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Iridium Hydride Complexes with Cyclohexyl-Based Pincer Ligands: Fluxionality and Deuterium Exchange

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Supporting Information

ABSTRACT: Two hydride compounds with aliphatic pincer ligands, $(PCyP)IrH_2$ $(PCyP = \{cis-1,3-bis[(di-tert$ $butylphosphino)methyl]cyclohexane}⁻ (1) and <math>(PCyP)IrH_4$ (2), have been studied, with emphasis on features where such systems differ from arene-based analogues. Both compounds reveal relatively rapid exchange between α -C-H and Ir-H, which can occur via formation of carbene or through demetalation, with nearly equal barriers. This observation is confirmed by deuterium incorporation into the α -C-H



position. Complex 1 can reversibly add an N_2 molecule, which competes with the α -agostic bond for a coordination site at iridium. The hydrogen binding mode in tetrahydride 2 is discussed on the basis of NMR and IR spectra, as well as DFT calculations. While the interpretation of the data is somewhat ambiguous, the best model seems to be a tetrahydride with minor contribution from a dihydrido-dihydrogen complex. In addition, the catalytic activity of 1 in deuterium exchange using benzene- d_6 as a deuterium source is presented.

INTRODUCTION

Iridium pincer complexes with terdentate PCP type ligands have been shown to be effective catalysts for various dehydrogenation reactions.¹ Depending on the substrate, both di-¹ and tetrahydride^{1,2} species may be relevant to a catalytic cycle and thus the study of such compounds has not only fundamental but also practical importance. Previously, we have studied many aspects of complexes with aliphatic pincer ligands based on a cyclohexyl framework³ and in dehydrogenation reactions we found that the catalytic activity of iridium pincer complexes with the cyclohexyl backbone is smaller than that of their arene-based counterparts.⁴ Furthermore, we found quite spectacular reactivity of these complexes, which included multiple C-H activations leading to formation of a C=C double bond⁵ and also completely reversible α -methyl migration via a carbene intermediate.⁶ This prompted us to investigate the dihydride complex $(PCyP)IrH_2$ (1)⁷ and tetrahydride complex (PCyP)IrH₄ (2; Chart 1) in order to understand how these systems differ from the arene-based analogues (PCP)IrH₂⁸ (PCP = $[2,6-({}^{t}Bu_{2}PCH_{2})_{2}C_{6}H_{3}]^{-}),$ $(POCOP)IrH_2^9 (POCOP = [2,6-(^tBu_2PO)_2C_6H_3]^-), (PCP)-$





 IrH_{4} ,¹⁰ and (POCOP) IrH_{4} .¹⁰ While these arene-based compounds have been properly studied, polyhydride pincer complexes with aliphatic ligands have received little attention. Previously, the synthesis and some studies of [(^tBu₂PCH₂)₂CH]IrH₄ and [(^tBu₂PCH₂)₂CH]IrH₂¹¹ as well as $[({}^{i}Pr_{2}P - o - C_{6}H_{4})_{2}CH]IrH_{4}^{12}$ were reported, but the rather limited amount of data provided did not allow an unambiguous clarification of the nature of these rather complex species. We have also previously shown, by spectroscopic methods and DFT calculations, that the geometry of 1 is dependent on the dielectric permittivity of the medium; ligands around the Ir atom adopt a trigonal-bipyramidal geometry in nonpolar solvents and square-pyramidal geometry in polar solvents. We also found that a weak agostic bond between α -C–H and Ir is present in 1.7 However, there are still many aspects of the chemistry of compounds 1 and 2 that are unknown and that could shed additional light on the general properties and reactivity of hydride complexes with an aliphatic pincer framework.

Here, we report on the exchange process between the α -C–H and Ir–H in compound 1, as well as on a full characterization of the tetrahydride 2, particularly with respect to the nature of the hydrides. Furthermore, we report on their use as deuterium exchange catalysts.

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^{*a*}For the analogous data for 1, see ref 10. For a brief comparison in aromatic solvent: 1, δ IrH₂ –22.85 ppm, $\delta \alpha$ -C–H 0.54 ppm, δ P 86.9 ppm; 2, δ IrH₄ –10.23 ppm, $\delta \alpha$ -C–H 2.42 ppm, δ P 71.7 ppm. ^{*b*}(δ IrH_{set 1} + δ IrH_{set 2})/2. ^{*c*}Positions of centers of multiplets for "upper" and "lower" sets of protons. ^{*d*}For α -C–H and IrH₄ exchange. ^{*e*}For averaged exchange between hydrides. ^{*f*}The signal of IrH₂D₂ was also resolved, with J_{HD} = 2.8 Hz and $\Delta \delta$ (IrH₄–IrH₂D₂) = +0.06.

EXPERIMENTAL SECTION

General Considerations. All manipulations were conducted under an inert gas atmosphere using standard Schlenk and glovebox techniques unless otherwise stated. All solvents were distilled under vacuum from Na/benzophenone. Hydrocarbon deuterated solvents were distilled under vacuum from Na/benzophenone; CD2Cl2 was distilled under vacuum from calcium hydride. Substrates used for catalytic deuteration were used as received, after degassing and refilling with nitrogen. Complexes 1 and 2 were synthesized according to previously published procedures.^{5,7} NMR spectra were recorded on Varian Unity INOVA 500 MHz and Bruker Avance 400 MHz instruments. ¹H and ¹³C NMR chemical shifts are reported in parts per million and referenced to the signals of deuterated solvents. ³¹P NMR chemical shifts are reported relative to external 85% solution of phosphoric acid. A calibration curve obtained using a neat methanol sample was used for variable-temperature measurements. Spin-lattice relaxation times (T_1) were measured using a standard inversion recovery pulse sequence. The line shape analysis was done using WinDNMR 7.1.¹³ IR spectra were recorded on a Bruker Alpha FT-IR spectrometer.

Synthesis of 2-D,HD₃. Deuterium gas was slowly bubbled through a solution of complex 2 (0.017 g, 0.029 mmol) in C_6D_6 (0.7 mL) in a rubber-septum-capped NMR tube equipped with an outlet needle for ca. 50 min. Complex 2-D,HD₃ was formed with >95% deuteration of hydridic positions. The compound suffers from slow incorporation of deuterium into ^tBu groups which makes J_{HD} irresolvable, and it was used immediately after preparation.

Synthesis of $1-d_{38}$. A solution of complex 1 (0.019 g, 0.032 mmol) in C₆D₆ (3 mL) was heated on an oil bath in a sealed Straus flask for ca. 3 h at 120 °C. Complex $1-d_{38}$ was formed with >95% deuteration of hydridic positions.

General Procedure for Catalytic Deuterium Exchange. A Straus flask was charged with (PCyP)IrH₂ (1; 0.3 mL of a stock solution in C_6D_6 , 0.00478 mmol), 0.7 mL of C_6D_6 , substrate (0.478 mmol, 100 equiv), and cyclooctane (0.010 mL, 0.074 mmol, internal standard) inside a nitrogen atmosphere glovebox. The flask was sealed and heated on an oil bath for 24 h at 150 °C, cooled to room temperature, and analyzed by NMR. The degree of deuteration was determined by integration of substrate signals versus cyclooctane prior to and after heating. In several cases (olefins, cyclooctane) external standards (both ¹H and ²H) were added after the reaction in order to quantify the degree of deuteration.

Crystallography. Crystals of complex 2 were grown by slow evaporation of a hexane solution of 2 at -35 °C under an N₂ atmosphere. Intensity data were collected at 120 K with an Oxford Diffraction Xcalibur 3 system using ω scans and Mo K α radiation ($\lambda =$ 0.71073 Å).¹⁴ The CCD data were extracted and integrated using Crysalis RED.¹⁵ The structures were solved using direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXL¹⁶ and SIR-92.¹⁷ Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. Although there is substantial electron density where the hydrides are expected, we were unable to refine them properly. The CCDC deposition number is 1473015.

RESULTS AND DISCUSSION

Variable-Temperature NMR Studies of 1 and 2. The dynamic behavior of 1 and 2 in three different solvents, toluene- d_{8} , methylcyclohexane- d_{14} , and dichloromethane- d_{2} , was investigated and revealed two types of exchange processes. The first process is responsible for broadened signals of the hydride ligands and the α -C-H of complex 1 at room temperature and is interpreted as an exchange of hydrogen atoms between these positions. At elevated temperatures this process results in very broad signals of α -C–H and IrH₂, while upon lowering the temperature to 0 °C and below it is frozen out. The Gibbs free energies of activation are 16.7, 16.3, and 15.7 kcal/mol in methylcyclohexane- d_{14} , toluene- d_8 , and dichloromethane- d_2 , respectively, at 25 °C. A line shape analysis through temperatures from 25 to 90 °C (in toluene d_8) resulted in $\Delta H^{\ddagger} = 14.3(\pm 0.4)$ kcal/mol and $\Delta S^{\ddagger} =$ $-6.6(\pm 1.2)$ cal/(mol K) (see the Supporting Information for details). The second dynamic process is an exchange of hydrides between each other and was discussed previously.

For tetrahydride complex 2 resonances corresponding to the α -C–H and Ir–H are sharp at room temperature, indicating that any exchange process is slower than for 1 (see Table 1). Indeed, ΔG^{\ddagger} measured using line-shape analysis at 100 °C in toluene- d_8 is 19.7 kcal/mol, which is ca. 3 kcal/mol higher than for complex 1. At low temperatures decoalescence of hydride resonances of 2 occurs, resulting in the appearance of a rather complex pattern (Figure 1) in the ¹H NMR spectrum; at the

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Figure 1. VT NMR spectra of 2 in methylcyclohexane- d_{14} . Asterisks indicate possible positions of maxima. The small triplet in the top spectrum is <0.1% impurity.

same time, only one signal is observed in the ³¹P{¹H} NMR spectrum. One could expect the existence of four lines in the proton spectrum of **2** in the case of a tetrahydride structure and three or six lines in the case of dihydrido-dihydrogen structure, depending on how fast H₂ rotation is on the NMR time scale. However, at least eight lines are observed in the spectrum of 2; moreover, the lines in each set of signals (likely corresponding to different sides of the plane formed by the two chelating fivemembered metallacycles) are moving closer to each other upon decreasing the temperature. Tentatively, we ascribe such behavior to the existence of several exchange couplings between hydrides, which leads to splitting and appearance of additional lines.¹⁸ Such couplings can be fairly large and temperaturedependent, decreasing with a decrease in the temperature, which is in line with the behavior of 2. Different line widths may be a result of several exchange processes. Taking the centers of the two sets of signals as $\Delta \nu_0$, it is possible to roughly estimate ΔG^{\ddagger} as 8.7 kcal/mol at coalescence (ca. -70 °C), which corresponds to the exchange between iridium hydrides. Differences between different solvents are fairly small for 2 and will not be discussed in detail.

Complexation of 1 with Nitrogen. Initial VT studies of 1, which were performed under an N_2 instead of an Ar atmosphere, revealed the formation of the dinitrogen complex 3 at low temperatures (Scheme 1). NMR signals of 3 are almost





indistinguishable from the baseline at room temperature, but upon cooling to 0 °C a new peak at 65.5 ppm in the ${}^{31}P{}^{1}H{}$ NMR spectrum as well as a broad triplet at -9.85 ppm in the ¹H NMR spectrum appear (Figure S1 in the Supporting Information). Chemical shifts around -10 ppm are characteristic of a hydride trans to a high-field ligand and indicates a mutual trans arrangement of hydrides, with the N₂ molecule occupying the site opposite to the α -C–H group. Further cooling to -30 °C transforms this broad triplet into a complex multiplet with sufficiently sharp lines, which seems to be no longer affected by exchange and consists of overlapping signals of nonequivalent hydrides. Interestingly, these signals move away from each other when the temperature decreases and finally are separated by 0.11 ppm (ca. 57 Hz) at ca. -100 °C. The ¹H{³¹P} spectrum recorded at -60 °C revealed an ABX system, with 8.5 Hz coupling between hydrides (which is believed to have a negative sign^{19,20}), as well as 4.0 and 2.0 Hz couplings between α -C–H and anti and syn hydrides, respectively. The ratio 1:3 changes from 7:1 at 0 °C to ca. 1:1 at -60 °C. Since the coordination of nitrogen replaces the agostic C–H bond in the coordination sphere of 1, the affinities of these two ligands for Ir seem to be roughly comparable. In contrast, complex 2 does not react with 1 atm of N₂.

Stoichiometric Deuterium Exchange in 1 and 2. In order to measure J_{HD} values, which are useful tools for determining H–H distances in hydride complexes, deuterium-labeled samples were prepared (Scheme 2). Deuteration of

Scheme 2. Deuterium Exchange with D_2 and C_6D_6 for Complexes 1 and 2



tetrahydride 2 was achieved by slow bubbling of deuterium gas through a solution of the complex for ca. 1 h. Isotope effects on hydride chemical shifts are small (see Table 1), and signals of individual isotopomers are severely overlapping. Therefore, the observation of a single isotopomer, 2-D,HD₂, required a high degree of deuteration (>95%); incorporation of deuterium into the α -C-H position confirmed the existence of the exchange process with the hydrides observed in the VT NMR spectra. The resulting samples of 2-D,HD₃ suffer from deuterium scrambling into tert-butyl groups and were measured immediately after preparation. Even a small amount of deuterium which migrates to tert-butyl groups upon evaporation of the solvent makes H-D couplings unresolvable; interestingly, exchange into one set of tert-butyl groups is significantly easier than into the other. For this reason, samples of 1-D,HD cannot be prepared by thermolysis of 2-D,HD₃; exchange with benzene- d_6 was used instead. Thus, heating of a solution of 1 in benzene- d_6 at moderate temperatures mainly results in deuteration of hydride and α -C-H positions, while above 100 °C the rate of exchange with tert-butyl groups becomes significant. Within several hours at 120 °C, complete deuteration of tert-butyl groups in 1 was achieved to give a sample suitable for $J_{\rm HD}$ measurement.^{7,21}

Mechanism of Exchange between α -C-H and Ir-H in **1 and 2.** The sp³ hybridization of the metalated carbon together with the presence of an α -hydrogen atom results in some unique properties of iridium pincers with aliphatic ligands. First of all, the dihydride complex **1** is an 18e compound in contrast to the 16e arene-based counterparts due to the agostic interaction between iridium and the α -C-H

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Figure 2. Energy profile for exchange between α -C-H and Ir-H for dihydride complex 1. The energy profile was calculated using LACVP**/B3LYP and single corrections for solvent (benzene) and dispersion: LACV3P**++/B3LYP-D3. The relative Gibbs free energies are given in kcal/mol.



Figure 3. Energy profile for exchange between α -C–H and Ir–H for tetrahydride complex **2**. The energy profile was calculated using LACVP**/B3LYP and single corrections for solvent (benzene) and dispersion: LACV3P**++/B3LYP-D3. The relative Gibbs free energies are given in kcal/mol.

bond. The second important thing is the existence of an exchange process between the α -C–H and hydride positions for both 1 and 2. For complex 1 there are two reasonable mechanisms for this process: demetalation and migration of the α -C–H hydrogen to give the carbene complex. DFT calculations provide some insight into the details of the exchange (Figure 2). The computed energies are in very good agreement with the experimental results. Thus, by calculations it is possible to identify two isomers of 1, namely triequatorial

1-*eee* and diequatorial **1**-*eae*, depending on whether an axial or equatorial C–H bond is metalated by Ir. The observed spectra correspond exclusively to **1**-*eee* due to its greater stability, which agrees with the calculations (**1**-*eae* is 7.1 kcal/mol higher in free energy). DFT calculations show that the complex **1**-*eee* can go through a demetalation process leading to complex **5**, followed by an oxidative addition to obtain the **1**-*eae* complex. The other possible mechanism for the formation of **1**-*eae* is 1,2-migration. The process begins with an α -elimination of a hydrogen atom

to give Ir carbene 4, which via an α -hydride migration (insertion) leads to the 1-eae complex. Both pathways have reasonably low barriers for a room-temperature reaction, where the carbene path has a lower free energy of activation that is closer to the experimentally observed value (20.3 (a) and 18.1 (b) kcal/mol vs 16.3 kcal/mol (experimental) in aromatic solvent). In contrast, for tetrahydride 2 the demetalation pathway (Figure 3) lies slightly lower in free energy than the dissociation of dihydrogen and exchange through a carbene (20.7 (a) and 19.7 (b) kcal/mol vs 19.7 kcal/mol (experimental) in benzene). Other possible mechanisms, for instance, direct formation of 4 from 2 via H-H coupling, were considered but were found to be energetically unavailable. It should be noted that the barriers for reductive elimination (around 15 kcal/mol), and especially the barriers for oxidative addition (metalation) (up to 1.2 kcal/mol for equatorial position and up to 6.9 kcal/mol for axial position) are remarkably low for both 1 and 2, indicating their fluxional nature. The related compounds with aromatic backbones are significantly more rigid; for comparison, barriers for reductive elimination/oxidative addition of Ph-H bond in the benzenebased complex trans-[2,6-(H2PCH2)2C6H3]IrH(CO)H (H atoms replaced real ⁱPr groups on P atoms) were calculated to be 29.9 and 16.4 kcal/mol, respectively.²² These results also imply that during the synthesis of the parent compound (PCyP)IrHCl^{3c} the highest barriers should be associated with bringing the pincer ligand to a desired conformation, since when this is done the C-H activation is nearly barrierless.

The deuterium scrambling into *tert*-butyl groups is also easier for 1 than for arene-based counterparts (for example, 4 h at 120 °C in benzene- d_6 for 1 vs 12 h at 150 °C for (*p*-Ar^F-POCOP)IrH₂ for complete deuteration²³), which is in line with the increased electron-donating ability of the aliphatic pincer ligand.²⁴

Hydride Bonding Mode in Complex 2. The XRD-based molecular structure of tetrahydride complex 2 is shown in Figure 4, revealing the triequatorial conformation of the



Figure 4. Molecular structure of tetrahydride complex **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–C1 2.187(5), Ir–P1 2.3218(11), Ir–P2 2.3214(11); P–Ir–P 165.64(4), C1–Ir–P1 82.83(12), C1–Ir1–P2 82.95(12).

cyclohexyl ligand. The P–Ir–P angle of $165.64(4)^{\circ}$ is close to typical values for Ir complexes with the PCyP ligand.³ A fairly long Ir–C bond length of 2.187(5) Å is consistent with its easy cleavage (see above). Unfortunately, we were not able to locate the hydrides properly in the Fourier map; thus, we have to rely on solution-state data. The tetrahydride complex 2 seems to be less affected by solvation effects than dihydride 1,⁷ as indicated by virtually the same values of $I_{\rm HD}$ and $T_1(\min)$ in different solvents. Isotope effects on chemical shift are positive (to high field) and small and do not exceed 0.09 ppm (for three deuterium atoms in 2-HD₃), which indicates that the distribution of deuterium in the molecule is close to statistical. This is also confirmed by the observation of $J_{\rm HD}$ for the 2-H₂D₂ isomer, which is resolved in dichloromethane- d_2 and equal to $J_{\rm HD}$ in 2-HD₃. At the same time, the interpretation of spectroscopic data is more complex, since the observed parameters are averaged between several hydride positions. Three possible structures were considered:¹⁰ classical tetrahydride 2A and trans and cis dihydrido-dihydrogen complexes 2B,C (attempts to locate the analogue of 2C with a syn orientation of the α -C-H and H₂ ligand were unsuccessful). For simplicity, during the analysis of $T_1(\min)$ and J_{HD} the two sides of the plane formed by the chelating metallacycles were taken as equivalent (Chart 2); in the real system fairly small differences between "upper" and "lower" $r_{\rm HH}$ could be observed by calculations.

Chart 2. Possible Structures of Tetrahydride Complex 2



Given the complexity of the system, it seems reasonable to start with the computational studies of **2**. Tetrahydride **2A** is found to be lowest in energy. Structure **2C** lies 3.0 kcal/mol above **2A** and thus most likely should be rejected; **2B**, however, is only 0.14 kcal/mol higher than **2A** (Figure 5). This difference



Figure 5. Free energy profile for **2A**–**C** and hydride exchange. The energy profile was calculated using LACVP**/B3LYP and single corrections for solvent (benzene) and dispersion: LACV3P**++/B3LYP-D3. The relative Gibbs free energies are given in kcal/mol.

is too small to be taken at face value, but taking into consideration the good agreement between measured and calculated energies for the studies of these systems it seems reasonable that such a difference at least semiquantitatively describes the reality and **2B** is to some extent populated. An extremely low barrier for interconversion between **2A** and **2B** is in agreement with the observation of only one signal in ³¹P{¹H} NMR spectra also at low temperatures. An exchange between

 $\rm H_a$ and $\rm H_b$, as well as between $\rm H_d$ and $\rm H_{c'}$ is thought to be frozen near $-100~^{\circ}\rm C$, since the calculated barrier is 8.1 kcal/mol; this is in line with the experimental barrier for decoalescence around 8.6 kcal/mol. At the same time, according to calculations, exchange between $\rm H_b$ and $\rm H_c$ (with a barrier of 5.6 kcal/mol) remains fast in comparison to the NMR time scale even at the lowest accessible temperature ($-110~^{\circ}\rm C$); it should be noted, however, that an error of 1–2 kcal/mol is enough to change the conclusion. We will go through the different indications concerning the bonding mode in the following paragraphs.

i. J_{HD} . Relationships between observed J_{HD} and individual couplings are given in eqs 1–3 for 2A–C, respectively (for details, see refs 9 and 25)

$$J_{\rm obs} = \frac{{}^{2t}J_{\rm HD} + 2^{2c}J_{\rm HD} + 2^{2t-\rm oid}J_{\rm HD} + 2^{2c-\rm oid}J_{\rm HD}}{6}$$
(1)

$$J_{\rm obs} = \frac{{}^{1}\!J_{\rm HD} + 2^{2c}\!J_{\rm HD}^{*} + 2^{2t}\!J_{\rm HD}^{*} + {}^{2}\!J_{\rm HD}}{6}$$
(2)

$$J_{\rm obs} = \frac{{}^{1}\!J_{\rm HD} + 4^{2}\!J_{\rm HD}^{*} + {}^{2}\!J_{\rm HD}}{6}$$
(3)

where ^{2t} $J_{\rm HD}$ and ^{2c} $J_{\rm HD}$ are two-bond couplings between mutually cis and trans H and D atoms (for example, a and b, a and d) and ^{2t-oid} $J_{\rm HD}$ and ^{2c-oid} $J_{\rm HD}$ are two-bond couplings between cisoid (for example, positions b and c) and transoid (for example, positions a and c) H and D atoms, while the symbol * indicates coupling (cis or trans) between a hydride and a dihydrogen ligand. Typically all two-bond couplings are taken as ±1 Hz;¹⁹ for **2B**,**C** this assumption will lead to $J_{\rm obs} = (^{1}J_{\rm HD} \pm$ 5)/6 and thus $^{1}J_{\rm HD} = 17 \pm 5$ Hz. This, in turn, implies the presence of an elongated dihydrogen ligand with $r_{\rm HH} = 1.06-$ 1.31 Å (Table 2 and eq 4^{19,26}).

$$r(H-H) = 0.74 - 0.494$$
$$\times \ln \left(\frac{16.1447 - \sqrt{260.65 - 4(1 + 0.32895(J_{HD}))}}{2} \right)$$
(4)

Structure **2A** also cannot be excluded; if one considers all pairs of adjacent hydrogens as compressed dihydrides, a similar procedure would lead to an estimation for $2^{2c}J_{HD} + {}^{2c-oid}J_{HD} = 14-20$ Hz, and thus individual couplings between mutually cis (a and b, c and d) and cisoid (b and c) H and D atoms would

Table 2. H–D Couplings and Possible H–H Distances within Dihydrogen Ligands in 2 and Related Compounds



^{*a*}Extracted using eqs 2 and 3. ^{*b*}Using eq 4 and ${}^{1}J_{HD}$.

be around 5-7 Hz, which falls in the range previously observed for compressed dihydrides. Since the correlation between $J_{\rm HD}$ and r(H-H) is far from accurate at long distances, ^{27,28} some additional assumptions are required for a reciprocal solution. It seems reasonable to take the value of -1 Hz as an estimation for two-bond trans H-D couplings in 2A,B, because the corresponding value in 3 is -1.3 Hz. If the principal shape of curve (4) is correct, this value is the most negative coupling possible for related systems, and at smaller H-H distances, corresponding to transoid interactions, couplings should decrease in module and pass through 0. Thus, we estimate these couplings as ± 1 Hz. For smaller distances, eq 4 is expected to give reasonably accurate results; therefore, the calculated H-H distances were used to obtain H-D coupling constants. Such a treatment gives $J_{\text{HDav}} \approx 1$ Hz for **2A** and J_{HDav} \approx 4 Hz for **2B**. From J_{obs} = 2.9 Hz, a ca. 40:60 ratio between **2A** and 2B under ambient conditions can be roughly estimated, in good agreement with the 55:45 ratio derived from calculations.

ii. $T_1(min)$. This value was calculated using the atomic positions of DFT optimized tetrahydride structure 2A using Halpern's method,; it is only slightly longer than that experimentally observed (174 ms vs 154-159 ms), and bearing in mind some underestimation of relaxation rate obtained by this method for (PCyP)IrHCl,7 these values should be considered as comparable. At the same time, both isomers of the dihydrido-dihydrogen structure are inconsistent with the experimental observations, giving rise to calculated $T_1(\min)$ values much smaller than 100 ms (for example, 20 ms for 2B). Fixing of the hydrides at the calculated positions for structures B and C and varying the angle between atoms in the dihydrogen ligand lead to an $r_{\rm HH}$ value above 1.5 Å in order to make the calculated $T_1(\min)$ value consistent with experiment, which argues against the existence of dihydrogen or elongated dihydrogen ligands. Relaxation rates for 2A,B are $R_{2A} = 5.7 \text{ s}^{-1} (174 \text{ ms}) \text{ and } R_{2B} = 50.0 \text{ s}^{-1} (20 \text{ ms}), \text{ respectively},$ which given $R_{obs} = 6.3-6.5 \text{ s}^{-1} (154-159 \text{ ms})$ is not consistent with a significant population of 2B, in contradiction with $J_{\rm HD}$ data. These calculations are done assuming a slow rotational regime for the H₂ ligand; indeed, the calculated barrier for rotation of 5.6 kcal/mol is much higher than that of molecular tumbling. It was noted, however, that if significant torsional librations of coordinated H₂ are present, a somewhat similar correction factor between 0.794 and 1 should be applied to the $r(H-H)-T_1(min)$ relationship,²⁹ depending on the angle of libration. Such a correction may increase the calculated $T_1(\min)$ value for **2B** up to 70 ms and thus may be consistent with up to 5-10% of population of 2B.

iii. Experimental IR Spectrum. The experimental IR spectrum of 2 in hexane matches that calculated for 2A quite well (although the calculated bands are somewhat blue shifted), but not that for 2B (Figure 6). The experimental band at 1940 cm^{-1} is slightly asymmetric, which in principle may be associated with the presence of a very low intensity additional absorption at ca. 1900 cm^{-1} , for example, from 2B; however, such a speculation should be treated with caution.

iv. Low-Temperature NMR Spectra. The low-temperature IR spectra can in principle represent $2A_{,B}$ or be a weighted average of those two. According to the calculated barriers, one set of signals should be assigned to H_a and H_d , while another set can be assigned to H_b and H_c , which are likely to be in exchange. Since only one large coupling between H_b and H_c may be present, 2A is expected to give rise to four lines, while other models give three or six lines. None of these models can



Figure 6. Stick diagram representing experimental and calculated IR spectra. Intensities are normalized to the most intense band. Experimental spectrum is given in Figure S2.

explain the observed NMR pattern; therefore, we suppose that additional splitting is a result of quantum-mechanical exchange couplings, likely between H_a and H_d, as well as H_b and H_c, as described above.¹⁸ While we cannot unambiguously assign the low-temperature NMR spectra to one of the possible structures, it is worth noting that T_1 values measured for the decoalesced signals at -80 °C of ca. 360 ms (methylcyclohexane- d_{14}) not only argue against the dihydrogen nature of any of these signals but also significantly limit the possible contribution of **2B** to the observed spectra.

v. Reactivity of **2**. The reactivity of **2** with deuterium clearly shows that dihydrogen-containing structures are energetically available at room temperature but does not prove that they are significantly populated, because the barriers for interconversion among **2A**–**C** are negligible in comparison to thermal energy.

All in all, DFT calculations suggest the tetrahydride 2A to be a global minimum, with the energy gap between 2A and 2B being comparable to the expected error of calculations. $T_1(\min)$ and IR data argue for tetrahydride structure 2A, with small or negligible contribution from 2B. H-D coupling, at the same time, is only consistent with significant (around 50%) population of 2B. In this respect, it is interesting that the related benzene-based complex (PCP)IrH₄ was found to have a tetrahydride structure at 100 K by neutron diffraction.¹⁰ Solution parameters for (PCP)IrH₄ were ambiguous; thus, IR spectra were better consistent with a tetrahydride: $J_{\rm HD}$ for a dihydrido-dihydrogen complex and $T_1(\min)$ for both of these structures. Complex 2 is apparently closer to a "classical" tetrahydride than (PCP)IrH₄, as seen from the smaller J_{HD} and longer $T_1(\min)$ values and decoalescence of the hydride resonances, which were not reported for the latter compound. Therefore, it seems likely that 2A is the predominating structure in the solution of 2. A precise estimation of the contribution of 2B is difficult. It is important to note that an analysis of $J_{\rm HD}$ is only approximate because several contributing couplings are unknown and correlation (4) at certain distances suffers from data scattering. At the same time, the PES is exceptionally flat toward movement of H_b and H_c; a change of the distance from 0.97 to 1.75 Å costs only 0.1 kcal/mol. For such shapes of the PES, occupation of vibrational states may affect the geometry;^{26,30} for example, r(H-H) values in elongated dihydrogen compounds can be underestimated by

0.2–0.3 Å.³⁰ If such an underestimation is present, it would significantly increase $T_1(\min)$ for **2B** and in turn give better agreement between the various methods.

Catalytic Deuterium Exchange. Catalytic deuterium exchange is an important method for the preparation of deuterium-labeled compounds, which find use in many areas.³¹ As complex 1 is capable of isotope exchange with benzene- d_{6} , it seemed reasonable that it could also mediate isotope exchange between benzene- d_6 and arenes. In line with this, it was found that other substrates, including those with activated and to some extent with nonactivated C_{sp}^3 -H bonds, can be successfully deuterated (Scheme 3).





 ${}^{a}\mathrm{The}$ values given with the structures show the percentages of deuteration.

Nonhindered positions in arenes are deuterated almost quantitatively, and the same is true for olefins which are not subjected to isomerization such as tert-butylethylene. 1-Hexene undergoes isomerization into internal hexenes, and deuterium scrambling takes place in all positions with the percentage of deuteration decreasing upon moving away from the double bond along the carbon chain. Importantly, not only could C_{sp}^2 -H bonds be involved in exchange but also activated and nonactivated C_{sp}^{3} -H bonds, a rarely observed event.³² Thus, ca. 15% deuteration of methyl groups in toluene and tertbutylethylene was observed. Up to 60% of C-H bonds of triethylamine were deuterated using increased catalyst loading (10 mol %). At the same time, the level of deuteration of purely aliphatic substrate cyclooctane is fairly low. Deuteration of arenes presumably proceeds via oxidiative addition of the substrate C-H bond to 1 with formation of an Ir(V) complex, followed by reductive elimination. In the case of triethylamine, traces of dehydrogenated products were observed during the

course of the reaction, and thus an insertion/ β -elimination mechanism can make a contribution for this substrate. Olefins are likely deuterated through removal of H₂ from Ir, resulting in an Ir(III)/Ir(I) catalytic cycle, similar to that previously observed by Hartwig for $[({}^{t}Bu_{2}PCH_{2})_{2}CH]IrH(NH_{2}).^{33}$ In general, the latter complex operates at lower temperatures and does not isomerize olefins, providing better selectivity. At the same time, the use of 1 allows for a decrease in catalyst loading and deuteration of C_{sp}^{3} -H bonds to some extent. For cyclooctane, it is not easy to unambigously determine which mechanism is operative. Deuteration of methyl groups in toluene and tert-butylethylene clearly shows that the Ir(III)/ Ir(V) cycle is possible, but we cannot completely exclude that some small unobserved amount of cyclooctene may form under experimental conditions to promote an Ir(III)/Ir(I) catalytic cycle.

Relevance to Catalytic Dehydrogenation. Previously we reported that the activity in catalytic dehydrogenations for complex 3 is lower than that of its arene-based counterparts.⁴ Observations of hydride complexes 1 and 2 shed some light on this problem. The reaction of (PCyP)IrHCl with ^tBuONa in neat cyclooctane produces exclusively dihydride 1 (together with 1 equiv of cyclooctene, COE), while mixtures of $(PCP)IrH_2$ and (PCP)Ir(COE) as well as $(POCOP)IrH_2$ and (POCOP)Ir(COE) in ratios ca. 9:1 and 1:1, correspondingly, were formed for complexes with benzene-based phosphine and phosphinite backbones,²³ in line with the increased electrondonating ability of the aliphatic pincer ligand. This stabilization of the Ir(III) oxidation state is, presumably together with increased steric barriers, responsible for the low dehydrogenation rates at moderate temperatures; thus, hydrogenation of tert-butylethylene, which is an important part of the catalytic cycle, is slower by approximately 1 order of magnitude for 1 in comparison to $(PCP)IrH_2^{34}$ at similar temperatures (65–70 °C). At high temperatures, complex 1 decomposes under catalytic conditions. While complex 1 is moderately stable in solution, as indicated by the performance in catalytic deuterium exchange, the addition of a hydrogen acceptor such as tertbutylethylene or cyclooctene causes relatively fast decomposition at temperatures around 150 °C. In addition to metalation of tert-butyl groups, which is possible for arene counterparts also, 1 and 2 undergo demetalation and activation of the α -C–H bond; these processes seem to be responsible for the low thermal stability of dihydride 1. Decomposition pathways may include formation of species with a demetalated cyclohexyl ring or formation of the olefin complex (Scheme 4), as we previously showed for these systems.^{5,6} The latter pathway is somewhat more likely, since addition of a hydrogen acceptor significantly facilitates decomposition of 1. In this

Scheme 4. Proposed Pathway for Decomposition of Complex 1 at High Temperatures



respect, it should be noted that $(PC_{sp}{}^{3}P)Ir$ complexes that do not have a α -C–H bond were recently found to be significantly more stable under alkane dehydrogenation conditions.³⁵

Regarding the tetrahydride 2, it has a higher stability with respect to loss of hydrogen in comparison to $(PCP)IrH_4$ and especially $(POCOP)IrH_4$. This means that at low temperatures complex 2 is unlikely to catalyze acceptorless dehydrogenation.

SUMMARY

In summary, we have presented some studies of the dihydride and tetrahydride iridium complexes (PCyP)IrH₂ (1) and $(PCyP)IrH_4$ (2) with a cyclohexane-based pincer ligand. These compounds are highly fluxional and complex systems with several dynamic processes present at room temperature. Thus, both compounds undergo exchange between α -C–H and Ir-H positions. For complex 1, two mechanisms-through carbene and through demetalation-have reasonably low barriers to be responsible for such exchange, with the former lying slightly lower in energy and closer to the experimentally observed ΔG^{\ddagger} values. In contrast, for complex 2 the demetalation mechanism is slightly more favorable. These data suggest that for complex 1 at least three additional structures-axially metalated isomer 1-eae, carbene 4, and demetalated complex 5-are kinetically accessible at room temperature (but not significantly populated) and may affect its reactivity.

NMR spectra of complex 2 are much less solvent dependent in comparison to those of 1. As for 1, a low-temperature decoalescence of hydride resonances was achieved, with the observed spectral pattern being very complex likely due to the presence of quantum-mechanical exchange couplings. IR spectra and $T_1(\min)$ analysis suggest a tetrahydride structure for 2, while J_{HD} is more consistent with a significant contribution of a dihydrido-dihydrogen structure. Bearing in mind the complexity of the system, and the fact that both $T_1(\min)$ and J_{HD} interpretation requires some assumptions, we rely on the more "straightforward" comparison of IR spectra and conclude that the tetrahydride is the main compound in solution, with possible minor contribution from the dihydridodihydrogen complex.

Finally, we have shown that complex 1 is a good catalyst for deuterium exchange using deuterobenzene as the deuterium source; C_{sp}^2 -H bonds of alkenes and arenes are deuterated almost quantitatively, while a moderate or low degree of deuetration was observed for substrates with C_{sp}^3 -H bonds. The reduced thermal stability of 1 in comparison to its arenebased counterparts is related to the processes involving the α -C-H bond; this should be kept in mind while designing new pincer ligands.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00324.

Eyring plot for exchange between α -C–H and Ir–H in toluene- d_8 , IR spectrum of complex **2**, ¹H NMR spectrum of **3** in toluene- d_8 , additional computational results, and atomic coordinates for all of the species (PDF)

Crystallographic data for 2 (CIF)

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Notes

The authors declare no competing financial interest.

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