}_2$  in the adducts  $\text{M}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{A}_2^+$  ( $\text{M} = \text{Rh}, \text{Ir}; \text{A}_2 = \text{O}_2, \text{S}_2$ ) is demonstrated. It is concluded that these complexes have a vibrational energy surface characteristic of six-coordinate  $\text{M}(\text{III})$ .

Recent publications<sup>1,2</sup> have reported on experiments designed to raise the barrier to rearrangement of the first coordination sphere of five-coordinate complexes. We describe here our work on the inverse problem: the lowering of the barrier to rearrangement of six-coordinate molecules. As a preliminary to this work, an experimental study of the effect of chelate ring size on rearrangement energetics has been carried out. Finally, having examined some of the molecular parameters which affect rearrangement barriers, we consider the application of these to a classic problem in coordination chemistry, the Dewar-Chat model for  $\pi$  ligands.

## Experimental Section

All operations were performed in a nitrogen atmosphere.  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was obtained from Varlacoid Chemical Co., while bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe), and 1,2-bis(diphenylphosphino)propane (dpp) were obtained from Alfa Inorganics, Pressure Chemical, and ROC/RIC, respectively. Infrared spectra were recorded on Perkin-Elmer 621 and Infracord 137 instruments, <sup>31</sup>P nmr spectra (pulsed Fourier transform, 40.5 MHz) on a Varian XL100/15, and <sup>1</sup>H nmr on a Varian HR 220 spectrometer. Unless otherwise noted, all <sup>31</sup>P spectra were recorded with white noise proton decoupling. Nmr spectra were simulated using the program DNMR of Binsch.<sup>3</sup> Activation parameters were determined by a least-squares criterion applied to Arrhenius and Eyring plots. Errors quoted represent *maximum possible deviations* from the least-squares values and were determined by changing each *T* and *k* by its maximum error so as to give slopes as large or as small as possible. Errors in *T* were determined to be  $\pm 1^\circ$ , while errors in *k* were established by multiple line shape calculations in the vicinity of the "best" *k* value. The errors in *k* are largest at high and low temperatures, but this effect is not usually taken into account by other workers. Although this makes the "errors" quoted here larger than those reported by others, we feel this to be a more objective procedure. Least-squares *esd*'s for the data in Table I, which are influenced only by scatter in the data, are 0.07 (log *A*), 0.2 (*E<sub>a</sub>*), 0.2 ( $\Delta H^*$ ), 0.3 ( $\Delta S^*$ ). In spite of our generous allocation of errors, the activation parameters in Table I show significant trends.

**[Ir(bidentate phosphine)<sub>2</sub>CO]Cl.** These complexes were prepared by stirring  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  with the appropriate bisphosphine ligand in benzene.<sup>4</sup> The complexes precipitated immediately, were filtered, washed with diethyl ether, and dried under vacuum.  $[\text{Ir}(\text{dpe})_2\text{CO}]\text{Cl}$  and  $[\text{Ir}(\text{dpp})_2\text{CO}]\text{Cl}$  were identified by their infrared and <sup>31</sup>P nmr spectra, while  $[\text{Ir}(\text{dpm})_2\text{CO}]\text{Cl}$  was characterized by its infrared spectrum and elemental analysis. *Anal.* Calcd for  $\text{C}_{51}\text{H}_{44}\text{ClIrOP}$ : C, 59.59; H, 4.28; Cl, 3.45; Ir, 18.69; P, 12.07. Found: C, 58.04; H, 4.67; Cl, 3.50; Ir, 20.37; P, 11.83.

**[Ir(dpp)<sub>2</sub>]Cl.** This salt was prepared by refluxing  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  with slightly more than 2 mol of dpp in *p*-xylene

for 2 hr: <sup>31</sup>P chemical shift, +3.3 ppm. *Anal.* Calcd for  $\text{C}_{54}\text{H}_{52}\text{ClIrP}_4$ : C, 61.65; H, 4.95; Ir, 18.26; P, 11.80. Found: C, 61.85; H, 5.06; Ir, 19.01; P, 11.99.

**[Ir(dpp)<sub>2</sub>H(Cl)]PF<sub>6</sub>.** Aqueous  $\text{HPF}_6$  (0.5 ml, 65%) was added to 200 mg of  $\text{Ir}(\text{dpp})_2\text{Cl}$  in 15 ml of ethanol. Within a few minutes, colorless crystals formed. Recrystallization from THF and ethanol produces white needles, yield 89%;  $\nu_{\text{Ir-H}}$  2210  $\text{cm}^{-1}$  (Nujol); conductivity (in acetonitrile)  $\Lambda_m = 88.5$ . *Anal.* Calcd for  $\text{C}_{54}\text{H}_{53}\text{ClF}_6\text{IrP}_5$ : C, 54.15; H, 4.43; Cl, 2.96; Ir, 16.04; P, 12.95. Found: C, 54.4; H, 4.54; Cl, 3.04; Ir, 16.60; P, 12.41.

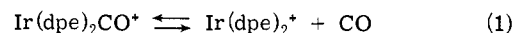
**[Ir(dpe)<sub>2</sub>H(Cl)]PF<sub>6</sub>.** Prepared as above. *Anal.* Calcd for  $\text{C}_{52}\text{H}_{49}\text{ClF}_6\text{IrP}_5$ : C, 53.38; H, 4.19; Cl, 3.03; Ir, 16.42; P, 13.26. Found: C, 52.98; H, 4.63; Cl, 3.10; Ir, 16.25; P, 12.87.

$\text{FeHCl}(\text{dpe})_2^6$  and the  $\text{O}_2$  and  $\text{S}_2$  adducts of  $\text{M}(\text{dpe})_2^+$  ( $\text{M} = \text{Rh}, \text{Ir}$ )<sup>7</sup> were prepared by literature methods. Oxygen addition to  $\text{Rh}(\text{dpe})_2^+$  is not entirely reversible.<sup>7</sup> Over a period of 12 hr, a singlet characteristic of  $(\text{OPh}_2\text{PCH}_2)_2$  ( $-30.9$  ppm) and a doublet ( $^2J_{\text{P-Rh}} = 84$  Hz,  $\delta$  39.8 ppm) consistent with  $\text{Rh}(\text{OPh}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{O})_2^+$  grow in. Because of the low equilibrium concentration of  $\text{Rh}(\text{dpe})_2\text{O}_2^+$ , the peaks due to irreversible oxidation quickly dominate the spectrum. This behavior is not observed for  $\text{Ir}(\text{dpe})_2\text{O}_2^+$ .

## Results

**Coordination Number Five.** The <sup>31</sup>P-<sup>1</sup>H nmr spectrum of  $[\text{Ir}(\text{dpp})_2\text{CO}]\text{Cl}$  was recorded at various temperatures in  $\text{CH}_2\text{Cl}_2$ . A spectrum characteristic of a trigonal bipyramid with CO equatorial is evident at  $-16^\circ$ . Since the pattern accidentally resembles that of an  $\text{A}_2\text{X}_2$  spin system, the only spectral parameters which can be determined are  $J_{\text{AX}} = 37.1$  Hz and  $\delta\nu = 445$  Hz. There is no evidence for peaks due to square-planar  $[\text{Ir}(\text{dpp})_2]\text{Cl}$ . Simulation of the coalescing spectra assuming simultaneous exchange of all four phosphorus nuclei (aeae)<sup>8</sup> yields the kinetic parameters shown in Table I.

The <sup>31</sup>P nmr spectrum of  $[\text{Ir}(\text{dpe})_2\text{CO}]\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  is also temperature dependent. In this case, the "frozen" spectrum is not quite achieved by  $-93^\circ$  (Figure 1). Nevertheless, nmr parameters can be determined:  $J_{\text{AX}} = 19$  Hz,  $\delta\nu = 364$  Hz. Assuming a natural line width of 4 Hz (estimated from internal  $[\text{Ir}(\text{dpe})_2]\text{Cl}$ ), rate data were determined as for  $\text{Ir}(\text{dpp})_2\text{CO}^+$ . Least-squares treatment of Arrhenius and Eyring plots<sup>9</sup> yields the activation parameters shown in Table I. The spectra at all temperatures also show a singlet at  $-50$  ppm due to  $\text{Ir}(\text{dpe})_2^+$ . This suggests the presence of eq 1, which is consistent with the observation that CO can



be removed from the adduct at elevated temperature in the solid state or in solution.<sup>4</sup>

Table I. Activation Parameters<sup>a</sup>

	$E_a$ (kcal/mol)	$\log A$	$\Delta H^*$ (kcal/mol)	$\Delta S^*$ (eu)
[Ir(dpp) <sub>2</sub> CO]Cl	12.9 (15)	11.8 (11)	12.2 (14)	-6.3 (102)
[Ir(dpe) <sub>2</sub> CO]Cl	10.6 (8)	14.1 (9)	10.2 (9)	4.9 (38)
[Ir(dpp) <sub>2</sub> HCl]PF <sub>6</sub>	11.6 (6)	13.1 (5)	11.3 (10)	-0.3 (25)

<sup>a</sup> Errors in parentheses represent maximum possible deviations from the quoted value (see Experimental Section for details).

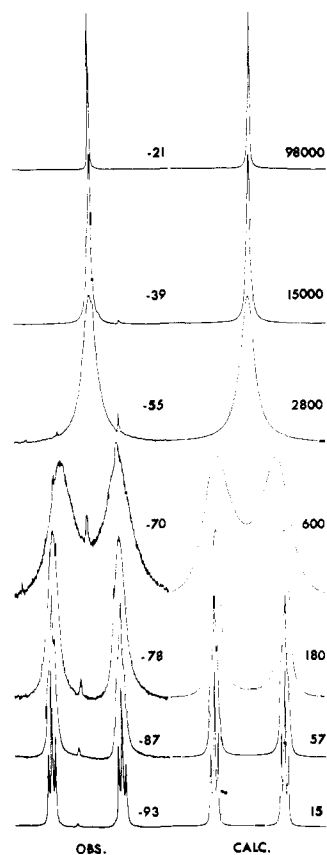
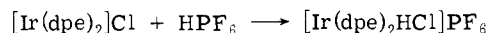


Figure 1. <sup>31</sup>P-<sup>1</sup>H} spectra of [Ir(dpe)<sub>2</sub>CO]Cl in CH<sub>2</sub>Cl<sub>2</sub>. Temperatures (°C) are shown on the observed spectra (left) and rate constants label the calculated spectra.

[Ir(dpm)<sub>2</sub>CO]Cl in CH<sub>2</sub>Cl<sub>2</sub> exhibits a <sup>31</sup>P singlet (line width 1 Hz) at 35°. At -92°, the <sup>31</sup>P signal is a singlet with a line width of 11 Hz. There is no nmr spectral evidence for Ir(dpm)<sub>2</sub><sup>+</sup> at either temperature.

**Coordination Number Six.** Ir(dpe)<sub>2</sub>HX<sup>+</sup> salts were prepared previously<sup>4</sup> in impure form by oxidative addition of HX to square planar Ir(dpe)<sub>2</sub><sup>+</sup>. High and variable halide analyses may have been due to coprecipitation of salts containing the bihalide anion, HX<sub>2</sub><sup>-</sup>. In the present work, this problem was avoided by maintaining precise stoichiometry with respect to halide. This was accomplished by making the square planar precursor complex the halide source.



Moderate excesses of HPF<sub>6</sub> had no obvious deleterious effect. Conductivity measurements prove that the product is indeed six-coordinate, and not a salt of the unknown cation HIr(dpe)<sub>2</sub><sup>2+</sup>. <sup>31</sup>P nmr was used to establish that the same product (*i.e.*, isomer) results from treatment of [Ir(dpe)<sub>2</sub>]Cl with aqueous HCl.

The <sup>31</sup>P nmr spectrum of the cation in [Ir(dpe)<sub>2</sub>HCl]PF<sub>6</sub> (all protons decoupled) is a sharp singlet (line width 2 Hz) at both +35 and -80°. The proton nmr at  $\tau$  29.6 is a quintet with  $J_{\text{PH}} = 12.5$  Hz at +20°. The variable temperature <sup>31</sup>P nmr spectrum of [Ir(dpp)<sub>2</sub>HCl]PF<sub>6</sub> is shown in Figure

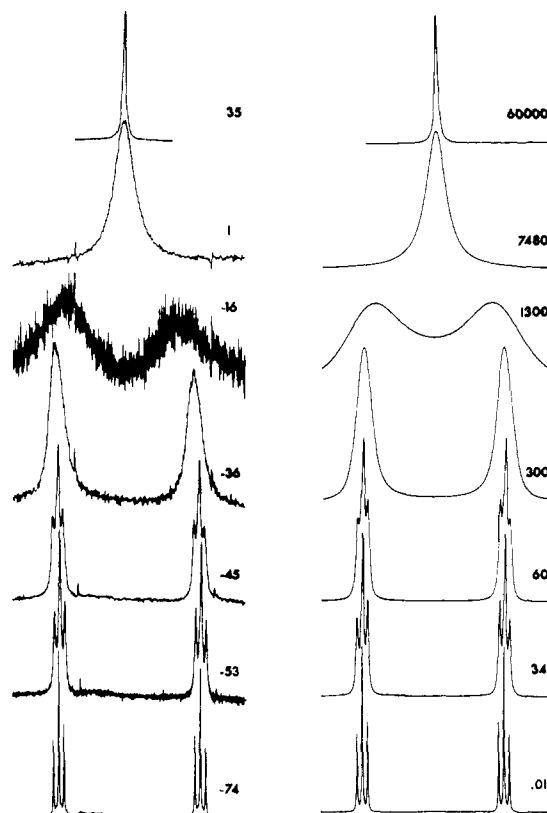


Figure 2. <sup>31</sup>P-<sup>1</sup>H} spectra of [Ir(dpp)<sub>2</sub>HCl]PF<sub>6</sub> in THF. Temperatures are shown on the observed spectra (left) and rate constants label the calculated spectra.

2; the PF<sub>6</sub><sup>-</sup> resonances have been omitted. At 35° a singlet is observed 15.8 ppm upfield from external 85% H<sub>3</sub>PO<sub>4</sub>. Although this is in apparent agreement with a *trans* stereochemistry, the line width, 17 Hz, is anomalously large. Low temperature spectra (Figure 2) prove that the 35° spectrum is time averaged and thus not diagnostic of stereochemistry. By -74° an apparent A<sub>2</sub>X<sub>2</sub> spectrum (a degenerate case of an AA'XX' spin system) is obtained and persists down to -100°. The spectral parameters are  $\delta_A - \delta_X = 743$  Hz and  $J_{\text{AX}} = 27.8$  Hz; the A and X resonances are symmetrically placed about the chemical shift observed at 35°. These temperature dependent spectral characteristics are reversible with temperature and independent of the concentration of complex or of added phosphine ligand. The proton nmr at +20° (220 MHz, 16 CAT scans) is a quintet at  $\tau$  29.0 with  $J_{\text{PH}} = 12.5$  Hz. An intramolecular process is indicated.

## Discussion

**Coordination Number Five.** The crystal structure of [Ir(dpe)<sub>2</sub>CO]Cl has demonstrated that the cation approximates trigonal bipyramidal geometry.<sup>10</sup> The complex therefore has two phosphorus environments, axial and equatorial. This same geometry will be assumed for the dpp and dpm analogs. The <sup>31</sup>P spectra show all three ions to be nonrigid with  $\Delta S^*$  values characteristic of an intramolecular process with no bond breaking.<sup>11</sup> This rules out the possibility that environmental averaging results from dissociation of CO. This is an important conclusion, since Ir(dpe)<sub>2</sub>CO<sup>+</sup> exists in equilibrium with Ir(dpe)<sub>2</sub><sup>+</sup>. Thus, although environmental averaging does occur by CO dissociation (eq 1), this pathway is much slower than the process actually being observed by <sup>31</sup>P nmr. It is not possible to obtain detailed information on the nature of the permutational process from the <sup>31</sup>P spectrum because of its simplicity. Calculations presuming *aeae* or *ae* permutations<sup>8</sup> yield activation param-

ters identical within experimental error. Attempts to utilize the diastereotopic methylene protons in the manner described previously<sup>12</sup> were frustrated by the overlapping resonances resulting from the  $\text{Ir}(\text{dpe})_2\text{CO}^+ - \text{Ir}(\text{dpe})_2^+$  equilibrium.

Activation parameters for the process (Table I) indicate that the barrier decreases in the order  $\text{dpp} > \text{dpe}$ ; the  $\text{dpm}$  complex seems to have the lowest barrier as judged by our inability to achieve a static spectrum. Thus, smaller ring size of the coordinated chelate facilitates rearrangement. This is consistent with the energy surface calculations of Kepert on  $\text{M}(\text{bidentate})_2(\text{monodentate})$  complexes.<sup>13</sup> Assuming only classical  $r^{-n}$  repulsions between points on the surface of a sphere, and assuming intrachelate repulsions to be independent of geometry, Kepert concludes that decreasing the "bite" parameter  $b = (\text{P} \cdots \text{P})/\text{M}-\text{P}$  decreases the energy separation between the more stable TBP and the less stable square pyramid (more properly rectangular pyramid). As  $b$  becomes very small, the square pyramid actually becomes the more stable structure. The structural study of  $\text{Ir}(\text{dpe})_2\text{CO}^+$  allows calculation of  $b = 1.34$ .  $\text{Ir}(\text{CH}_3)(\text{COD})(\text{dpp})$ , the only  $\text{dpp}$  complex studied crystallographically,<sup>14</sup> has  $b = 1.43$ .  $\text{Mo}(\text{CO})_4(\text{dpm})$ <sup>15</sup> has  $b = 1.11$ . An additional factor is also relevant. As the monodentate ligand (CO in this study) binds more tightly than the other ligands, the square pyramid becomes still more favored.<sup>16</sup>

A related example of this effect has been demonstrated.<sup>17</sup> The barrier to interchange of carbonyl groups in (1,3-diene) $\text{Fe}(\text{CO})_3$  complexes is larger than for 1,4- and 1,5-diene analogs, presumably because of the larger "bite" of the latter class of ligands.

Shapley and Osborn<sup>18</sup> have shown that "site preferences" in trigonal bipyramidal molecules can be used to alter rearrangement barriers. On the basis of the present work and that of Takats and Kruczynski, it appears that variation of the chelate ring size may also be useful in modifying some excessively low or high rearrangement barriers so that they become experimentally accessible. For example  $\text{Fe}(\text{bidentate phosphine})(\text{CO})_3$  complexes are nonrigid to the lowest accessible temperatures when one<sup>19</sup> or two<sup>20</sup> methylene groups connect the phosphorus nuclei. Ligands such as  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  with  $n = 3$  or 4, may make these complexes more amenable to analysis. Note, however, that  $\text{HM}(\text{dpe})_2$  and  $\text{HM}(\text{PR}_3)_4$  appear to have comparable activation parameters;<sup>21</sup> it appears that chelate ring strain is not a significant factor in the "tetrahedral jump" transition state.

**Coordination Number Six.** The hydride ligand is unusual in a structural sense since its steric requirements are minimal.<sup>22</sup> The hydride ligand also confers unusual dynamic properties on molecules. This has been amply demonstrated for  $\text{HML}_4$ <sup>21</sup> and  $\text{H}_2\text{ML}_4$ <sup>23</sup> complexes, as well as hydride complexes with higher coordination numbers.<sup>24</sup> In general, molecular rearrangements are facilitated by the presence of one or more hydride ligands. Although the experimentally observed result is permutation of nonhydridic ligands, it has been argued that for  $\text{cis-MH}_2\text{L}_4$  the physical process involved is mainly a motion of the hydrides. Intramolecular rearrangement of complexes with six nonhydridic monodentate ligands has been observed only for  $\text{Os}(\text{SiMe}_3)_2(\text{CO})_4$ .<sup>25</sup> Here,  $\text{cis-trans}$  isomerization proceeds with an activation enthalpy of 17.9 kcal/mol. Tris chelate complexes of the transition metals have been studied extensively.<sup>26-30</sup> In cases where the data exclude bond breaking, the lowest barriers to rearrangement of the first coordination sphere are in excess of 8-10 kcal/mol. These occur for tropolonate and dithiocarbamate ligands. In these latter situations it is likely that the barrier is as low as it is because of intrachelate constraints on bond angles at the metal.<sup>31</sup> In

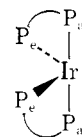
contrast to dithiocarbamates and tropolonates, bidentate phosphines have the virtue of easy alteration of "bite size" with a negligible change in electronic characteristics.

The dynamics of six-coordinate monohydrides have not been studied previously. Indeed, previous workers have presumed these molecules to be rigid and taken room temperature nmr data at face value;  $\text{Ir}(\text{dpe})_2\text{HX}^+$  and the bis(dimethylphosphino)ethane analogs have been assigned structures with H trans to X on the basis of quintet patterns in the hydride resonances.<sup>4,32</sup> The trends emerging from the work of others coupled with our observation of nonrigidity in five-coordinate bis(bidentate phosphine) complexes, led us to examine the molecules studied here.

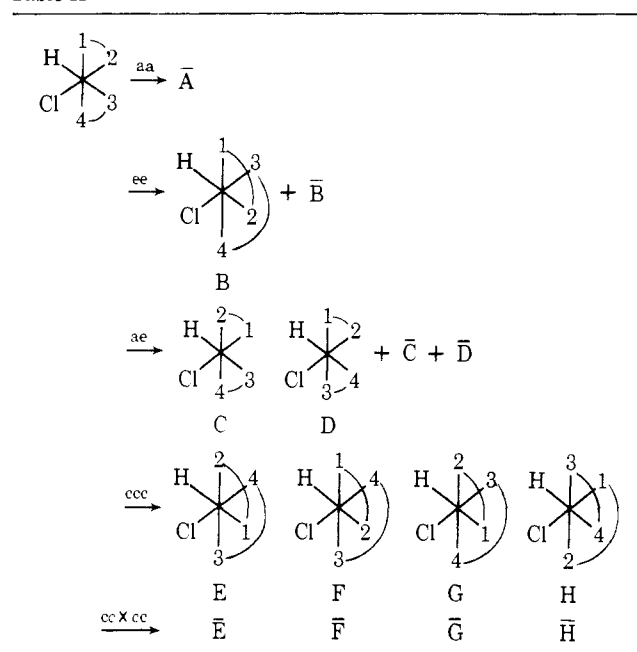
Low temperature <sup>31</sup>P nmr shows unambiguously that  $\text{Ir}(\text{dpp})_2\text{HCl}^+$  is the  $\text{cis}$  isomer.<sup>33</sup> The situation for  $\text{Ir}(\text{dpe})_2\text{HCl}^+$  is less clear, since we are unable to observe any nmr spectral changes on lowering the temperature. However, we feel that the similarity of  ${}^2J_{\text{P-H}}$  observed at  $+20^\circ$  for the two complexes suggests similar stereochemistry. The time-averaged  ${}^2J_{\text{P-H}}$  for the  $\text{dpp}$  complex is the average of three  $J_{\text{P-H}}$  terms at  $90^\circ$  and one  $J_{\text{P-H}}$  at  $180^\circ$ . The latter is large and thus we expect  ${}^2J_{\text{P-H}}$  for an authentic  $\text{trans}$  isomer to be considerably diminished in magnitude from the time-averaged value in a  $\text{cis}$  isomer. Since rearrangement barriers decrease with decreasing ring size (see above) the failure to achieve a limiting spectrum for  $\text{Ir}(\text{dpe})_2\text{HCl}^+$  is understandable.

$\text{cis-Ir}(\text{dpp})_2\text{HCl}^+$  has no molecular symmetry; even the phosphorus nuclei lying above and below the  $\text{IrHCl}$  plane (the apical phosphorus nuclei) are inequivalent. Thus, the static structure requires four phosphorus chemical shifts. Even at  $-93^\circ$  there is no evidence for more than two chemical shifts; by this temperature some rearrangement has been slowed sufficiently for detection by <sup>31</sup>P nmr, but some process is still occurring so as to leave the molecule with apparent  $C_2$  symmetry. The nmr pattern observed at  $-93^\circ$  must actually be an  $\text{AA}'\text{XX}'$  pattern with  $J_{\text{AX}} - J_{\text{AX}'} \ll \delta_{\text{A}} - \delta_{\text{X}}$  where  $\delta$  represents chemical shift in hertz. Under these conditions an apparent  $\text{A}_2\text{X}_2$  pattern results. Physically this condition means that coupling between nuclei on the same bidentate ligand is similar to that between nuclei in different bidentate ligands.

The process observed between  $-74$  and  $+35^\circ$  is thus the equilibration of axial ( $\text{P}_a$ ) and equatorial ( $\text{P}_e$ ) nuclei of the unit  $\text{Ir}(\text{dpp})_2$  with effective  $C_2$  symmetry.



This problem has been treated earlier.<sup>12</sup> One possible choice of three independent permutations for this molecule is  $ee$ ,  $ae$ , and  $aeae$ .<sup>34,35</sup> The first permutation alone does not equilibrate axial and equatorial sites and is thus inconsistent with experiment. The second and third permutations do. A choice between these cannot be made by line shape analysis of the coalescing <sup>31</sup>P nmr spectra; both modes yield satisfactory fits with similar activation parameters. Proton nmr in the rapid exchange region is diagnostic, however. With <sup>31</sup>P decoupling, the chelate ring methylene protons of  $[\text{Ir}(\text{dpe})_2\text{HCl}]\text{PF}_6$  appear as an  $\text{AA}'\text{BB}'$  pattern (Figure 3). The permutations  $ae$  and  $aeae$  correspond to distinct observable processes using the methylene protons as probes. In brief, the chemically equivalent protons are on the same side of the chelate ring if the permutation is  $aeae$ ; this permutation retains a proximal and distal relationship with respect to the chloride and hydride ligands. The permutation  $ae$ , on the other hand equilibrates  $\text{trans}$  vicinal protons

Table II<sup>a</sup>

<sup>a</sup> A and  $\bar{A}$  denote enantiomers.

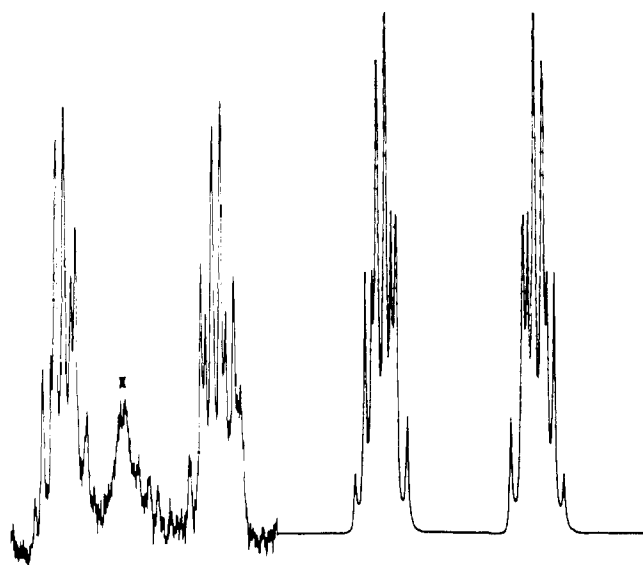
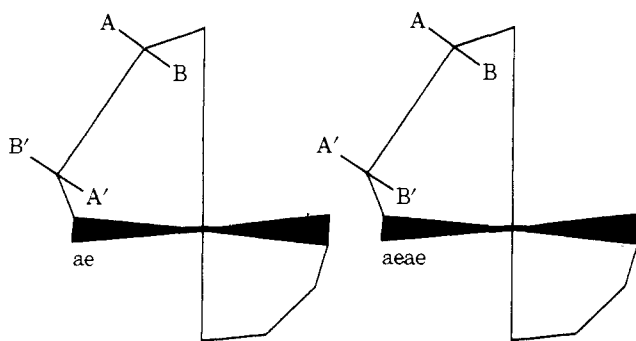


Figure 3. The 220-MHz <sup>1</sup>H-[<sup>31</sup>P}] spectrum of Ir(dpe)<sub>2</sub>HCl<sup>+</sup> in acetone-*d*<sub>6</sub> at 20°. × denotes a solvent spinning side band. Calculated spectrum is at right.



within one chelate ring. The observed methylene resonances can be reproduced with the parameters  $\delta_{AB}$  0.50 ppm,  $J_{AA'}$  = 6.3,  $J_{AB}$  = -14.3,  $J_{BB'}$  = 6.2, and  $J_{AB'}$  = 8.0 Hz.

Using an argument based on the Karplus relationship,<sup>12</sup> these parameters indicate that the aeae permutation is op-

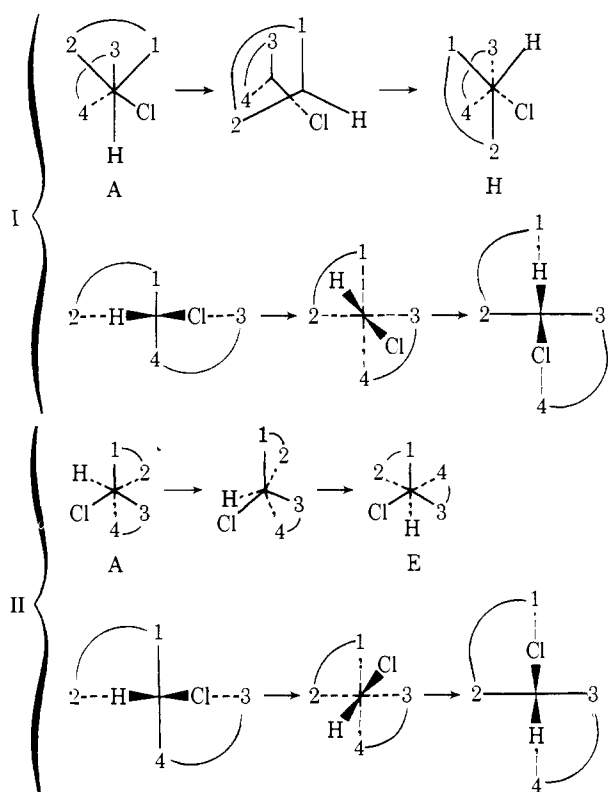
erative.<sup>36</sup> Note that the persistence of an AA'BB' methylene pattern also rules out rapid dissociation of H and Cl; such a process would render all methylene protons equivalent.

The bis chelate hydrido-chloride species studied here exhibit remarkably low rearrangement barriers for six-coordinate complexes. Hf(acac)Cl<sub>2</sub> is the only other example of a nonrigid six-coordinate complex of the third transition series. In fact, only a partial determination of the nmr parameters for the static structure has been possible since one aspect of the rearrangement, the permutation of H and Cl, apparently has an extremely low barrier.<sup>37</sup> The significant aspect of this observation is that we have, in a single complex, two rearrangements of the first coordination sphere occurring at different rates.

Table II exhibits the results of a permutational analysis of a *cis*-M(bidentate)<sub>2</sub>XY isomer. Permutations which place H trans to Cl have been omitted.<sup>38</sup> In the interest of completeness and in order to avoid initial prejudice toward one physical pathway for rearrangement, the procedure of Musher is adopted.<sup>8,34</sup> The notations a and e refer to positions out of or lying in the IrHCl plane, respectively. Since our experiments do not distinguish between retention and inversion of absolute configuration, optical isomers are grouped together.<sup>39</sup> Two points are to be emphasized. First, since the molecule has no symmetry, every permutation listed in Table II has a different activation energy. As a result, rearrangement by a stepwise sequence of permutations along an energy surface with many local minima cannot be rigorously excluded. Second, the labeling of permuted nuclei is purely a formal "bookkeeping" device. These labels do not uniquely specify the nuclei which are displaced in the actual physical rearrangement. For example, interchange of P<sub>3</sub> and P<sub>4</sub> generates D, while interchange of H with P<sub>1</sub> generates the enantiomeric species  $\bar{D}$ . Similarly, the single species G results from the following three energetically distinct cc x cc processes: (H, P<sub>4</sub>) x (P<sub>2</sub>, P<sub>3</sub>); (H, Cl) x (P<sub>1</sub>, P<sub>2</sub>); (Cl, P<sub>4</sub>) x (P<sub>1</sub>, P<sub>3</sub>). The valuable characteristic of any permutational analysis is its generality. Because of this generality, all previously proposed physical pathways<sup>27,28</sup> ("mechanisms") for rearrangement are contained in Table II. In particular the permutation of three *cis* ligands (ccc) encompasses both Bailar and Ray-Dutt processes. In the low symmetry system considered here, however, one is faced with a staggering array of choices, and some speculation is inevitable. A brief example follows.

Two kinetic processes with distinct energetics are implied by the data at hand. The slower process is a pairwise permutation of axial with equatorial phosphorus nuclei; the faster one permutes the equatorial sites trans to H and Cl. The latter corresponds directly to the ee process on Table II. The former is consistent with either the numerous ccc permutations which produce E or the numerous ccc permutations which produce H. The permutations which produce F and G are inconsistent with the methylene proton nmr and are therefore excluded. At this point (see Scheme I), it is worth describing one physical pathway for the formation of H (process I) and one for formation of E (process II). The upper representation in each case corresponds to the classical view down a pseudo-threefold axis about which a 120° rotation is performed. The motions thus correspond to Bailar or Ray-Dutt twists. The lower representation is useful in drawing a parallel to the process of Berry pseudo-rotation in coordination number five. In each case, the transition state has the phosphorus nuclei in the basal positions of a square pyramid (H and Cl together formally occupy the apical position). The need for rotation of the plane of the Ir-H and Ir-Cl bonds (or of the O<sub>2</sub>, S<sub>2</sub>, or olefin moiety in the following section) in the rearrangement is clearly

Scheme I



shown. Moreover, it is clear that processes I and II will have different activation energies; the transition states are distinguished by H and Cl eclipsing or being staggered with respect to the chelate methylene groups. It is repetitive to say that these physical processes are not uniquely implied by the data. However, their simplicity and their relationship to the five-coordinate rearrangements discussed here make them useful as working hypotheses.

It is appropriate to attempt to separate the factors of chelate effect and hydride mobility on lowering the rearrangement barrier in bis chelate hydrido-chloride complexes. In an attempt to determine to what extent the hydride ligand facilitates axial-equatorial phosphorus permutation, we sought to determine whether *cis*-Ir(dpe)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> exhibits stereochemical nonrigidity. This compound has apparently not been made<sup>40</sup> before, and oxidative addition of I<sub>2</sub> to Ir(dpe)<sub>2</sub><sup>+</sup> is known to produce the *trans* isomer.<sup>41</sup>

Addition of a deficiency of dry chlorine in CH<sub>2</sub>Cl<sub>2</sub> to [Ir(dpe)<sub>2</sub>]Cl produces new <sup>31</sup>P resonances (in addition to a singlet at -50.2 ppm due to Ir(dpe)<sub>2</sub><sup>+</sup> at -24.9, -20.1, -12.6, and -2.1 ppm (Figure 4). The strong singlet at -2.1 ppm is attributed to *trans*-Ir(dpe)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>;<sup>42</sup> this signal is temperature independent. The singlet at -20.1 ppm is due to Ir(dpe)<sub>2</sub>HCl<sup>+</sup>.<sup>43</sup> The signals at -24.9 and -12.6 ppm are structured (<sup>2</sup>J<sub>P-P</sub> = 5.5 Hz) and are consistent with *cis*-Ir(dpe)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> as a static molecule.<sup>44</sup> Two five-membered chelate rings alone thus are inadequate to cause nonrigidity at +35°. Conversely, the mere presence of a single hydride ligand in a six-coordinate complex is also insufficient. RuHCl[P(OPh)<sub>3</sub>]<sub>4</sub> is rigid at room temperature.<sup>45</sup> In fact, the Ir(III) dihydride IrH<sub>2</sub>CO(PPh<sub>3</sub>)<sub>3</sub><sup>+</sup> is also rigid.<sup>46</sup> It must be concluded that the nonrigidity observed here for Ir-(bidentate phosphine)HX<sup>+</sup> species results from the summation of two effects which tend to lower the rearrangement barrier.

**Intermediate Cases.** The qualitative aspects of the binding of diatomic or planar ligands, "sideways" or by a face, are widely known.<sup>47</sup> The symmetry of the systems allows factorization of the bonding into a  $\sigma$  component from filled

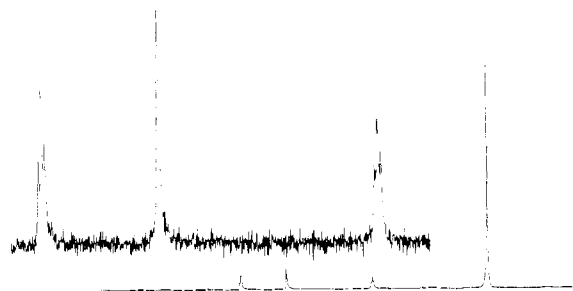


Figure 4. <sup>31</sup>P-{<sup>1</sup>H} spectrum (-78°, CH<sub>2</sub>Cl<sub>2</sub>) of the products resulting from chlorination of [Ir(dpe)<sub>2</sub>]Cl. The singlet due to unreacted [Ir(dpe)<sub>2</sub>]Cl has been omitted. The inset shows an expanded view of the region -35 to -10 ppm.

ligand  $\pi$ -orbitals to empty metal orbitals (I) and  $\pi$  bonding from filled metal d orbitals to empty ligand  $\pi^*$  orbitals (II).



Any real situation will of course contain some contribution from each of these bonding modes; to seek an exclusive "either/or" choice between these two is to oversimplify reality. Quantitative assessment of the relative contribution of these bonding modes is of real importance, however, since these are tied to the commonly used terms "oxidative addition" and "coordination number." For example, limiting case I formally has the ligand functioning as a monodentate ligand and there is no oxidation of the metal. Case II, because it involves bonds from M toward each atom of the ligand A<sub>2</sub>, is best considered as bidentate bonding by A<sub>2</sub>; further, in the limiting case where the ligand  $\pi^*$  orbital lies below the metal d orbital on the energy scale this picture represents oxidation of the metal by two electrons. The hypothetical situation of pure case I behavior is thus viewed in valence bond structure as III, while equal contributions of I and II correspond to the metallocycle structure IV. Past at-



tempts to assess the relative importance of  $\sigma$  and  $\pi$  bonding have utilized structural, vibrational, and nuclear coupling constant data.<sup>47</sup> We propose here still another experimental criterion.

Ligand-to-metal  $\sigma$  bonding, by virtue of its rotationally invariant overlap, allows free rotation of the ligand A<sub>2</sub> about the M-A<sub>2</sub> bond. Metal to ligand  $\pi$  bonding, when it occurs, introduces a rotational barrier; this results from an energetic differentiation of the d $\pi$  orbitals in, and perpendicular to, the MA<sub>2</sub> plane. To this electronic barrier must be added any barrier due to internuclear repulsions. In several planar complexes, where the separation between these orbitals is presumably maximized, the overall barrier has been established as 12-15 kcal/mol.<sup>48</sup>

It has been established above that rearrangement of axial and equatorial phosphorus nuclei in *cis*-Ir(dpe)<sub>2</sub>HCl<sup>+</sup> requires an apparent net rotation of the IrHCl plane by 90°. Since the same holds true for adducts of Ir(dpe)<sub>2</sub><sup>+</sup> with small molecules, we suggest that the magnitude of the rearrangement barrier in Ir(dpe)<sub>2</sub>A<sub>2</sub><sup>+</sup> species be used as an additional experimental criterion for the extent of metal-to-ligand  $\pi$  bonding. In the particular case at hand, the distinction to be drawn is between a five-coordinate Ir<sup>I</sup> complex (V) and a complex which, by this energy criterion, is

effectively six-coordinate Ir<sup>III</sup> (VI). In the work of the Tak-



ats and Osborn groups,<sup>12</sup> exchange of carbonyl groups in Fe(CO)<sub>4</sub>L has been inhibited by incorporating ligands which give the metal some of the characteristics of six-coordinate iron(II). In contrast, Fe(CO)<sub>4</sub>(amine) and Fe(CO)<sub>4</sub>(CHO)<sup>-1</sup> retain the very low energy barrier characteristic of Fe(CO)<sub>5</sub> since these ligands are nearly pure  $\sigma$  donors.<sup>49,50</sup>

The <sup>31</sup>P nmr spectrum of Ir(dpe)<sub>2</sub>O<sub>2</sub><sup>+</sup>, indicates that this is a rigid molecule.<sup>51</sup> As a result of the lower electronegativity of sulfur, back-bonding to the S<sub>2</sub> moiety should be less than that to O<sub>2</sub>; the rearrangement barrier for Ir(dpe)<sub>2</sub>S<sub>2</sub><sup>+</sup> should therefore be lower than that for the O<sub>2</sub> analog. However, Ir(dpe)<sub>2</sub>S<sub>2</sub><sup>+</sup> is also rigid at 35°. Binding of O<sub>2</sub> to rhodium(I) is weaker than to iridium(I). This is evident in the <sup>31</sup>P nmr spectrum, since Ir(dpe)<sub>2</sub><sup>+</sup> is no longer spectroscopically detectable when it is exposed to 1 atm of O<sub>2</sub>. In contrast, in acetone at 35° 1 atm of O<sub>2</sub> leaves Rh(dpe)<sub>2</sub><sup>+</sup> mainly as the square planar species with only about 12% Rh(dpe)<sub>2</sub>O<sub>2</sub><sup>+</sup>. However, the signal of this latter species is two doublets of triplets characteristic of a rigid molecule.

Our attempts to further probe the extent of back-bonding in  $\pi$ -acid complexes were frustrated by the low formation constants for M(dpe)<sub>2</sub>(olefin)<sup>+</sup> complexes. We find, both by visual observation and <sup>31</sup>P techniques, no significant complex formation by C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>, maleic anhydride, fumaronitrile, and TCNE. Since the equilibrium constant for oxygen addition to Ir(dpe)<sub>2</sub><sup>+</sup> exceeds that to Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>, the cation is an intrinsically better substrate.<sup>52</sup> We therefore attribute the low formation constants of other adducts to steric effects. These are presumably repulsions between phenyl rings of the phosphine chelate and olefin substituents. Such interactions have been noted in the solid state with the small ligands CO,<sup>10</sup> O<sub>2</sub>,<sup>53</sup> and S<sub>2</sub>,<sup>54</sup> and they presumably persist in solution for the latter.<sup>41</sup> It is to be noted that the concept of repulsive interactions between the addend and the axial ligands may be used to rationalize the stereochemistry of adducts of Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>. Thus, the adduct has trans (axial) phosphines in adducts of CO<sup>55</sup> and O<sub>2</sub>,<sup>56</sup> while the phosphines go to the more distant cis (equatorial) positions in the adducts of C<sub>2</sub>F<sub>4</sub> and TCNE. Similarly, the complexes Ir(C<sub>6</sub>N<sub>4</sub>H)CO(TCNE)(PPh<sub>3</sub>)<sub>2</sub> and Ir(H)CO(*trans*-1,2-dicyanoethylene)(PPh<sub>3</sub>)<sub>2</sub> have cis phosphines while Ir(1,2-dicyanovinyl)CO(NCCCCN)(PPh<sub>3</sub>)<sub>2</sub>, with the smaller acetylene ligand, has the phosphines trans.<sup>57</sup> Congestion is particularly acute in tetrakis phosphine complexes. Formal cleavage of the methylene bridges of Ir(dpe)<sub>2</sub><sup>+</sup> to produce Ir(PPh<sub>2</sub>Me)<sub>4</sub><sup>+</sup> produces a species which no longer binds oxygen.<sup>58</sup>

In summary, although Ir(dpe)<sub>2</sub><sup>+</sup> will not support the range of addends that Fe(CO)<sub>4</sub> does, it appears that rearrangement barriers may prove generally useful in ranking metal-to-ligand donation among  $\pi$ -acid ligands. Back-bonding to the electronegative groups O<sub>2</sub> and S<sub>2</sub> is strong enough to inhibit rotation, and therefore also phosphine rearrangement at accessible temperatures. Ir(dpe)<sub>2</sub>O<sub>2</sub><sup>+</sup> and Ir(dpe)<sub>2</sub>S<sub>2</sub><sup>+</sup> thus possess a vibrational energy surface characteristic of six-coordinate Ir(III).

Table III summarizes <sup>31</sup>P nmr parameters. Any attempt at extracting trends seems doomed. Values of  $J_{P-P}$  show marginal evidence for decreasing with increasing metal oxidation state. Changes in chemical shifts on coordination are

Table III. <sup>31</sup>P Nmr Data

Compound	$J_{P-P}$	$\nu_A$	$\nu_X$	$T$ (°C)
dpp		17.3		+35
dpe		12.5		
dpm		23.6		
Rh(dpe) <sub>2</sub> <sup>+</sup> <sup>a</sup>		-56.8		
Ir(dpe) <sub>2</sub> <sup>+</sup>		-50.2		
[Ir(dpp) <sub>2</sub> CO]Cl	37.1	16.9	27.9	
[Ir(dpe) <sub>2</sub> CO]Cl	19.1	-28.7	-19.7	-93
		-24.4		+35
[Ir(dpm) <sub>2</sub> CO]Cl		38.9		+35, -92
[Ir(dpp) <sub>2</sub> HCl]PF <sub>6</sub>	27.8	5.2	23.6	-74
		15.8		+35
[Ir(dpe) <sub>2</sub> HCl]PF <sub>6</sub>		-20.1		+35, -80
Fe(dpe) <sub>2</sub> (H)(Cl)		-78.2		+35, -95
[Ir(dpe) <sub>2</sub> O <sub>2</sub> ]Cl	3.4	-16.5	-13.4	+35
[Ir(dpe) <sub>2</sub> S <sub>2</sub> ]Cl	7.7	-21.9	-19.3	+35
[Rh(dpe) <sub>2</sub> O <sub>2</sub> ]Cl <sup>b</sup>	7.7	-51.3	-44.3	-80
<i>trans</i> -[Ir(dpe) <sub>2</sub> Cl <sub>2</sub> ]Cl		-2.1		+35
<i>cis</i> -[Ir(dpe) <sub>2</sub> Cl <sub>2</sub> ]Cl	5.5	-24.9	-12.6	+35

<sup>a</sup>  $J_{Rh-P} = 133$  Hz, <sup>b</sup>  $J_{Rh-PA} = 126$ ,  $J_{Rh-PX} = 92$  Hz.

irrational; dpe and dpp undergo downfield coordination chemical shifts in the square planar complexes. In the carbonyl adducts, however, dpe moves downfield while dpp and dpm move upfield with respect to free ligand. Oxidative addition to the square planar species generally moves the <sup>31</sup>P resonances upfield. However, direct oxidation of Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> to the dioxide causes a downfield shift. The axial-equatorial chemical shift difference is similar in the O<sub>2</sub> and S<sub>2</sub> adducts of Ir(dpe)<sub>2</sub><sup>+</sup>. This difference is substantially larger in the weaker adduct Rh(dpe)<sub>2</sub>O<sub>2</sub><sup>+</sup>. It may be useful for future studies of oxidative addition to note that the <sup>31</sup>P chemical shifts of *cis*- and *trans*-Ir(dpe)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> differ markedly. Similarly, the *trans* dichloro species is easily distinguished from the *trans* diiodo cation (chemical shift +6.7 ppm).<sup>41</sup> Finally, <sup>1</sup> $J_{P-Rh}$  decreases on oxidation and shows substantial variation with phosphorus environment within one molecule (Rh(dpe)<sub>2</sub>O<sub>2</sub><sup>+</sup>).

## Conclusion

Stereochemical assignments of molecules M(bidentate phosphine)XY must be approached with caution. These molecules have been shown to be nonrigid in some instances. In other cases, we have been unable to clearly distinguish a static structure with X and Y *trans* from a nonrigid *cis* geometry with a low rearrangement barrier. In view of these results, past stereochemical determinations<sup>59</sup> should be reconsidered on their individual merits and future work should utilize all applicable physical methods. Negative spectroscopic results are particularly suspect. For example, although FeHCl(dpe)<sub>2</sub> shows a hydride quintet ( $J_{P-H} = 50.5$  Hz) at 20° and a sharp <sup>31</sup>P doublet (hydride not decoupled) down to -90°, its structure remains uncertain. Vibrational spectra in the "methylene rock" region may be of use for cases where X = Y.<sup>60</sup> Finally, rearrangement barriers provide an additional experimental criterion of back-bonding, oxidation state, and, to some degree, coordination number for complexes of formula ML<sub>4</sub>(addend) provided L contains spin-active nuclei which can potentially achieve time-average equivalence.

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