

similar, i.e. -85 and -76 Hz, respectively. The $^2J_{\text{Pt-P}_B}$ coupling constant for 7 should be greater than that for 6 because of the greater trans influence of the H⁻ ligand in 6. For 7, $^2J_{\text{Pt-P}_B}$ is -119 Hz whereas, for 6, $^2J_{\text{Pt-P}_B}$ is -12 Hz.

The basis for this correlation to the trans effect may be related to the difference in the electronic distribution about each platinum atom in these dimers, which is indicated by the P-Pt-P bond angles and Pt-P bond lengths.³² From the crystal structure data of complexes 5,¹⁹ 8,³³ and 9,²⁷ it can be seen that, in each of these dimers, the P-Pt-P angles at Pt_X and Pt_{X'} are different. For example, in 5, the P_A-Pt_X-Pt_{A'} angle is 177° whereas the P_B-Pt_X-P_{B'} angle is 160°. For 8 and 9, not only are these angles different but the Pt-P bond lengths are also different. In 8, the Pt-P_A and Pt-P_B bond lengths are 2.248 and 2.264 Å, respectively. Although the steric requirements of the ligands trans to the Pt-Pt bond will partially contribute to the observed structural differences, the σ -donor ability of these ligands, which is related to the trans effect order, will also play a role in these differences. As a result, the relative magnitudes of $^2J_{\text{Pt-P}_A}$ and $^2J_{\text{Pt-P}_B}$ will reflect not only a difference in the type of ligands which are trans to the Pt-Pt bond but also their σ -donor ability.

Conclusion

Studies presented in this paper of symmetrical and unsymmetrical dinuclear Pt(II) complexes containing phosphine ligands

clearly demonstrate that two-dimensional ^{31}P correlated spectroscopy (COSY) available on high-field NMR spectrometers is a powerful technique for determining important coupling constant information. It has been shown for nine complexes, that the signs and magnitudes of the $^2J_{\text{Pt-P}}$ coupling constant can be directly determined from the experimental two-dimensional spectrum by the appearance and position of cross correlations of the Pt-P satellite peaks. This method is especially valuable for systems of high complexity, where the internal multiplets of the Pt-P satellite peaks are poorly resolved or are obscured by the more intense central phosphorus resonance. In these cases, the two-bond Pt-P coupling constants cannot be determined from one-dimensional data. The determination of the $^2J_{\text{Pt-P}}$ coupling constant is important for this class of compounds because it yields valuable information concerning the nature of the Pt-Pt bond and the effect of the ligands on this bond.

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Supplementary Material Available: The one- and two-dimensional ^{31}P NMR spectra of complexes 3, 4, and 7-9 (6 pages). Ordering information is given on any current masthead page.

(32) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 107.

(33) Manojlovic-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1981**, 219, 129.

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Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 4. Oxidative Addition of Dihydrogen to d⁸ Square-Planar Iridium Complexes with Trans Phosphines

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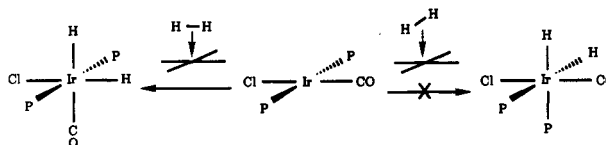
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The oxidative addition of H₂ to Vaska-type complexes, *trans*-IrX(CO)(PR₃)₂, is investigated with ab initio quantum chemical calculations. The direction of addition in these complexes is controlled by how the ligands in the plane of addition react to a close encounter with concentrations of charge density around the metal center as the complex evolves from a four-coordinate to a six-coordinate species. Strong electron-donating ligands destabilize the five-coordinate transition state while electron-withdrawing ligands stabilize the transition state. When X is a weak electron donor ligand such as Cl⁻, H₂ adds in the Cl-Ir-CO plane. When X = H⁻ or Ph⁻, however, H₂ adds in the PR₃-Ir-PR₃ plane; the destabilizing influence of these strong electron-donating ligands on the transition state outweigh those of the PR₃ ligands. The electronic contribution to the relative stabilities of the six-coordinate final products can be predicted based on the relative orientations of the strongest trans-influence ligands. The isomers in which these ligands are facial are lower in energy than those in which they are meridional.

Introduction

The activation of H₂ through an oxidative-addition reaction with a transition-metal complex is a fundamental step in several important catalytic cycles.¹ In catalytic hydrogenation and hydroformylation, for example, H₂ is activated by oxidative addition to a transition-metal center.² The oxidative addition of H₂ to *trans*-IrCl(CO)(PPh₃)₂, Vaska's complex, has been extensively studied,³ and the generally accepted mechanism of the reaction involves the concerted addition of H₂ to form pseudooctahedral products with a cis orientation of the hydride ligands.

Two isomeric products are possible in this reaction, and their formation can be viewed as the result of the concerted addition in one of the two vertical L-M-L planes of the d⁸ square-planar transition-metal complex. For Vaska's complex, only one isomer is observed, as shown in eq 1, and despite the large quantity of



(1)

- (1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1186.
- (2) Parrshall, G. W. *Homogenous Catalysis*; Wiley: New York, 1980.
- (3) (a) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, 88, 3511. (b) Halpern, J. *Acc. Chem. Res.* **1970**, 3, 386. (c) Vaska, L. *Ibid.* **1968**, 1, 335. (d) Ugo, R.; Pasini, A.; Fusi, A.; Cenini, S. *J. Am. Chem. Soc.* **1972**, 94, 7364. (e) Collman, J. P. *Acc. Chem. Res.* **1968**, 1, 136.

work that has been devoted to the reaction, the specific factors which determine this stereochemistry remain largely unknown.

The analysis of the factors, which control the direction of H₂ addition to Vaska's complex, is complicated by their sheer number. These factors include the combined steric and electronic contri-

butions from the pairs of ligands along each axis. Sorting out which of these contributions determine to which L-M-L plane the H₂ unit adds is a complicated task. The task, however, is simplified somewhat for the oxidative addition of H₂ to complexes with a cis orientation of the phosphine ligands, such as IrCl(CO)(dppe), which was thoroughly studied by Eisenberg and co-workers.⁴ In this reaction, because one phosphine ligand is present in both planes of addition, the electronic and steric contributions from these ligands to the factors which control the direction of addition effectively cancel. The analysis is reduced to a comparison between the CO and Cl⁻ ligands. Our *ab initio* quantum chemical analysis of this reaction⁵ concluded that the principal factor controlling the direction of addition was how well the ligands in the plane of addition compensated for the interelectronic repulsion that existed between the ligands and the metal as the complex evolved from a four-coordinate to a six-coordinate species. The electron-withdrawing CO ligand stabilized the repulsive five-coordinate transition state by delocalizing some of the excess electron density. The electron-donating Cl⁻ ligand simply contributed to the excess repulsive interaction in the reaction plane.

In studies of the oxidative addition of H₂ to derivatives of Vaska's complex, Crabtree and co-workers have demonstrated that the H₂ unit does not always add in the plane of the strongest electron-withdrawing ligand,⁶ as might be expected based on the experimental and theoretical results for the cis-phosphine complexes. Determining what effects influence the direction of H₂ addition in the more complicated trans-phosphine complexes is the objective of this paper.

The results are organized into three general sections. The first describes the results obtained from our calculations of H₂ addition to Vaska's complex and highlights the importance of accurately modeling the phosphine ligands. The second section focuses on understanding the relative thermodynamic stabilities in six-coordinate products of H₂ addition to d⁸ square-planar iridium complexes with both cis and trans orientations of the phosphine ligands. Finally, we examine reaction pathways for the H₂ addition to various derivatives of Vaska's complex, including reactions in which the H₂ unit preferentially adds in the L-M-L plane which does not contain the strongest electron-withdrawing ligands. We conclude with a summary of the factors which control the direction of addition and the relative stabilities of the final products in H₂ addition reactions to d⁸ square-planar iridium complexes.

Methods

Reaction coordinates corresponding to the addition of H₂ in the two vertical ligand planes of the square-planar *trans*-IrX(CO)(PR₃)₂ complex were constructed from a series of full-gradient geometry optimizations⁷ on model 1 at the restricted Hartree-Fock-Roothaan (HFR) level of

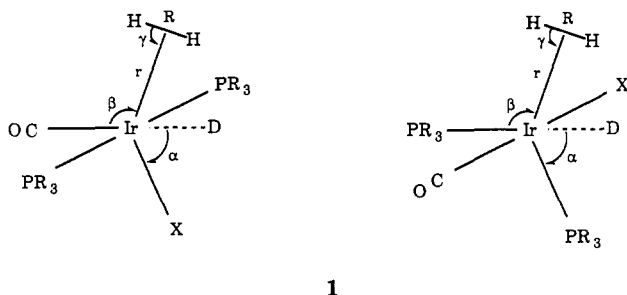


Figure 1. Reaction coordinate for the oxidative addition of H₂ to *trans*-IrCl(CO)(PH₃)₂. The point at $r = 4.0$ Å corresponds to the summation of the total energies from independent optimization calculations on H₂ and the square-planar metal complex.

approaches. All metal-ligand bond distances, as well as the H-H and C-O bond distances were allowed to vary. The distance from the metal atom to the centroid of the H₂ unit, r , was fixed at several values along the reaction coordinate while the other geometric variables were allowed to optimize. The two metal-phosphine bond distances were constrained to be equal only when H₂ adds in the X-Ir-CO plane, to retain C_s symmetry. The phosphine ligands were replaced by PH₃ or P(CH₃)₃ (i.e. PMe₃) groups. Unless otherwise noted, the geometries were not reoptimized in the calculations which employed the PMe₃ groups but rather utilized the optimized geometries from the calculations with the PH₃ groups.

The ECP2-type pseudopotential basis set of Hay and Wadt⁹ was employed for the iridium atom. In this basis, the outermost core electrons, the 5s and 5p, were treated explicitly along with the valence electrons. With the exception of the 5s function, all functions were split to form double- ζ contractions. All non-hydrogen ligand atoms utilized the split valence form of Huzinaga's fully contracted basis sets;¹⁰ Huzinaga's (33/3) basis sets for carbon, nitrogen and oxygen were split to (321/21), and the (333/33) sets for phosphorus and chlorine were split to (3321/321). The hydrogen basis set was the (21) contraction of an STO-3G representation.¹¹ Fully contracted basis sets for the C and H atoms of the Me groups were employed in the calculations of IrH₂X(CO)(PMe₃)₂.

Results and Discussion

H₂ Addition to Vaska's Complex. The theoretical reaction coordinate for the oxidative addition of H₂ to *trans*-IrCl(CO)(PH₃)₂ is shown in Figure 1. These results predict that, in contrast to the experimental results, the isomer formed from addition in the P-Ir-P plane would be observed at low temperatures. Since our previous study⁵ indicated that the differences in the correlation energy of these two paths could not explain the lack of agreement between the theory and the experiment, we reexamined certain points along the reaction coordinate with a more accurate model. PMe₃ groups were used instead of the PH₃ groups as a more accurate model of the PPh₃ ligands found in Vaska's complex. The results, shown in Figure 2, illustrate that when more realistic phosphine ligands were used, the energy of the pathway corresponding to addition in the P-Ir-P plane increased relative to that in the Cl-Ir-CO plane for intermediate to small values of r . The difference in energy between the final products increased from 0.87 kcal/mol to 11.89 kcal/mol (favoring the isomer formed from addition in the Cl-Ir-CO plane), while the relative stabilities near the transition states, at $r = 1.70$ Å, reversed (the calculations with PH₃ ligands favored addition in the P-Ir-P plane by 8.88 kcal/mol, while those with PMe₃ ligands favored addition in the

theory.⁸ In 1, D is a dummy atom used to define the movement of one ligand out of the plane of the square-planar complex as the H₂ unit

- (4) (a) Fisher, B. J.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 3216. (b) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (c) Johnson, C. E.; Eisenberg, R. *Ibid.* **1985**, *107*, 3148. (d) Johnson, C. E.; Eisenberg, R. *Ibid.* **1985**, *107*, 6531.
- (5) Sargent, A. L.; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.*, in press.
- (6) Burk, M. J.; McGrath, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034.
- (7) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.
- (8) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

- (9) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
- (10) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.
- (11) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

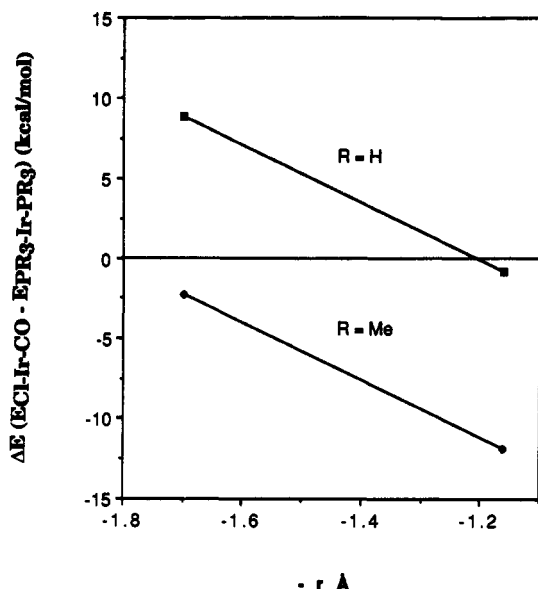


Figure 2. Energy difference of the isomers formed from the addition of H₂ to *trans*-IrCl(CO)(PR₃)₂ for R = H and R = Me at two points along the reaction coordinate: near the transition state ($r = 1.70$ Å) and for the final products. The energies are plotted in kcal/mol.

Cl-Ir-CO plane by 2.27 kcal/mol).¹² Unlike addition reactions to *cis*-phosphine complexes, the error, due to the misrepresentation of the phosphine ligands in addition reactions to *trans*-phosphine complexes, manifests itself unequally in the two reaction pathways. What electronic factors account for the difference in the behavior of these two phosphine groups?

The PH₃ ligands are weaker σ -donors and stronger π -acceptors than are the PMe₃ ligands. Our previous study on *cis*-phosphine complexes found that as the metal complex evolves from a four-coordinate to a six-coordinate species during the addition reaction, the ligands in the plane of addition move past regions of charge concentration around the metal center,⁵ as shown in Figure 3. Notice that, in the equatorial plane of the five-coordinate pseudo-trigonal-bipyramidal transition state, the metal-ligand bond axes are aligned along regions of charge concentration rather than along holes in the concentrations, as in the four-coordinate and six-coordinate species. A similar topology of the charge density has been noted in studies of Fe(CO)₅.¹³ Electron-withdrawing ligands in the plane of addition stabilize the five-coordinate transition state by delocalizing some of the charge from the metal center, thereby reducing the repulsive interaction between its own charge density and that concentrated around the metal center. The deformation density plots which appeared in our previous study⁵ illustrated this kind of electron delocalization. In our present calculations, addition in the PH₃-Ir-PH₃ plane is unrealistically stabilized by the weaker σ -donating and stronger π -accepting ability of the PH₃ groups. When the more realistic PMe₃ groups are employed, this relative stability is removed. Although the PMe₃ groups may still underestimate the σ -donor strength of the actual PPh₃ ligands, the poorer π -accepting ability of the former versus the latter may offset the additional stability due to the lack of σ -donor strength.

Apparently, as the H₂ unit adds in the Cl-Ir-CO plane, the repulsions between the concentrations of charge around the metal center and the combined charge concentrations on the Cl⁻ and CO ligands are less than those between the metal concentrations and the combined charge concentrations from the PMe₃ groups for addition in the P-Ir-P plane. Our previous study demonstrated the destabilizing and stabilizing effects that the Cl⁻ and CO

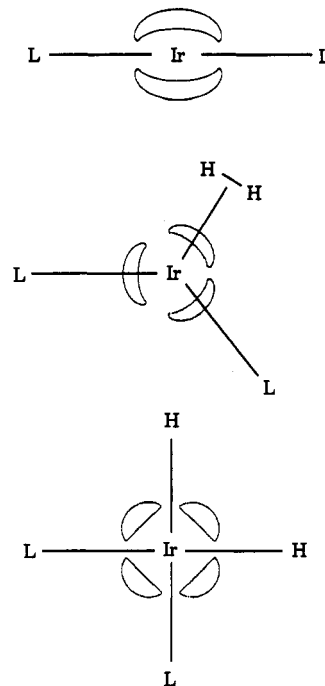
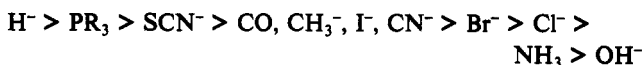


Figure 3. Schematic representation of the movement of the charge concentrations around the metal center in the plane of addition as the four-coordinate square-planar complex evolves to a six-coordinate species during the addition reaction. The schematic is modeled after plots of the Laplacian of the total charge density.⁵

ligands, respectively, have on a related five-coordinate transition state. Understanding the relative effects of different combinations of ligands in the plane of addition is a complicated task; the theoretical and experimental results for the oxidative addition of H₂ to Vaska's complex set the precedent that two strong σ -donor PMe₃ ligands in the plane of addition repel the concentrations of charge around the metal to a greater degree and thereby destabilize the five-coordinate transition state more than do the Cl⁻ and CO ligands.

These results underscore the importance of accurately modeling the phosphine ligands in reactions involving H₂ addition to complexes with *trans* phosphines. The calculations indicate that the π -accepting ability of PH₃, compared to that of PMe₃ or PPh₃, provides enough stability to the five-coordinate transition state that addition is favored in the PH₃-Ir-PH₃ plane. On the basis of these results, we predict that electronic factors would favor H₂ addition in the P(OR)₃-Ir-P(OR)₃ plane in *trans*-IrCl(CO)(P(OR)₃)₂.

Relative Thermodynamic Stabilities. Qualitatively, the relative thermodynamic stabilities of the isomeric products of H₂ addition to IrX(CO)(dppe) and IrX(CO)(PR₃)₂ can be predicted from the relative orientations of the strongest *trans*-influence ligands. The relative *trans*-influence strengths follow the order¹⁴

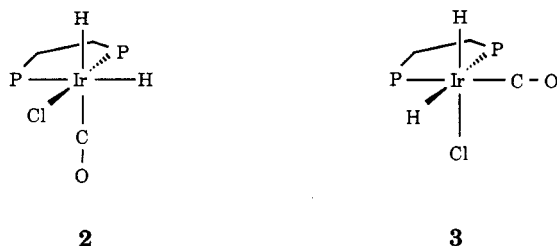


Strong *trans*-influence ligands form strong bonds with the metal atom at the expense of the *trans* metal-ligand bond.¹⁴ The geometric result of this weakened metal-ligand bond is a longer bond distance. Orientations in which strong *trans*-influence ligands are *trans* to each other are higher in energy than those in which they are mutually *cis*. For instance, in the two isomers formed from the oxidative addition of H₂ to IrCl(CO)(dppe), shown in 2 and 3, the two strongest *trans*-influence ligands are the hydrides, followed closely by the phosphines. In both isomers, one hydride is *trans* to a phosphine ligand. The other hydride is *trans* to CO

(12) While some of this difference may be due to the lack of geometric flexibility in the complexes with PMe₃ ligands, our experience suggests that this contribution is small.

(13) MacDougall, P. J. Ph.D. Thesis; McMaster University, Hamilton, Ontario, Canada, 1989.

(14) (a) Cotton, F. A.; Wilkinson, G. Reference 1, p 1299. (b) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishing Co.: Monterey CA, 1985; p 51.

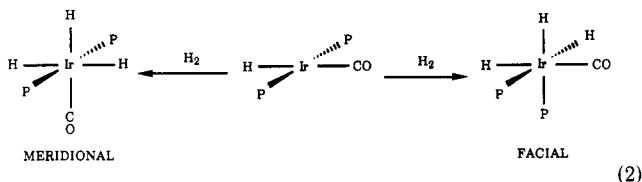


in **2** and Cl^- in **3**. CO is a stronger trans-influence ligand than Cl^- . The Ir–CO bond is a strong bond, due to the substantial synergistic σ -donating, π -back-bonding interactions. The energetic price that is paid for orienting this ligand trans to a hydride is high. In contrast, the Ir–Cl bond is relatively weak. Contributing to this weakness is the occupied metal–ligand antibonding interaction of π symmetry that exists for this π -donor ligand in the d^6 pseudooctahedral product. The energetic price that is paid for orienting this ligand trans to a hydride is relatively small. Thus, **2** is higher in energy than **3**. In other words, the orientation in which the two hydrides and the next strongest, unique ligand (the CO in this case) are facial is the lowest in energy.

The decreasing K_{eq} for $\text{X} = \text{Cl}^-$, Br^- , and I^- that is observed between the two final isomers in $\text{IrX}(\text{CO})(\text{dppe})_4$ is consistent with this view of the relative thermodynamic stabilities. I^- is a stronger trans-influence ligand than Cl^- .¹⁵ Orienting the former ligand trans to a hydride will be less stable than orienting the latter ligand trans to a hydride; the relative stability of the thermodynamic isomer over the kinetic isomer will therefore be less for $\text{X} = \text{I}^-$ than for $\text{X} = \text{Cl}^-$.

In H_2 addition to Vaska's complex, the product formed from addition in the Cl–Ir–CO plane is the most stable. This product has the two hydrides trans to Cl^- and CO, whereas the less stable isomer has them trans to the two phosphine ligands. The difference in the stability is understandable since the two phosphine ligands are stronger σ -donors (and, hence, stronger trans-influence ligands) than the Cl^- and CO ligands; the lowest energy orientation occurs with the three strongest trans-influence ligands, the two hydrides and a phosphine, are facial.

H_2 Addition to Derivatives of Vaska's Complex. The room-temperature oxidative addition of H_2 to the hydride derivative of Vaska's complex, *trans*- $\text{IrH}(\text{CO})(\text{PPh}_3)_2$, yields two products,¹⁶ as shown in eq 2. At equilibrium, the isomer in which the three



hydride ligands are mutually cis, the facial isomer, is more stable than the meridional isomer by only 0.2 kcal/mol. While purely electronic arguments might predict that the facial isomer would be significantly more stable than the meridional isomer, steric influences of the bulky phosphine groups may destabilize the facial isomer relative to the meridional isomer. The electronic factors, however, still appear to control the relative stabilities. In both isomers, a hydride is trans to the CO ligand; the principal difference between them is whether the remaining two hydrides are trans to each other or trans to the phosphine ligands. As expected, the latter orientation is more stable than the former. The change from $\text{X} = \text{Cl}^-$ to $\text{X} = \text{H}^-$ completely reverses the relative thermodynamic stabilities of the isomers. What about the relative stabilities of the transition states?

To our knowledge, no low-temperature experimental studies have been performed to determine whether the meridional isomer is formed preferentially over the facial isomer. Our theoretical efforts in this regard involved optimizing the geometries of the two isomers near their transition states (at $r = 1.7 \text{ \AA}$) and at equilibrium. When the phosphine ligands were represented by PH_3 groups, the energy differences were 9.7 and 8.9 kcal/mol for the transition states and equilibrium structures, respectively, favoring the facial isomer. These complexes were reoptimized with the more accurate PMe_3 groups, and, as expected, the relative stability of the facial isomer decreased with respect to the meridional isomer. However, the relative stability of the facial isomer decreased beyond the 0.2 kcal/mol difference observed experimentally at equilibrium, to the point where the meridional isomer was favored by 2.2 kcal/mol. Near the transition state, the meridional isomer was favored by 1.8 kcal/mol.

While several factors are potential contributors to the lack of agreement between theory and experiment for the equilibrium structures, such as the misrepresentation of the PPh_3 ligands by the PMe_3 groups, the lack of complete flexibility in the geometry optimizations, the basis set incompleteness, and the lack of electron correlation, all of the approaches to rectify them are prohibitively expensive. Instead, we adjusted the energies near the transition state by the amount necessary to bring the theory into agreement with the experiment for the equilibrium structures. Assuming the validity of this linear, empirical correction, the results suggest that the transition state leading to the facial isomer is lower than that leading to the meridional isomer by 0.6 kcal/mol.

These results are the opposite to what was found for H_2 addition to Vaska's complex. Changing $\text{X} = \text{Cl}^-$ to $\text{X} = \text{H}^-$ reverses the stereochemistry of addition and is testimony to the fact that the hydride ligand destabilizes the five-coordinate transition state to a greater extent than the chloride ligand, when present in the plane of addition. We attribute this to the closer relative proximity of the hydride ligand to the charge concentrations around the metal center. The presence of the hydride, a very strong σ -donor ligand, in the square-planar complex encourages addition of H_2 in the other, perpendicular, ligand plane.

The results presented so far indicate that the σ -donor strength of the X ligand in *trans*- $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ complexes plays an important role in both the stereochemistry of addition and the relative stabilities of the final products. When X is a strong σ -donor ligand such as H^- , addition is preferred in the P–Ir–P plane, whereas when X is a weak σ -donor such as Cl^- , addition is preferred in the X–Ir–CO plane. But what about when the σ -donor strength of X is intermediate between $\text{X} = \text{H}^-$ and $\text{X} = \text{Cl}^-$? Two such cases, where $\text{X} = \text{CH}_3^-$ (Me^-) and $\text{X} = \eta^1\text{-C}_6\text{H}_5^-$ (Ph^-), are investigated below.

Recent experimental work has demonstrated that at low temperatures, the addition of H_2 to *trans*- $\text{IrMe}(\text{CO})(\text{PMe}_3)_2$ proceeds in the P–Ir–P plane.^{6,17} Whether or not this isomer is also the most thermodynamically stable isomer has not yet been determined due to complications arising from a competing reaction pathway of reductive elimination of methane at temperatures as low as -40°C . Our calculations (based on optimizations of the *trans*- $\text{IrMe}(\text{CO})(\text{PH}_3)_2$ model, subsequently corrected for the presence of the PMe_3 groups) suggest that if this competing pathway was not present, the other isomer, formed from addition in the Me–Ir–CO plane, would be more stable. Decreasing the σ -donor strength of X from $\text{X} = \text{H}^-$ to $\text{X} = \text{Me}^-$ was sufficient to reverse the relative stabilities of the products, but not that of the transition states. More accurate calculations, with correlated wave functions and phosphine ligands which are allowed to distort (changing the cone angle and the P–C bond distances) and rotate about the P–Ir axis, are necessary to verify these findings prior to undertaking an analysis of the subtle differences exerted in the transition states and final products by $\text{X} = \text{H}^-$ and $\text{X} = \text{Me}^-$.

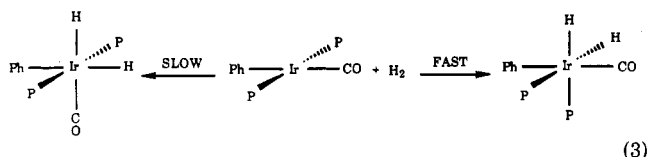
Another case in which the σ -donor strength of the X ligand is intermediate between H^- and Cl^- is $\text{X} = \text{Ph}^-$. Experimentally,

(15) While the I^- ligand is a stronger σ -donor than the Cl^- ligand, a secondary π effect is also expected to contribute to the decreased K_{eq} as X changes from Cl^- to I^- . The π -donor ability of the halides decreases rapidly from F^- down to I^- , since the overlap of the halide π orbitals with the metal falls off much more rapidly than the expansion of the valence electron clouds of the larger atoms.

(16) Harrod, J. F.; Yorke, W. J. *Inorg. Chem.* **1981**, *20*, 1156.

(17) Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727.

H₂ adds to *trans*-IrPh(CO)(PMe₃)₂ to yield distinct kinetic and thermodynamic products (eq 3).⁶ Addition in the PMe₃-Ir-PMe₃



plane is favored. Notice that, in contrast to the stereoselective H₂ addition to IrCl(CO)(dppe), the lowest energy pathway to addition does not involve addition in the Ir-CO plane. As the σ -donor strength of the X ligand decreases, we expect the relative barrier heights for the two pathways to addition to eventually resemble those in Vaska's complex, where addition in the X-Ir-CO plane is lower in energy. The σ -donor strength of Ph⁻ is certainly lower than that of H⁻ and is also lower than that for Me⁻; the sp²-hybridized carbon atom of Ph⁻ is a poorer σ -donor than is the sp³-hybridized carbon of CH₃⁻. Despite this difference, addition is preferred in the P-Ir-P plane. Although the σ -donor strength of the Ph⁻ group does not contribute as much to the destabilization of the transition state, a secondary interaction of π symmetry adds to this destabilization. The delocalized π -electron density above and below the phenyl ring repels the concentrations of charge around the metal center, as did the lone-pair electrons on the Cl⁻.

To what extent is the π -donor ability of the Ph⁻ group different from that of the Cl⁻ group? Previous studies which examined the singlet-triplet splitting in models¹⁸ of TiX₂(dmpe)₂ (X = Cl⁻ or CH₃⁻; dmpe = bis(1,2-dimethylphosphino)ethane)²¹ were extended to include X = Ph⁻. The singlet-triplet splitting for X = Cl⁻ was 8.2 kcal/mol,¹⁹ whereas for X = Ph⁻ the corresponding value was 17.4 kcal/mol. These energy splittings provide a direct means with which to compare the π -donor strengths of the two ligands. The greater π -donor strength of Ph⁻ relative to that of Cl⁻ is due to the combined effects of enhanced overlap, which results from the relatively short bond between the metal and the second-row Ph⁻ ligand versus the third-row Cl⁻ ligand, and the decreased electronegativity of the former versus the latter. That the Ph⁻ ligand is a strong π -donor, as well as a moderately strong σ -donor, accounts not only for the increased destabilization of the transition state when H₂ adds in the Ph-Ir-CO plane, but also for the relative stability of the isomer with the Ph⁻ group trans to a hydride. As with Cl⁻, the occupied Ir-Ph antibonding interaction of π symmetry will decrease the strength of this bond and allow for a lower energy interaction when a hydride ligand is in the trans position of the d⁶ final product. The steric influences of the Ph⁻ and the

bulky PPh₃ ligands have been addressed elsewhere and were not found to alter these conclusions.²²

Conclusion

The direction of addition in oxidative-addition reactions of H₂ to d⁸ square-planar transition-metal complexes is controlled by the interactions between the ligands in the plane of addition and the concentrations of charge around the metal center. As the square-planar complex evolves to a six-coordinate species during the course of the reaction, the ligands in the plane of addition move past regions of charge concentration on the metal atom which are due to the metal lone-pair electrons. Strong σ - and π -donor ligands destabilize the five-coordinate transition state by contributing to the repulsion between the electronic charge density of the ligands and that concentrated around the metal center. Electron-withdrawing ligands stabilize the five-coordinate transition state by delocalizing some of the charge density contributing to this repulsive interaction.

The electronic contribution to the relative stabilities of the six-coordinate d⁶ final products can be predicted based on the relative orientations of the strongest trans-influence ligands. The lowest energy configuration involves a facial orientation of these ligands. Additional stability in the final product is gained by orienting a strong trans-influence ligand trans to a strong π -donor ligand.

In the oxidative addition of H₂ to Vaska-type complexes, *trans*-IrX(CO)(PR₃)₂, the nature of the X ligand is crucial to determining the direction of addition. Weak electron donor ligands, such as Cl⁻, favor addition in the X-Ir-CO plane, whereas for stronger electron donor ligands, such as Ph⁻, Me⁻, and H⁻, addition is preferred in the P-Ir-P plane. For Ph⁻ and Me⁻ (if reductive elimination was not a competing pathway for the latter), the more stable isomer of the final products corresponds to the species formed from addition in the X-Ir-CO plane. This isomer gains stability by orienting a weaker σ -donor and/or stronger π -donor ligand trans to a hydride ligand. The weak σ -donor character strengthens the strong Ir-H σ bond to which it is trans, while the strong π -donor character, which results in an occupied antibonding interaction of π symmetry, is able to minimize the impact of the antibonding interaction by being trans to the strong trans-influence hydride ligand.

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Registry No. *trans*-IrCl(CO)(PH₃)₂, 58201-19-7; *trans*-IrCl(CO)-(PMe₃)₂, 21209-86-9; H₂, 1333-74-0.

Supplementary Material Available: Tables I and II, containing the optimized geometric parameters and total energies for the six values of r along the reaction coordinates shown in Figure 1 (2 pages). Ordering information is given on any current masthead page.

- (18) Open-shell RHF calculations on TiBe₄Cl₂ and TiBe₄Ph₂ (Ph = η^1 -C₆H₅) substituted Be ligands for the chelating phosphine groups.¹⁹ The metal basis set was the split-valence set of Williamson and Hall.²⁰ Chlorine, carbon, and hydrogen employed the basis set described above, while beryllium used the fully contracted (33/3) basis of Huzinaga.¹⁰ The geometry for TiBe₄Cl₂ was taken from a previous study.¹⁹ For the calculations involving TiBe₄Ph₂, the phenyl groups were oriented to bisect the smaller Be-Ti-Be angle, and the Ti-C bond distance was based on the known Ti-CH₃ distance in Ti(CH₃)₂(dmpe)₂²¹ but was adjusted to account for the change in hybridization (sp³ to sp²) at the carbon atom.
- (19) Simpson, C. Q.; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.* **1991**, *113*, 2898.
- (20) Williamson, R. L.; Hall, M. B. *Int. J. Quantum Chem.* **1987**, *21*, 503.
- (21) (a) Jensen, J. A.; Wilson, S. R.; Schultz, A. J.; Girolami, G. S. *J. Am. Chem. Soc.* **1987**, *109*, 8094. (b) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thorton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339.

- (22) Sargent, A. L.; Hall, M. B. *Topics in Physical Organometallic Chemistry*; Gielen, M., Ed.; Vol. 4, in press.