Minimum Energy Structure of Hydridotris(pyrazolyl)borato Iridium(V) Tetrahydride Is Not a C_{3v} Capped Octahedron

Charles Edwin Webster,[†] Daniel A. Singleton,*,[†] Michael J. Szymanski,[†] Michael B. Hall,*,[†] Cunyuan Zhao,[‡] Guochen Jia,*,[‡] and Zhenyang Lin*,[‡]

Contribution from the Department of Chemistry, Texas A&M University,
College Station, Texas 77843-3255, and the Department of Chemistry,
The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received April 10, 2000. Revised Manuscript Received May 18, 2001

Abstract: Recent synthesis and NMR spectroscopy of neutral Ir(V) complexes hydridotris(3,5-dimethylpyrazol-1-yl)borato tetrahydride (Tp*IrH$_4$) and hydridotris(pyrazol-1-yl)borato tetrahydride (TpIrH$_4$) have been interpreted as supporting face-capped octahedral structures (C_{3v}) with each of three Ir−H bonds trans to an Ir−N bond and the fourth hydride capping the IrH$_3$ face. Here, density functional geometry optimizations and coupled cluster calculations on hydridotris(pyrazol-1-yl)borato iridium tetrahydrogen find that a C_s edge-bridged octahedral tetrahydride structure and a C_1 η^2-dihydrogen, dihydride structure are local minima and find that the C_{3v} structure is a local maximum (second-order saddle point). Several low energy transition states connecting the local minima have been located, and these minima can be used to simulate the experimental NMR spectra. A comparison of the experimental infrared spectrum of Tp*IrH$_4$ and the harmonic frequency calculations on the C_s, C_1, and C_{3v} structures also supports the assignment of the C_s and C_1 structures as the observed ones.

Introduction

The determination of the structure of fluxional transition metal polyhydride complexes has been an intricate challenge. Neutron diffraction studies provide reliable structures when applicable, but most structural studies rely on spectroscopic observables, such as ^{1}H NMR chemical shifts, H−D coupling constants, NMR relaxation times, and infrared spectra; with such indirect probes of structure, multiple interpretations may arise. Quantum mechanical calculations have proven extremely valuable in structural and mechanistic studies of polyhydride complexes,[1] particularly when experimental methods have been less than adequate. However, the reliability of even the best of calculations may be uncertain, especially when the potential energy surface is complicated and there are several structures of similar energy. Theory and experiment must then work in concert to resolve these structures.

Recently, neutral Ir(V) complexes hydridotris(3,5-dimethylpyrazol-1-yl)borato tetrahydride (Tp*IrH$_4$) and hydridotris(pyrazol-1-yl)borato tetrahydride (TpIrH$_4$) were proposed to be face-capped octahedral structures (C_{3v}) with each of three Ir−H bonds trans to an Ir−N bond and the fourth hydride capping the IrH$_3$ face.[2] This proposal was based on ^{1}H and ^{2}H NMR observations for the relevant Ir tetrahydrogen and deuterium substituted (H$_{4-n}$D$_n$; $n = 1-4$) species, on the IR spectrum of Tp*IrH$_4$, and on the structure of the analogous triethylsilyl trihydride complex, where the triethylsilyl group caps the trihydride octahedral face. In the ^{1}H NMR of Tp*IrH$_4$, the four "hydrides" remain equivalent on the NMR time scale down to −70 °C. However, the hydride peak is shifted substantially in partially deuterated complexes. This "isotopic perturbation of resonance" (IPR)[3] effect is indicative of a structure in which there are at least two inequivalent hydride positions.[2] This contrasts with the analogous Cp*IrH$_4$ complex,[4] for which theoretical[5] studies of CpIrH$_4$ support a pseudo-C_{4v} "piano stool" geometry.[6] The rhodium analogue, Tp*RhH$_4$, has a C_1 η^2-dihydrogen, dihydride equilibrium geometry,[7] but the observation of a relatively long T_1(min) in Tp*IrH$_4$ weighs against an analogous structure.

In this paper, a theoretical study of the TpIrH$_4$ system is described. The potential energy surface for TpIrH$_4$ is predicted to involve several low-energy structures, including two compet-

---

[†] Texas A&M University.

[‡] The Hong Kong University of Science and Technology.

(1) (a) Lin, Z. Y.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135*, 845−879. (b) Bayse, C. A.; Couty, M.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 8916−8919. (c) Abugideiri, F.; Fettinger, J. C.; Pleune, B.; Poli, R.; Bayse, C. A.; Hall, M. B. *Organometallics* **1997**, *16*, 1179−1185. (d) Bayse, C. A.; Hall, M. B. *Inorg. Chim. Acta* **1997**, *259*, 179−184. (e) Bayse, C. A.; Hall, M. B.; Pleune, B.; Poli, R. *Organometallics* **1998**, *17*, 4309−4315. (f) Bayse, C. A.; Hall, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 1348−1358. (g) Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601−636.

(2) (a) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Taboada, S.; Trujillo, M.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 346−354. (b) Paneque, M.; Poveda, M. L.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519−4520.

(3) (a) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071−8072. (b) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072−8073. Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726−7727. (c) *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Crabtree, R. H., Ed.; John Wiley and Sons: New York, 1994; pp 256−258. For more recent examples see ref 12 and the following: (d) Perrin, C. L.; Kim, Y. J. *J. Phys. Org. Chem.* **2000**, *13*, 752−756. (e) Heinekey, D. M.; van Roon, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134-12140. (f) Kuhlman, R.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 6934−6945.

(4) Gilbert, T. M.; Bergman, R. G. *Organometallics* **1983**, *2*, 1458−1460.

(5) Lin, Z. Y.; Hall, M. B. *Organometallics* **1992**, *11*, 3801−3804.

(6) A theoretical study of the analogous CpRhH$_4$ also found a piano-stool tetrahydride structure to be lowest in energy. See: Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *Organometallics* **1997**, *16*, 3805−3814.

(7) Clot, E.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 8855−8863. Eckert, J.; Albinati, A.; Bucher, U. E.; Venanzi, L. M. *Inorg. Chem.* **1996**, *35*, 1292−1294.

10.1021/ja001233t CCC: $20.00

ing minima. These predictions are tested against the experimental NMR observations in a novel manner, by using the theoretical calculations to predict the equilibrium isotope effects involved in the IPR phenomenon. The comparison of NMR and IR predictions with experiment supports the calculational results and their revised view of the structure of these complexes.

Results and Discussion

Calculated Structures and Energies. The calculations described here find two minima for $TpIrH_4$ (Figure 1). The first is a C_s edge-bridged octahedron (C_s MIN) with the fourth hydrogen on an $Ir(H)_2$ edge in a pseudoplane with the two other hydrides and two nitrogens of the Tp ligand (a distorted pentagonal bipyramid). The second is a C_1 η^2-dihydrogen, dihydride structure (C_1 MIN) with a canted H_2 ligand (see Figure 1). The path for exchange of the inequivalent hydrides of the C_s structure involves the central, edge-bridged hydride simultaneously shifting with one of its two equatorial neighbors to form the C_1 MIN η^2-dihydrogen, dihydride structure through a C_1 transition state (C_1 TS). Two equivalent C_1 MIN structures are connected by two low energy transition states, each C_s symmetric, η^2-dihydrogen, dihydride structures. The first structure (C_s TSE) has the η^2-dihydrogen parallel to the plane created by the three N atoms of the Tp ligand bound the metal center, and the second structure (C_s TSR) has the η^2-dihydrogen perpendicular to the plane of the N atoms. Note that both C_s TSE and C_s TSR connect two equivalent C_1 η^2-dihydrogen, dihydride local minima, while C_1 TS connects a C_s MIN tetrahydride local minimum with a C_1 MIN local minimum (see Figure 1). Rotation of the η^2-dihydrogen through either C_s TSE or C_s TSR exchanges the relative position of the two hydrogens in C_1 MIN. The C_1 MIN structure could then reform C_s MIN, again through C_1 TS. This path thereby exchanges two hydride positions of C_s MIN; that is, one of the equatorial hydrogens becomes the edge-bridged hydride and vice versa. The C_{3v} tetrahydride Ir(V) structure (with the fourth hydride capping the IrH_3 face) is a second-order saddle point (SOSP) characterized by two imaginary frequencies (see Figure 1). The C_s MIN structure can be reached by one of the downhill directions from the C_{3v} SOSP, while the other leads to the C_s TSR structure.

The relative energies of the key species are collected in Table 1. B3LYP favors C_s MIN (a tetrahydride) over C_1 MIN (a η^2-dihydrogen, dihydride) by only 0.30 kcal mol^{-1} without zero point energies (ZPEs). On the other hand, at the B3LYP level with ZPE, the C_s MIN and the C_1 MIN structures are equivalent in energy, while, at the CCSD (with geometries and ZPE from B3LYP) level, the C_s MIN structure is favored by 0.64 kcal mol^{-1}. All methods that include electron correlation find that the C_s TSE structure is slightly less stable than C_s MIN without ZPE and remains close in energy to C_1 MIN with ZPE. Similarly, without ZPE, the C_1 TS structure is above C_s MIN and is at approximately the same energy as C_1 MIN, but it appears to be lower in energy than both minima with ZPE, because the harmonic approximation overestimates the ZPE for the local minima (see Theoretical Details). The B3LYP//B3LYP energies (relative to C_s MIN) of the two transition states that connect mirror image C_1 MIN structures are 0.30 kcal mol^{-1} for C_s TSE and 2.00 kcal mol^{-1} for C_s TSR; the less stable TSR has more dihydrogen character. Inclusion of ZPE for these transition states lowers their relative differences to 0.0 and 1.24 kcal mol^{-1}, for C_s TSE and C_s TSR, respectively, compared to C_s MIN. The CCSD//B3LYP single point energy of the C_s TSE with ZPE from B3LYP is 0.65 kcal mol^{-1} above the C_s MIN energy. For the previously proposed C_{3v} tetrahydride structure, all methods clearly show that this structure is highest in energy, at least 2.4 kcal mol^{-1} above C_s MIN by all methods. Both B3LYP and BP86 frequencies authenticate the C_{3v} structure as a second-order saddle point (SOSP), that is, a local maximum of the potential energy surface (PES).

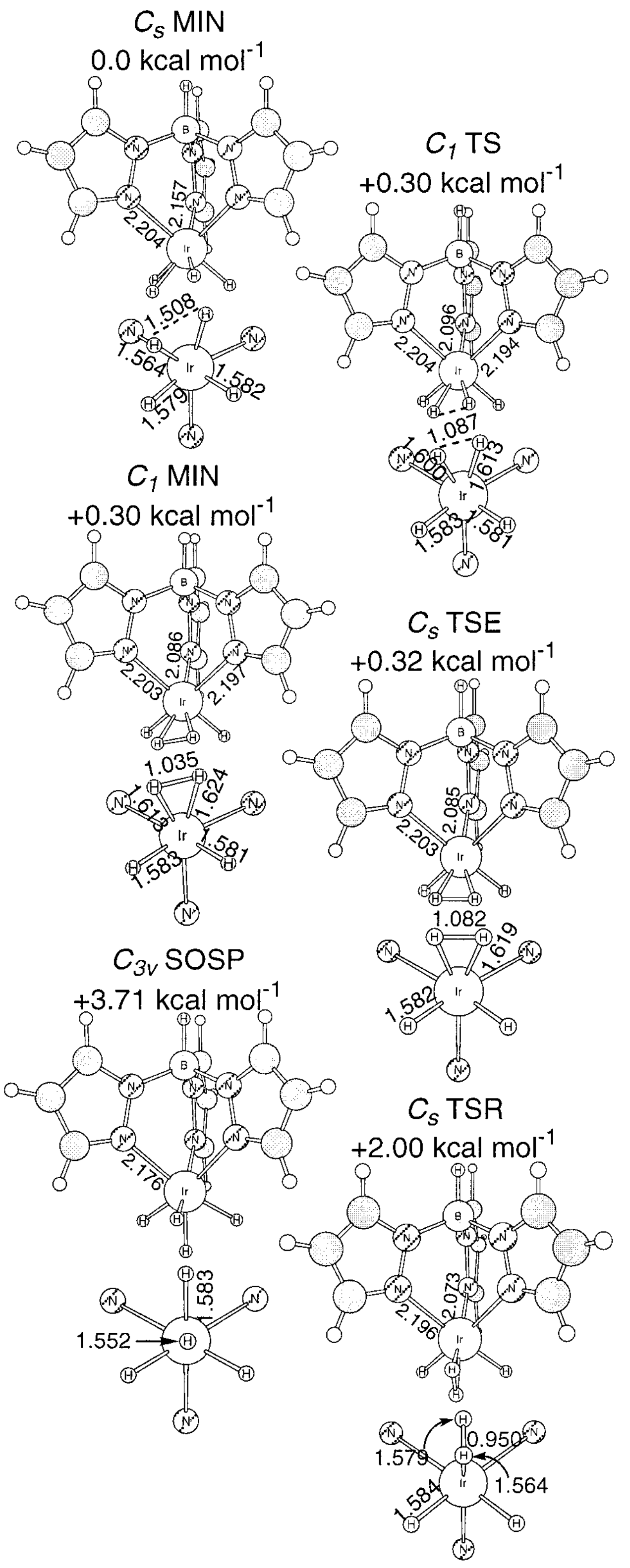

Figure 1. B3LYP calculated structures and non-ZPE relative energies of the tris(pyrazol-1-yl)borate iridium complexes. Below each structure is the view down the Ir−B axis with the pyrazolylborate framework removed for clarity.

Table 1. Comparison of Relative Energies[a]

	C_s MIN[b]	C_1 MIN[c]	C_s TSE[d]	C_{3v} SOSP[e]
B3LYP//B3LYP (ΔE)[f]	0.0	+0.30	+0.32	+3.71
MP2//MP2 (ΔE)[g]	0.0		+0.67	+3.53
BP86//BP86 (ΔE)[h]	0.0		+0.71	+3.33
HF//B3LYP (ΔE)	0.0	−3.95	−4.08	+4.76
MP2//B3LYP (ΔE)	0.0	+3.76	+3.90	+3.90
MP3//B3LYP (ΔE)	0.0	+0.58	+0.59	+4.77
MP4D//B3LYP (ΔE)	0.0	+2.24	+2.31	+4.22
MP4DQ//B3LYP (ΔE)	0.0	+2.09	+2.16	+4.12
MP4SDQ//B3LYP (ΔE)	0.0	+1.63	+1.69	+4.11
CCSD//B3LYP (ΔE_o)	0.0	+0.64	+0.65	+3.45
B3LYP//B3LYP (ΔE_o)[f]	0.0	+0.01	+0.00	+2.78
MP2//MP2 (ΔE_o)[g]	0.0		+0.35	+2.60
BP86//BP86 (ΔE_o)[h]	0.0		+0.46	+2.37

[a] Values are in kcal mol^{-1}. The relative energies without zero-point energy (ZPE) are ΔE, and those with ZPE are ΔE_o. ΔE_o values for CCSD and MP2 use ZPE from B3LYP frequency calculations; ΔE_o values for BP86//BP86 have ZPE from BP86 frequency calculations. Similarly, B3LYP//B3LYP have ZPE from B3LYP frequency calculations. [b] Local minimum: an edge-bridged octahedral (distorted pentagonal bipyrimid), tetrahydride structure. [c] Second local minimum: a C_1, η^2-dihydrogen, dihydride structure. [d] Transition state for hydrogen exchange: a C_s, η^2-dihydrogen, dihydride structure. [e] Second-order saddle point: a C_{3v}, tetrahydride structure. [f] At B3LYP//B3LYP: for the C_1 TS structure, ΔE is 0.30 kcal mol^{-1} and ΔE_o is −0.50 kcal mol^{-1} (a value which reflects an error in the harmonic approximation for calculating the zero-point energy); for the C_s TSR structure, ΔE is 2.00 kcal mol^{-1} and ΔE_o is 1.24 kcal mol^{-1}. [g] At MP2//MP2: the H−H distance in C_s TSE is 1.375 Å. Using BP86 ZPE results in 0.42 and 2.56 kcal mol^{-1} for C_s TSE and C_{3v} SOSP, respectively. [h] At BP86//BP86: for the C_s TSR structure, ΔE is 2.84 kcal mol^{-1} and ΔE_o is 2.18 kcal mol^{-1}. At BP86//BP86, the H−H distance is 1.296 Å in C_s TSE and 1.123 Å in C_s TSR.

The BP86 PES contains the C_s MIN, C_s TSE, C_s TSR, and C_{3v} SOSP structures, but not structures analogous to either the C_1 MIN or the C_1 TS as found on the B3LYP surface. The fact that a C_1 η^2-dihydrogen, dihydride was not found on the BP86 PES is not an issue of the quality of the basis set on the ligated hydrogens. Separate geometry optimizations in an improved basis set (BS2) still did not find a C_1 structure. The BP86 optimized structures are qualitatively similar to the B3LYP structures, but in C_s TSE (0.5 kcal mol^{-1} above C_s MIN) and C_s TSR (2.2 kcal mol^{-1} above C_s MIN), the bond distances between the hydrogens of the η^2-dihydrogen are longer than those found with B3LYP, owing to the slight preference of BP86 for a higher oxidation state. Furthermore, in agreement with experiment for the analogous Tp*RhH$_4$ system,[7] BP86 does find a C_1 MIN structure that is of a dihydrogen, dihydride nature.[8] The C_1 MIN was not examined on the MP2 PES, because the C_s TSE structure found on the MP2 surface is formally an Ir^V tetrahydride. Even more than BP86, MP2 favors the higher oxidation state, and for this Ir system, the dihydrogen species do not exist on the MP2 PES. Again, this phenomenon is not an issue of the basis set quality on the metal and/or ligated hydrogens. Separate geometry optimizations in a larger basis set (BS3) at the MP2 level consistently found oxidative addition tetrahydride structures to the exclusion of dihydrogen ones.

Steric effects of methyl substitution on the Tp* ligand were examined by performing B3LYP optimizations on the 5-methylated Tp tetrahydrogen complex. The results (which are not presented) were closely analogous to those on the Tp complex: the C_{3v} structure is a SOSP, and the minima are the same C_s and C_1 structures.

Although the experimental observations appeared consistent with the C_{3v} structure, the calculational results consistently disfavor this structure and favor two low energy structures, one of which is a dihydrogen complex. The calculations would suggest that the experiment can be interpreted on the basis of a series of triple-welled potentials with the most stable C_s MIN structure coupled to chiral C_1 MIN structures on either side. In the next section, the experimental NMR and IR spectra are examined in detail using calculated structures and vibrational frequencies to reinterpret the experimental observations. The relative energies and the calculated vibrational frequencies of the structures are used to produce simulated ^{1}H and ^{2}H NMR spectra, which are compared to the experimental spectra. The calculated vibrational frequencies of the C_s MIN, C_1 MIN, and C_{3v} SOSP are compared to the reported vibrational frequencies.

NMR Spectra. The key NMR observations for Tp*IrH$_4$ follow. (1) There are large downfield shifts in the ^{1}H signal for the hydride ligands in partially deuterated complexes (Figure 4c), proposed to result from an "isotopic perturbation of resonance" (IPR) effect. The chemical shift difference between complexes was strongly temperature-dependent and decreased with increasing deuteration. (2) There is a significant upfield shift, by ~0.4 ppm, of the ^{2}H resonance for the d_4 complex compared to the ^{1}H resonance of the d_0 complex. This is much larger than expected from an *intrinsic* isotope effect on the chemical shift, and the ^{2}H spectrum of a mixture of partially deuterated complexes exhibits a pattern of separate peaks similar to the ^{1}H spectrum. (3) There are apparent H−D coupling constants of 2.5−3.3 Hz, increasing with increasing deuteration. (4) There is a T_1(min) of ~400 ms. The current goal is to explore whether the calculational prediction of low-energy C_s MIN and C_1 MIN can specifically account for these observations. The approach is to first calculate isomer and isotopic equilibria for the C_s/C_1 equilibrium. The calculated equilibria are then used to simulate NMR spectra for comparison with the experimental spectra, varying freely the chemical shifts of the protons involved.[9] Finally, it is examined whether any single structure (C_s MIN, C_1 MIN, or C_{3v} SOSP) can by itself account for the NMR findings.

The IPR effects in NMR result from nonunity equilibrium isotope effects affecting isotopomer populations in the partially deuterated complexes. The critical starting point in the analysis here is the calculation of these isotope effects. Recent work has shown that heavy atom and secondary ^{2}H *kinetic* isotope effects can usually be predicted quite accurately from DFT or ab initio calculations, provided that the calculated transition structures are themselves accurate.[10] *Equilibrium* isotope effects, which are not complicated by tunneling or the limitations of transition state theory, should be more accurately calculable. However, the intrinsically high flexibility of metal polyhydride M−H bending vibrations and the anharmonicity of H−H stretching in metal dihydrogen complexes[11] made the accuracy of isotope

---

(8) Webster, C. E.; Hall, M. B. Unpublished results.

(9) An attempt was made to calculate the ^{1}H NMR chemical shifts of these various complexes using the Gauge-Independent Atomic Orbital method (Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807.), but reasonable chemical shifts were not obtained. Even the calculated chemical shifts for model complex TpIrH$_2$H(PH$_3$)$^+$, which is known to be a dihydrogen hydride, did not compare well with the experimental observations in reference 12 for TpIrH$_3$(PR$_3$)BF$_4$; the calculated chemical shifts were actually in the reverse order of the experiment.

(10) (a) Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 3385−3386. (b) DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907−9908. (c) Keating, A. E.; Merrigan, S. R.; Singleton, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 3933−3938. (d) Meyer, M. P.; DelMonte, A. J.; Singleton, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 10865-10874. (e) Singleton, D. A.; Hang, C. *J. Am. Chem. Soc.* **1999**, *121*, 11885-11893. (f) Beno, B. R.; Houk, K. N.; Singleton, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 9984−9985.

(11) Law, J. K.; Mellows, H.; Heinekey, D. M. *J. Am. Chem. Soc.* **2001**, *123*, 2085−2086.

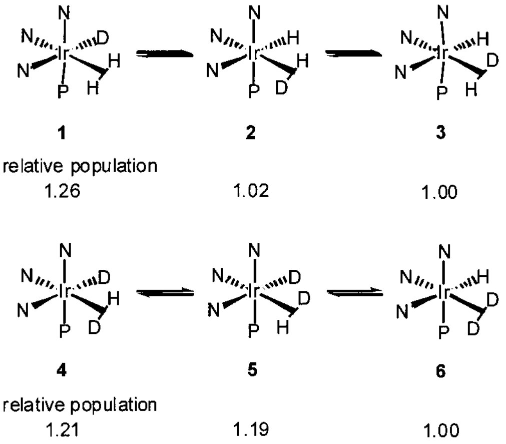

Figure 2. Representation of the possible isotopomers for $TpIrH_2D(PH_3)^+$ and $TpIrHD_2(PH_3)^+$ and their calculated relative populations at 240 K.

effects calculated from harmonic frequencies uncertain. Therefore, to test the prediction of isotope effects in such systems, the simpler and more-understood $TpIrH_3(PR_3)^+$ complexes[12] were studied.

As Poveda et al. found for Tp^*IrH_4, Heinekey and co-workers found that $TpIrH_3(PR_3)BF_4$ complexes (R = Me or Ph) exhibit temperature-dependent downfield shifts in the ^1H signal for the hydride ligands in partially deuterated complexes.[12] A variety of observations pointed to a dihydrogen/hydride ground-state structure, and the ^1H spectrum for $TpIrH_{3-n}D_n(PR_3)BF_4$ was consistent with an IPR effect. From the observed shifts and coupling constants, it was possible to determine approximately the component chemical shifts for the dihydrogen and hydride positions. Deuterium was found to favor occupying the hydride over a dihydrogen position.

In an effort to calibrate our calculations with experimental observations, the structure of simplified model complex $TpIrH_3(PH_3)^+$ (where trimethylphosphine has been replaced with simple phosphine) has been calculated. The isotopic substitutions predicted from the calculated frequencies were compared to the observed experimental preference, and the simulated NMR spectra derived from the calculations were compared to the experimental spectra. In keeping with Heinekey's observations, the minimum energy structure calculated for the model complex is an η^2-dihydrogen, hydride structure [$TpIrH_2H(PH_3)^+$]. For a mixture of partially deuterated complexes, the three isotopomers **1**, **2**, and **3** will contribute to the time-averaged signal for the d_1 complex and the isotopomers **4**, **5**, and **6** will contribute to the signal for the d_2 complex (Figure 2). The equilibrium isotope effects determining the relative populations of these isotopomers were calculated by the method of Bigeleisen and Mayer[13] from the scaled theoretical harmonic vibrational frequencies[14] calculated for the $TpIrH_2H(PH_3)^+$ structure. The results, as shown in Figure 2, accurately predict the preference for deuterium to occupy the classical hydride position. The average energetic preferences for $TpIr(H_2)D(PH_3)^+$ over $TpIr(HD)H(PH_3)^+$ and $TpIr(HD)D(PH_3)^+$ over $TpIr(D_2)H(PH_3)^+$ are 107 and 86 cal mol^{-1}, respectively. These calculated values are within experimental error of the values found at 240 K for $TpIrH_{3-n}D_n(PMe_3)BF_4$.[12] Using the calculated isotope effects, a simulation of the ^1H NMR spectrum of $TpIrH_{3-n}D_n(PMe_3)BF_4$ had optimized component chemical shifts of −7.88 and −15.36 for the dihydrogen and hydride positions, respectively, and a dihydrogen H−D coupling constant of 24.6 Hz. These values are very close to those determined by Heinekey.[12] The resulting spectrum reproduces the reported chemical shifts for $TpIrH_{3-n}D_n(PMe_3)BF_4$ within 0.002 ppm and the H−D coupling constants in $TpIrH_2D(PMe_3)BF_4$ and $TpIrHD_2(PMe_3)BF_4$ within 0.1 Hz. Overall, these results support the accuracy of isotope effect calculations for metal polyhydrides.[15]

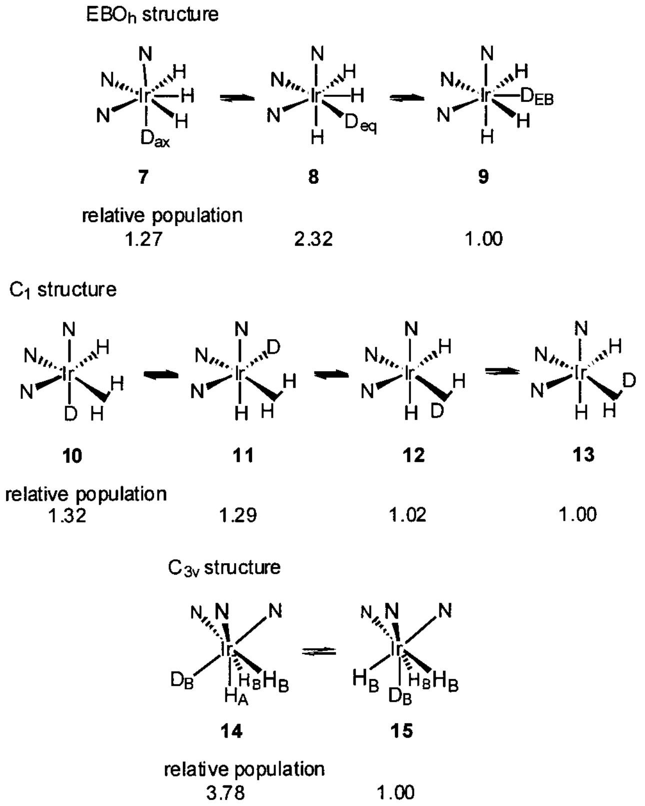

Figure 3. Representation of the possible isomers and isotopomers for $TpIrH_3D$ and their calculated relative populations at 25 °C.

Turning to the $TpIrH_4$ and Tp^*IrH_4 systems, there are many more structures to consider (for example, six isotopomers for the d_2 C_1 complex alone). Figure 3 shows the calculated relative isotopomer populations for the d_1 C_s MIN, C_1 MIN, and C_{3v} SOSP complexes after allowing for symmetry numbers. (A complete set of the relevant calculated isotope effects is given in the Supporting Information.) Deuterium favors being in isolated positions for which the Ir−H bending vibrations are strong, for example, the axial position of the C_s MIN structure (cf., **7** versus **9**). Deuterium also prefers classical hydride positions to dihydrogen. Thus, **10** and **11** are favored over **12** and **13**. The d_4 complex, compared to the d_0 complex, would favor the all-classical C_s MIN structure relative to the C_1 MIN structure by a factor of 1.11. As anticipated by Poveda and co-workers,[2] deuterium would favor the three "B" sites over the lone apical site in the C_{3v} structure by a predicted factor of 1.26 per site.[16]

Allowing for the CCSD energy difference of 0.64 kcal mol^{-1} and an entropy of mixing for the chiral C_1 MIN complex, the

---

[12] (a) Oldham, W. J., Jr.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028-11036. (b) Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137−3138.

[13] (a) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261−267. (b) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225−233.

[14] The calculations used the program QUIVER (Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989−8994.) with B3LYP frequencies scaled by 0.9614 (Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.).

[15] High-energy vibrational frequencies contribute much more to isotope effects than low-energy modes do. This likely aids the accuracy of the isotope effect calculations, because the low-energy modes are most affected by anharmonicity and are most difficult to calculate accurately.

ratio of C_s MIN and C_1 MIN complexes at 25 °C would be 1.47:1. From this number and the isotope effects, the relative amounts of each isotopomer in an equilibrium of C_s MIN and C_1 MIN complexes were calculated. A predicted NMR spectrum then requires only some assumptions of coupling constants and chemical shifts for the individual hydride positions in the complexes. From the formula $r_{HH} = 1.44 - 0.0168(J_{HD})$,[17] the J_{HD} for the dihydrogen positions ($r = 1.035$ Å) in the C_1 MIN complex would be 24.1 Hz. All other couplings are expected to be small. If all of these couplings are set at 1.5 Hz, the predicted average H−D coupling constants for d_1-, d_2-, and d_3-TpIrH$_4$ would be 2.8, 3.0, and 3.1 Hz, respectively, exactly matching the couplings from one of the experimental spectra.[2]

The component chemical shifts for the hydride positions in the complexes are more difficult to ascertain. Chemical shifts in similar complexes vary over a wide range (from −0 to −45 ppm[18]), with a clear tendency for dihydrogen to favor the downfield end of this range. If all of the classical hydride positions are assigned chemical shifts of δ_{ppm} −18, and a shift of δ_{ppm} −4 is assigned to the dihydrogen positions of the C_1 MIN structure, the spectrum of Figure 4a results for a mixture of partially deuterated complexes. In this spectrum, there is a downfield shift of the hydride peaks with partial deuteration, with the shift difference decreasing with increasing deuteration. The ^{2}H resonance for the d_4 complex would be shifted upfield by 0.17 ppm relative to the ^{1}H resonance of the d_0 complex. In short, all of the qualitative features of the experimental spectrum are reproduced. This is, in fact, true of *any* model that (1) uses the calculated isotope effects, (2) involves significant amounts of both C_s MIN and C_1 MIN complexes, (3) places the contributing shift of the dihydrogen ligand downfield from the classical hydrides, and (4) involves a large dihydrogen coupling constant with all other couplings small.

By adjusting the chemical shifts for the individual hydride positions, the experimental ^{1}H NMR spectrum may be quantitatively reproduced easily. In fact, diverse sets of assumptions lead to equivalent spectra,[19] the result of having seven parameters (the component chemical shifts) to model the shift of only four peaks. However, it is much more difficult to simultaneously account for the four peaks of the ^{2}H spectrum. The upfield shift of 0.4 ppm of the ^{2}H resonance for the d_4 complex compared to the ^{1}H resonance of the d_0 complex may result from either an intrinsic isotope effect[20] or the presence of two structures with an equilibrium affected by the isotopic substitution (or a combination of the two). Intrinsic deuterium isotope effects in

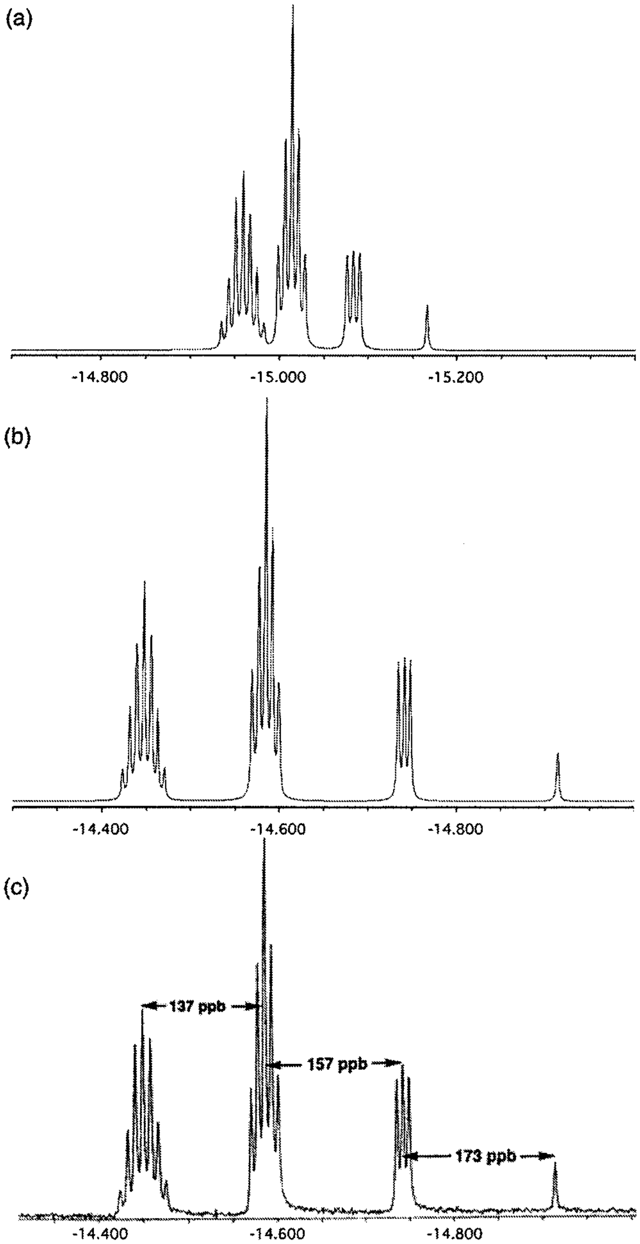

Figure 4. (a) Simulated ^{1}H NMR spectrum for a mixture of partially deuterated isomers of TpIrH$_4$, based on the calculated isotope effects, the calculated energy difference between C_s MIN and C_1 MIN complexes, assumed shifts of δ_{ppm} −18 for all classical hydride positions and δ_{ppm} −4 for dihydrogen positions, and assumed H−D dihydrogen coupling of 24.1 and 1.5 Hz couplings in all other positions. Lorentzian peaks with half-widths of 0.5 Hz are assumed. (b) Simulated spectrum as in (a), using shifts of −10.00, −18.13, −18.13, and −30.83 for the edge-bridged, equatorial, and axial positions of C_s MIN complex and shifts of −16.96, −16.76, −0.10, and −0.20 for the two classical hydride and two dihydrogen positions of the C_1 MIN structure, respectively, and an intrinsic isotope effect on the shift of −37.5 ppb per deuterium. (c) Experimental spectrum (see ref 2).

---

(16) Because this prediction is based on a second-order saddle point, it does not take into account two frequencies that would be present if indeed the C_{3v} structure were a ground state. However, the imaginary frequencies in the calculated C_{3v} structure would likely translate into low-energy modes in a "ground-state" C_{3v} structure. Because low-energy frequencies contribute relatively little to isotope effects, a "ground-state" C_{3v} structure would likely exhibit a qualitatively similar isotope effect.

(17) Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127−132.

(18) For example NMR spectra of iridium hydrides, see: Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017−11018. Wiley, J. S.; Oldham, W. J., Jr.; Heinekey, D. M. *Organometallics* **2000**, *19*, 1670−1676. McLoughlin, M. A.; Keder, N. L.; Harrison, W. T. A.; Flesher, R. J.; Mayer, H. A.; Kaska, W. C. *Inorg. Chem.* **1999**, *38*, 3223−3227. Sjövall, S.; Johansson, M.; Andersson, C. *Organometallics* **1999**, *18*, 2198−2205. Cooper, A. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **1998**, 307−309. Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974−1978. Lindner, E.; Gierling, K.; Keppeler, B.; Mayer, H. A. *Organometallics* **1997**, *16*, 3531−3535. Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353−5361. Park, S.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 3001−3006.

(19) For example, shifts of −15.80, −11.83, −11.83, and −26.18 ppm for the edge-bridged, equatorial, and axial positions of the C_s MIN complex, along with shifts of −21.42, −20.30, −4.00, and −5.13 ppm for the two classical hydride and two dihydrogen positions of the C_1 MIN structure, respectively, reproduce within 1 ppb the experimental ^{1}H shifts. However, so do shifts of −15.83, −12.54, −12.54, −20.55, −24.50, −22.03, −4.00, and −6.47 for the same positions, respectively.

(20) We use "intrinsic isotope effect" to refer to any change in chemical shifts on isotopic substitution due to the changes in average nuclear positions (such as bond lengths) within a single structure (i.e., near a single minimum on the potential energy surface). Isotopic substitution may have an intrinsic effect on the chemical shift of both the position being substituted and other positions in the molecule. In our modeling, we arbitrarily assume that all such effects are similar.

similar complexes have ranged from 0 to 76 ppb per deuterium,[21] making it unlikely that an intrinsic effect alone accounts for the 0.4 ppm d_0/d_4 shift. However, modeling the spectra well without any intrinsic isotope effect on the shift requires a chemical shift of −38.85 for the axial position of the C_s MIN structure and +0.34 and +1.49 for the dihydrogen positions of the C_1 MIN structure. Assumption of some intrinsic shift allows more moderate component chemical shifts to simulate the spectrum. For example, with an intrinsic shift of −37.5 ppb per deuterium, optimized shifts of δ_{ppm} −10.00, −18.13, −18.13, and −30.83 for the edge-bridged, equatorial, and axial positions of C_s MIN complex and shifts of δ_{ppm} −16.96, −16.76, −0.10, and −0.20 for the two classical hydride and two dihydrogen positions of the C_1 MIN structure, respectively, were obtained. From these shifts, the simulated ^{1}H NMR (Figure 4b) reproduces within 1 ppb the experimental ^{1}H shifts and the simulated ^{2}H spectrum reproduces within 0.02 ppm the ^{2}H shifts. These best-fit component shifts should not be taken too seriously, as they would vary with varying assumptions (an error in the calculated C_s/C_1 equilibrium or the calculated isotope effects, or an error in the experimental d_0/d_4 shift difference). We are also modeling eight chemical shifts with eight adjustable parameters (the seven component shifts and the intrinsic shift).[22] Overall, however, it is clear that the IPR effects in the ^{1}H and ^{2}H spectra are consistent with a C_s/C_1 equilibrium.

Because dihydrogen complexes typically exhibit short T_1(min) values, the relatively long T_1(min) of ~400 ms at 212 K and 500 MHz for Tp*IrH$_4$ appears to limit the contribution of the C_1 MIN structure to a C_s/C_1 equilibrium. However, this limitation is not severe, as the rate of decay would be a weighted average of the decay rates for the various positions within the two complexes.[23] For a calculated C_s/C_1 equilibrium constant of 1.8 at 212 K (favoring C_s MIN), a given hydrogen would spend only 15% of its time in a dihydrogen position. Assuming fast internal "rotation" of the H$_2$ ligand,[24] an H−H distance of 1.035 Å corresponds to a rate of 15.8 s^{-1}.[25] If the rate constant for decay in a dihydrogen position were 16 s^{-1} (well within the observed range for dihydrogen complexes[23,26]) and decay in all other positions was negligible, then the T_1(min) value would be 411 ms. This analysis shows that the predicted C_s/C_1 equilibrium constant is plausibly consistent with T_1(min). However, the analysis here would be more comfortable if the preference for the C_s MIN structure were somewhat higher. If the C_s MIN structure were favored by 0.94 kcal mol^{-1} instead of the calculated 0.64 kcal mol^{-1} (within the error of the calculation), then a given hydrogen would spend only 9% of its time in a dihydrogen position. In this case, a rate constant for decay in a dihydrogen position of 28 s^{-1}, much more typical of dihydrogen complexes, would account for the observed T_1(min).

Can a single complex account for the observed spectra? This would require an unusually large intrinsic isotope effect on the chemical shift (averaging ≈−100 ppb per deuterium to model the observed 0.4 ppm d_0/d_4 shift). It is reasonable to suppose that a high degree of anharmonicity could produce a large intrinsic isotope effect.[27] If the C_1 MIN structure were not truly a local minimum, but merely an extreme of a vibrational motion of the edge-bridged hydrogen in the C_s MIN structure, the potential energy well for the edge-bridged hydrogen would not be triple-welled, but rather a highly anharmonic surface. Then, the intrinsic isotope effect on the chemical shift for the edge-bridged hydrogen could be substantial. With an assumed average intrinsic isotope effect of −100 ppb, the C_s MIN complex accounts reasonably for the observed spectra (within 1 ppb on ^{1}H and within 0.03 ppm on ^{2}H) using component shifts of −5.74, −8.88, and −39.31 ppm for the equatorial, edge-bridged, and axial positions, respectively. Although the long T_1(min) appears inconsistent with an exclusive C_1 complex, C_1 MIN can also lead to a good fit of modeled and experimental spectra.[28]

Using the calculated isotope effects, the C_{3v} structure does not lead to an acceptable simulation of the observed chemical shifts, providing at best errors of >20 ppb in the ^{1}H spectrum and >0.1 ppm in the ^{2}H spectrum. Even if the deuterium preference for the B sites is varied uniformly from the calculated isotope effects, a good fit does not result. However, as described by the previous workers,[2] the ^{1}H chemical shifts can be fit well if the isotopic fractionation factors are allowed to vary independently with the degree of deuteration of the complex. Although such violations of the general proscription against "isotope effects on isotope effects" are possible,[29] they are rarely significant for equilibrium isotope effects. The experimental precedent given for variation of the isotopic fractionation factors was the observations of Heinekey with TpIrH$_2$H(PR$_3$)BF$_4$. The calculations above with TpIrH$_2$H(PH$_3$)$^+$ predict the observed change in fractionation factors well (ΔΔE predicted, 21 cal mol^{-1}; observed for TpIrH$_{3-n}$D$_n$(PMe$_3$)BF$_4$, 22 cal mol^{-1}). In TpIrH$_2$H(PH$_3$)$^+$, this appears because of a nonadditivity of changes in the Ir−H$_2$ symmetric and asymmetric stretching frequencies on adding one deuterium versus a second.[30] There is no such effect in the C_{3v} structure of TpIrH$_4$, and the calculated preferences for B-site deuteration vary by < 0.1% with increasing deuteration.

---

[21] Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353−5361. Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876−4887. Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909−919. Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

[22] The number of adjustable parameters does not affect the fundamental argument, because our goal is simply to show that the spectrum is consistent with the theoretical prediction. However, this understates the significance of our observations; while there are eight adjustable parameters, they do not have an orthogonal impact on the predicted spectrum. It is in no way possible to simulate an arbitrary spectrum. The fact that the experimental spectrum can be simulated with reasonable input parameters is not without significance.

[23] Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133.

[24] Aside from rotation via C_s TSR, effective rotation of the hydrogens of the dihydrogen can occur with very little barrier by interconversion between chiral C_1 MIN structures (through a C_s MIN structure), an exchange resulting "in a motion that is indistinguishable from spinning of the H$_2$ ligand".[25]

[25] Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031−7036.

[26] For some relatively long T_1(min)s in dihydrogen complexes, see: Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652−1660. Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396−5407. Earl, K. A.; Jia, G. C.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027−3039.

[27] The effect of anharmonicity on chemical shifts supports the intuitive expectation that anharmonicity could lead to significant intrinsic isotope shifts, though, as pointed out by one of the referees, anharmonicity certainly does not always do so. See: Ruud, K.; Åstrand, P.−O.; Taylor, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 4826−4833.

[28] Even though the C_s TSE structure (which resembles a four-legged piano stool structure) is a transition state, an attempt was also made to simulate the NMR spectra solely with C_s TSE; these simulation results were unacceptable.

[29] Hamilton, D. G.; Luo, X.−L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198−3203.

[30] Interestingly, the C_1 MIN [TpIrH$_2$(H$_2$)] and TSE [the C_s TpIrH$_2$(H$_2$) transition state for hydrogen exchange] are similar to those of TpIrH$_2$H(PH$_3$)$^+$ in that, in each case, the isotope effect for adding a second deuterium to a dihydrogen position is significantly less than expected from adding the first deuterium. No such effect is predicted for any of the complexes when a deuterium is put into a classical hydride position.

Finally, for either the C_{3v} SOSP or C_s MIN classical hydride structures to explain the observed H−D coupling constants of 2.5−3.3 Hz and their increase with increasing deuteration, some unusually large $^2J_{HD}$ couplings must be present. For example, a possibility previously suggested for the C_{3v} structure was a $^2J_{HD}$ between A and B sites of 4.7 Hz along with a $^2J_{HD}$ between two B sites of 1 Hz. However, using the previously suggested isotopic fractionation factors of 1.15 for Tp^*IrH_3D and 1.13 for Tp^*IrHD_3, the difference in coupling constants between the two complexes would be only 0.12 Hz. Simulation of the observed increase in J_{HD} of 0.3−0.8 Hz[2b] between Tp^*IrH_3D and Tp^*IrHD_3 requires a greater difference between the large A−B and small B−B couplings, pushing the A−B coupling further above precedented values. As described above, the theoretically predicted mixture of C_s MIN and C_1 MIN structures economically accounts for the observed coupling constants.

In summary, it is difficult to reconcile many of the NMR observations with a single classical hydride structure. The calculational prediction of low-energy C_s MIN and C_1 MIN minima in rapid equilibrium appears consistent with all of the NMR observations for these complexes, while the previously postulated C_{3v} structure is not.

Infrared Spectra. Additional evidence for our proposed C_s MIN/C_1 MIN structures comes from the infrared spectroscopy of the complex. The Ir−H stretches in the experimental IR spectrum of the tetrahydrogen complex “are identified as a relatively broad absorption centered at 2163 cm^{-1}”.[2] Analytical frequency calculations of the C_{3v} SOSP structure reveal two bands arising from three frequencies (wavenumbers followed by relative intensities and symmetry in parentheses): one band consisting of 2266 cm^{-1} (97, E) and 2278 cm^{-1} (63, A_1) and the second band consisting of 2440 cm^{-1} (60, A_1). These calculated frequencies for the C_{3v} structure, two bands separated by ∼160 cm^{-1}, are not in accord with the experimental observation of a single absorption band.

The four calculated Ir−H frequencies for the C_s MIN minimum energy structure are in agreement with experiment: one observed broad band, consisting of three frequencies, 2262 cm^{-1} (111, A′), 2292 cm^{-1} (56, A″), and 2294 cm^{-1} (110, A′) and another unobserved band (too weak) at 2397 cm^{-1} (11, A′). The Ir−H frequencies of the C_1 MIN structure are over the same frequency range as those of the C_s MIN structure and would also produce one broad band, consisting of four frequencies, 2256 cm^{-1} (102), 2261 cm^{-1} (82), 2285 cm^{-1} (163), and 2298 cm^{-1} (29). Thus, only the C_s/C_1 structures or their mixture, and not the C_{3v} structure, is consistent with the infrared spectroscopy.

Conclusions

Density functional calculations for hydridotris(pyrazol-1-yl)borato iridium tetrahydrogen species predict that there are two minimum energy structures, a C_s edge-bridged octahedral structure (formally Ir^{V}) and a C_1 η^2-dihydrogen, dihydride structure (formally Ir^{III}), which are nearly isoenergetic. Furthermore, the calculated analytical frequencies reveal that the previously proposed C_{3v} structure is actually a local maximum (a second-order saddle point) on the potential energy surface. Several low energy transition states have been located that account for the observation of equivalence of the hydrides at −70 °C on the NMR time scale. High-level ab initio calculations have also been used to substantiate the small energy differences of the two local minima found with B3LYP, as well as the high relative energy found for the C_{3v} structure. By using the calculated equilibrium and vibrational frequencies of the two minima (C_s MIN and C_1 MIN), the NMR spectra were successfully simulated, but attempts to simulate the NMR spectra with the frequencies of the C_{3v} structure were not successful. A comparison of the experimental infrared spectrum of the hydridotris(3,5-dimethylpyrazol-1-yl)borato iridium tetrahydrogen complex and harmonic frequency calculations on $TpIrH_4$ with the C_s, C_1, and C_{3v} structures also supports the assignment of the minimum energy structures to C_s and C_1 to the exclusion of the C_{3v} structure.

Theoretical Details

The density functional calculations were performed with B3LYP [Becke three-parameter exchange functional (B3)[31] and the Lee−Yang−Parr correlation functional (LYP)[32]] and BP86 [Becke one-parameter exchange functional (B)[33] and the correlation functional of Perdew et al. (P86)[34]] density functional theory[35] as implemented in Gaussian 98.[36] Frozen core Möller−Plesset perturbation theory calculations (MP*x*, $x = 2$, 3, and 4)[37] and coupled cluster calculations involving single and double excitations (CCSD)[38] were also performed with Gaussian 98 in selected cases. The basis set for iridium is the modified LanL2DZ[39] of Couty and Hall [where the two outermost *p* functions have been replaced by a (41) split of the optimized iridium 6*p* function[40]] as well as *f* polarization functions on the Ir.[41] Spherical *d* functions were used for iridium; that is, there are five primitive basis functions per *d* function. The effective core potentials (ECP) of Hay and Wadt were used for iridium.[39] The standard D95 basis sets[42] were used for all peripheral nitrogen, carbon, boron, and hydrogen atoms. For all metal ligated atoms, polarization functions were added to the ligated N(*d*) and H(*p*) atoms (D95**).[42] This basis set will be referred to as BS1. Additional calculations were performed on selected structures with improved basis sets as defined here: BS2 replaces the basis set of the ligated hydrogens in BS1 with a triple-ζ plus double polarization basis set (cc-pVTZ);[43] BS3 expands BS2 by uncontracting the Couty and Hall modified Hay and Wadt basis set to triple-ζ in the valence space supplemented by a set of *f* polarization functions for Ir. All structures were optimized with and without symmetry at the B3LYP and the BP86 levels, while selected structures were optimized at the MP2 level. Analytical frequency calculations were performed on all B3LYP and BP86 structures to ensure a local minimum or *n*th order saddle point was achieved, while an MP2 analytical frequency calculation was only performed on the MP2 derived C_s TSE structure. All ZPE energies use the zero point energy (ZPE) from B3LYP frequency calculations,

---

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(33) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(34) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824; **1986**, *34*, 7406.

(35) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, A. C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revisions A.6 and A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(37) Moller, C.; Plesset, M. C. *Phys. Rev.* **1934**, *46*, 618−622.

(38) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(39) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298.

(40) Couty, M.; Hall, M. B. *J. Comput. Chem.* **1996**, *17*, 1359−1370.

(41) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111−114. Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237−240; **1994**, *224*, 603.

(42) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976, 1−28.

(43) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

except for BP86 energies, where ZPEs from those frequency calculations were used. In some instances, the relative zero point energy of the transition state lies below the two local minima it connects. This apparent inconsistency of the relative energies is primarily due to the harmonic approximation, which overestimates the ZPE at the two minima.[44] The non-ZPE relative values do reflect the higher energy of the transition state. One might note that the relative energy of C_s TSE and C_s MIN is much larger at MP2//B3LYP than the same difference at MP2//MP2. This large discrepancy is caused by the preference of MP2 for the higher oxidation state. When the geometry is reoptimized at MP2, the η^2-dihydrogen, dihydride becomes a tetrahydride and the small relative energy difference between C_s TSE and C_s MIN is recovered. Calculations of solvent effects were not considered, because the calculated dipole moments of all of the various structures were very similar; therefore, solvent effects would be minimal, especially in the nonpolar solvents used (d_6-benzene, d_8-toluene, and d_2-dichloromethane).[2] Calculations on the $TpIrH_2H(PH_3)^+$ model complex have been performed for comparison to the NMR observations of Heinekey and co-workers for the $TpIrH_2H(P(CH_3)_3)^+$ complex.[12] B3LYP (with BS1 and the Hay and Wadt ECP and LanL2DZ basis set supplemented by a set of *d* polarization functions[41] for phosphorus) geometry optimizations and analytical frequency calculations were performed on the cationic C_1 hydridotris(pyrazolyl)borato phosphino iridium η^2-dihydrogen, hydride and the cationic C_s hydridotris(pyrazolyl)borato phosphino iridium trihydride complexes. For this model complex, the C_1 η^2-dihydrogen, hydride structure was found to be slightly favored over the C_s trihydride structure in agreement with experiment.

Acknowledgment. C.E.W. and M.B.H. thank the National Science Foundation (Grant CHE-9800184) and the Welch Foundation (Grant A-648) for financial support. D.A.S. and M.J.S. thank the National Institutes of Health (Grant NIH GM-45617) for financial support. C.Z., G.J., and Z.L. thank the Research Grants Council of Hong Kong and the Hong Kong University of Science and Technology for financial support.

Supporting Information Available: Diagrams describing relevant equilibrium isotope effects (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001233T

---

[44] Jordon, M. J. T.; Del Bene, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 2101−2115.