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Dihydrogen Complexes of Iridium and Rhodium

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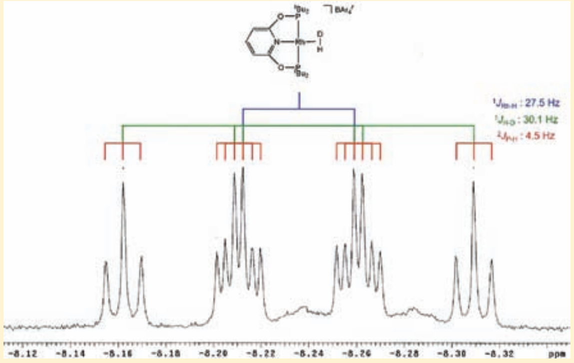
S Supporting Information

ABSTRACT: A series of iridium and rhodium pincer complexes have been synthesized and characterized: $[(POCOP)Ir(H)(H_2)]$ $[BAr^f_4]$ (**1-H_3**), $(POCOP)Rh(H_2)$ (**2-H_2**), $[(PONOP)Ir(C_2H_4)]$ $[BAr^f_4]$ (**3-C_2H_4**), $[(PONOP)Ir(H)_2)]$ $[BAr^f_4]$ (**3-H_2**), $[(PONOP)Rh(C_2H_4)]$ $[BAr^f_4]$ (**4-C_2H_4**) and $[(PONOP)Rh(H_2)]$ $[BAr^f_4]$ (**4-H_2**) (POCOP = κ^3-C_6H_3-2,6-$[OP(t\mathrm{Bu})_2]_2$; PONOP = 2,6-$(t\mathrm{Bu}_2PO)_2C_5H_3N$; BAr^f_4 = tetrakis(3,5-trifluoromethylphenyl)borate). The nature of the dihydrogen−metal interaction was probed using NMR spectroscopic studies. Complexes **1-H_3**, **2-H_2**, and **4-H_2** retain the H−H bond and are classified as η^2-dihydrogen adducts. In contrast, complex **3-H_2** is best described as a classical dihydride system. The presence of bound dihydrogen was determined using both T_1 and $^1J_{HD}$ coupling values: T_1 = 14 ms, $^1J_{HD}$ = 33 Hz for the dihydrogen ligand in **1-H_3**, $T_1(\mathrm{min})$ = 23 ms, $^1J_{HD}$ = 32 Hz for **2-H_2**, $T_1(\mathrm{min})$ = 873 ms for **3-H_2**, $T_1(\mathrm{min})$ = 33 ms, $^1J_{HD}$ = 30.1 Hz for **4-H_2**.



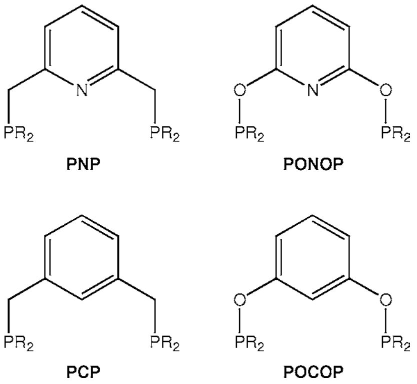
INTRODUCTION

Since the seminal work of Kubas[1] and co-workers, the coordination chemistry of the dihydrogen ligand has been studied extensively and expanded rapidly.[2] The bonding features in such complexes have now been well-described, with electron-deficient metal centers favoring the support of dihydrogen ligands since there is a decrease in the electron-density, back-bonding into the σ^* orbital is reduced and prevents rupture of the H−H bond. Thus, it is unsurprising that the vast majority of dihydrogen complexes reported to date are cationic and that neutral dihydrogen complexes remain rare.

The importance of transition metal hydrides in catalysis has long been recognized.[3] More specifically, and in the context of pincer chemistry, it has been shown that the complex (POCOP)IrH_2 (POCOP = 2,6-bis(di-*tert*-butylphosphinito) benzene) is a highly effective catalyst for dehydrogenation of ammonia borane.[4] When this reaction was carried out at ambient temperatures, the major Ir-containing species in solution was a tetrahydride comprised of both dihydrogen and dihydride ligands. A combined experimental and computational study by Goldman and Heinekey probed the structure of pincer iridium polyhydride species.[5] Recently we have also explored the nature of iridium and rhodium hydrido−olefin pincer complexes[6] as models of key catalytic intermediates. These studies elucidated the remarkable influence of coordination geometry upon the migratory aptitude of the hydride ligand in such systems, which displayed a significant departure from earlier work in cyclopentadienyl-supported iridium and rhodium hydrido−olefin complexes.[7]

The POCOP and PCP ligands (Chart 1) have been employed by several groups for the preparation of iridium complexes which were mainly applied as alkane transfer dehydrogenation catalysts.[8] The dihydride complexes (POCOP)IrH_2 and (PCP)IrH_2 are key intermediates in these dehydrogenation reactions and the synthesis, chemistry, and structures of these complexes and closely related derivatives have been thoroughly investigated.[4,5,9]

Chart 1



Milstein and co-workers have reported a family of iridium complexes supported by the neutral pincer ligand 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (PNP) (Chart 1).[10]

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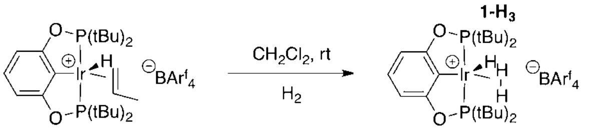
These species show a range of intriguing reactivity and thorough mechanistic investigations indicated that the methylene groups on the PNP ligand play an important role in the reactivity of the metal complex. These CH_2 groups are susceptible to deprotonation by external base or the transition metal itself resulting in dearomatization of the pyridine ligand. More recently, Nozaki has reported the synthesis of an iridium trihydride complex supported by the PNP ligand.[11] Intuitively, modification of the PNP scaffold in a vein similar to the PCP system (replacement of the methylene bridges with O atoms) may result in different reactivity patterns. Thus, an alteration of the PNP ligand would yield the pincer ligand, 2,6-bis(di-*tert*-butylphosphinito)pyridine (PONOP, Chart 1). This ligand framework offers the advantage of exchanging the reactive methylene bridges with an -O- bridging unit which precludes ligand deprotonation. We have recently reported the use of the PONOP ligand to support a variety of iridium and rhodium complexes including an observable methane complex.[12]

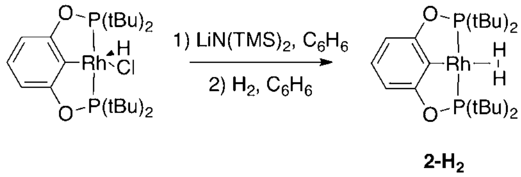
Herein we report the synthesis of several new POCOP and PONOP iridium and rhodium hydride complexes. The nature of the hydride ligands (classical vs nonclassical) was determined using established NMR techniques.[13,14] The dynamic behavior of the $[(POCOP)-Ir(H)(H_2)][BAr^f_4]$ complex was studied by variable temperature ^1H NMR spectroscopy. These studies further demonstrate the role of ligand electronic effects, charge, and metal oxidation state in dictating the structure of metal hydrogenation products.

■ RESULTS

Syntheses of POCOP/PONOP Iridium and Rhodium Hydride Complexes. Complex **1-H_3** was obtained by hydrogenation of the cationic propylene complex $[(POCOP)-Ir(H)(C_3H_6)][BAr^f_4]$[6] in methylene chloride (eq 1). The cationic trihydride complex, **1-H_3**, is cleanly generated with concomitant production of one equivalent of propane, which does not interfere with the NMR characterization. While complex **1-H_3** can be quantitatively generated in situ in methylene chloride, fluorobenzene, and $CHCl_2F$, the coordinated dihydrogen is labile and attempts to isolate this complex have so far been unsuccessful. Complex **1-H_3** has been observed to be quite stable in fluorobenzene, while slow decomposition occurs in the chlorinated solvents. Additionally, **1-H_3** is inert to oxygen and stable to mild heating in fluorobenzene.



(1)



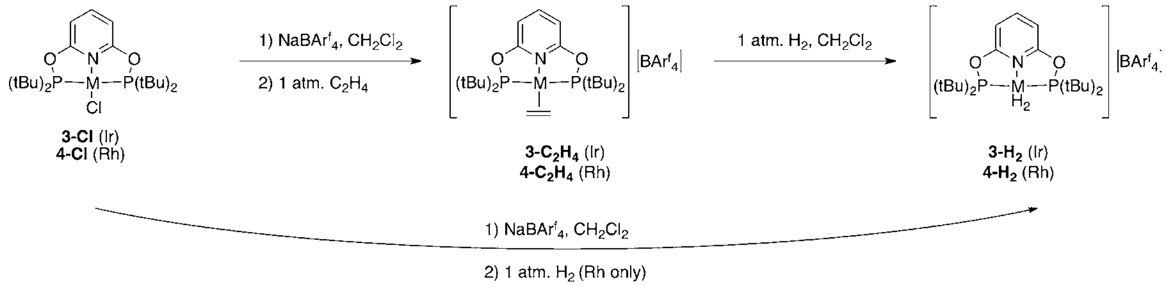
(2)

Rhodium(I) dihydrogen complexes supported by the PCP ligand framework have been prepared previously.[15] The corresponding POCOP-based rhodium complex, **2-H_2**, can be accessed directly from the hydrido−chloride complex (POCOP)Rh(H)(Cl).[16] Thus, treatment of (POCOP)Rh(H)(Cl) with $LiN(SiMe_3)_2$ in benzene under a hydrogen atmosphere affords the desired complex (eq 2), which may be isolated as a red−brown powder via filtration and subsequent solvent evaporation. Complex **2-H_2** undergoes hydrogen−deuterium exchange in C_6D_6 and thus was characterized in deuterated cyclohexane to preclude deuterium scrambling. The solubility of this complex is greatly diminished in cyclohexane.

Initial attempts to prepare cationic $(PONOP)IrH_2$, **3-H_2**, via simple chloride abstraction from **3-Cl**[12a] using $[Na][BAr^f_4]$ in methylene chloride under an H_2 atmosphere were frustrated by generation of unidentified hydride species, as indicated by ^1H NMR spectroscopy. However, the cationic **3-C_2H_4** could be cleanly generated using similar halide abstraction under an atmosphere of ethylene. Subsequent hydrogenation of **3-C_2H_4** in methylene chloride solution under ambient conditions allowed access to the desired **3-H_2** in good yield (Scheme 1) with concomitant formation of one equivalent of ethane. Both **3-C_2H_4** and **3-H_2** were isolated as orange−brown powders and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The analogous cationic PONOP rhodium dihydride, **4-H_2**, can be generated directly from halide abstraction of **4-Cl**[12b] in methylene chloride solution under an H_2 atmosphere, without the need to generate the rhodium-ethylene complex as an intermediate. However, the ethylene complex **4-C_2H_4** can be easily accessed in a manner analogous to **3-C_2H_4** and also affords **4-H_2** upon treatment of solutions of **4-C_2H_4** with an atmosphere of H_2. Both routes afford **4-H_2** in near quantitative yield as a brown powder. This complex was also characterized using multinuclear NMR spectroscopy.

Characterization of POCOP/PONOP Iridium and Rhodium Hydride Complexes by NMR Spectroscopy. *$[(POCOP)Ir(H)(H_2)][BAr^f_4]$ (1-H_3).* At room temperature the proton NMR spectrum of **1-H_3** shows a very broad iridium hydride resonance centered at −14 ppm integrating for three protons. At temperatures below *ca.* 200 K, this resonance separates into two broad signals at 0.3 and −41.9 ppm in a 2:1 integral ratio, respectively. Attempts to measure the minimum spin−lattice relaxation time (T_1(min)) for each resonance were unsuccessful, since at the lowest accessible temperatures the relaxation times were still decreasing. At 150 K in $CDCl_2F$ at

Scheme 1



500 MHz, the resonance at 0.3 ppm had a T_1 of 14 ms, while the resonance at −41.9 ppm had a T_1 of 175 ms.

A value of the one-bond HD coupling ($^1J_{HD}$) was obtained by examining a partially deuterated sample. To observe HD coupling arising primarily from the **1-HD$_2$** isotopologue, a deuterated sample of **1-H$_3$** in fluorobenzene-d_5 was prepared by establishing a 90% D_2/10% H_2 atmosphere in the headspace of a J. Young NMR tube. This generated a sample that contained a mixture of **1-HD$_2$** and **1-H$_2$D** in a 12:1 ratio. Large temperature-independent downfield isotope shifts are noted for the hydride resonances of the deuterated complexes; these isotopologues are observable in the ^{1}H NMR spectrum as two distinct signals separated by 0.6 ppm. The ^{1}H{^{31}P} NMR signal of **1-HD$_2$**, even when observed at a lower field (200 MHz) and elevated temperatures (up to 328 K), was too broad to allow for resolution of HD coupling

In a separate experiment, complex **1-H$_3$** was partially deuterated by purging both D_2 and H_2 through the solution. This generated a sample that contained a mixture of **1-H$_3$**, **1-H$_2$D**, **1-HD$_2$**, and **1-D$_3$** complexes. The ^{1}H NMR signal at 0.3 ppm was too broad and complex to determine a J_{HD} coupling constant. In the normal ^{2}H NMR spectrum at 173 K, the peaks representing HD and D−D coordinated to the iridium could be seen in approximately a 1:1 ratio. Although the HD coupling could be observed (Figure 1), it was difficult to obtain an accurate measurement of the HD coupling constant.

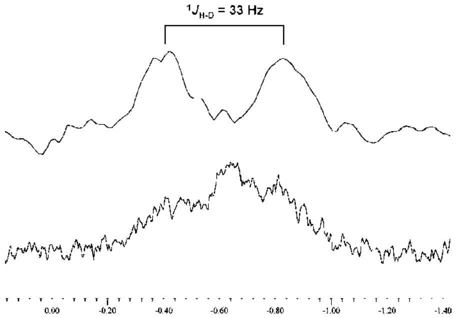


Figure 1. Overlay of the ^{2}H NMR spectrum of the dihydrogen region of a partially deuterated sample of **1-H$_3$** in CH_2Cl_2. The top spectrum is a deuterium observed 1D-HMQC. The bottom spectrum is a ^{2}H NMR.

To circumvent this problem and determine the coupling constant, a one-dimensional HMQC NMR experiment was performed in which the observed nucleus is deuterium. This experiment allowed only signals that contain HD coupling to be visible, suppressing all signals that do not have coupling to ^{1}H (i.e., the D_2 signal). This HMQC experiment is depicted in Figure 1 where the bottom spectrum shows the normal ^{2}H NMR spectrum, and the top spectrum shows the result of the one-dimensional ^{2}H-HMQC experiment, where the doublet resonance for the partially deuterated complex is clearly observed. The measured J_{HD} coupling constant was 33 Hz.

(POCOP)Rh(H$_2$) (2-H$_2$). At room temperature a single hydridic resonance is observed in the ^{1}H NMR spectrum of **2-H$_2$** at −3.00 ppm, corresponding to two hydrogen atoms. The T_1(min) for **2-H$_2$** was observed at 222 K as 23 ms in methylene chloride-d_2 (500 MHz). Above 283 K this resonance appeared as a broad doublet. From 283 K down to 223 K, coupling to phosphorus atoms was resolved; below 223 K this coupling was no longer resolved. Partially deuterated **2-HD** was generated in a manner similar to **2-H$_2$** using HD gas instead of H_2. The observed $^1J_{HD}$ coupling constant was 32 Hz.

[(PONOP)IrH$_2$][BAr$^f_4$] (3-H$_2$). In the room temperature ^{1}H NMR spectrum of **3-H$_2$**, a single hydridic resonance integrating to two H atoms was observed as a triplet at −25.07 ppm (J_{P-H} = 14.6 Hz). The T_1(min) for **3-H$_2$** was observed to be 873 ms (264 K, methylene chloride-d_2, 500 MHz). Partially deuterated **3-HD** displays a single hydridic resonance at −25.29 ppm in the ^{1}H NMR spectrum with no evidence of HD coupling.

[(PONOP)Rh(H$_2$)][BAr$^f_4$] (4-H$_2$). A single hydridic resonance was observed in the room temperature ^{1}H NMR spectrum of **4-H$_2$** as a doublet of triplets (J_{Rh-H} = 28 Hz, J_{P-H} = 4.5 Hz), at −8.26 ppm corresponding to two hydrogen atoms. The T_1(min) for **4-H$_2$** was observed to be 33 ms (methylene chloride-d_2, 500 MHz, 264 K). Labeling experiments conducted with HD generated a complex splitting pattern in the hydride region (Figure 2) confirming the presence of HD coupling ($J_{H\text{-}D}$ = 30.1 Hz).

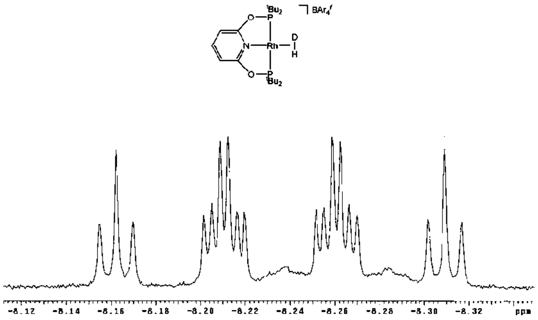


Figure 2. Partial (hydride region) ^{1}H NMR spectrum of **4-HD** in CD_2Cl_2.

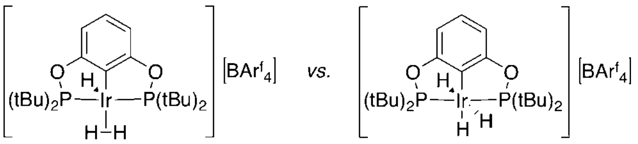
The observed splitting pattern arises from a combination of the hydride coupling with rhodium (J_{Rh-H} = 27.5 Hz), deuterium ($J_{H\text{-}D}$ = 30.1 Hz), and with phosphorus (J_{P-H} = 4.5 Hz).

■ DISCUSSION

POCOP Complexes. *(a). [(POCOP)Ir(H)(H$_2$)][BAr$^f_4$] (1-H$_3$).* Formation of transition-metal dihydrogen complexes and their structures have been of interest since the first report of a stable M−(η^2-H_2) complex by Kubas.[1] For complexes with three H atoms in the coordination sphere of the metal, there are two possible structures: a classical trihydride complex and a nonclassical dihydrogen/hydride complex. T_1(min) values and HD coupling constants have been employed to distinguish these two structures. The structural assignment is made more difficult by the generally low barriers to site exchange usually observed when hydride and dihydrogen ligands are adjacent in high symmetry complexes.[17] For example, Oldham and co-workers reported a *cis*-dihydrogen/hydride structure with a very low barrier to site exchange in the case of an iridium tris-pyrazolylborate complex.[18] A similar rapid permutation of dihydrogen and hydride ligands was described by Parkin and co-workers in an *ansa*-molybdenum species.[19]

Examination of the HD coupling constants in a partially deuterated sample provides a way to differentiate the structures. The $^1J_{H\text{-}D}$ coupling constant for free HD is 43 Hz. When dihydrogen coordinates to a metal, the $^1J_{H\text{-}D}$ coupling constant is diminished, usually to 25−35 Hz (e.g., 33.5 Hz in Kubas' complex).[1,20] The $^2J_{H\text{-}D}$ coupling constant between two terminal hydrides is much lower and tends to be ca. 1 Hz or less. For example, the classical anionic trihydride [(POCOP)IrH$_3$][Na] exhibits $^2J_{H-H}$ = 4.3 Hz, so $^2J_{H\text{-}D}$ will be 0.7 Hz for this species.[9m]

For comparison to this anionic species, we were interested in generating the cationic iridium "trihydride" complex $[(POCOP)Ir(H_3)][BAr^f_4]$, **1-$H_3$**, and determining if the structure is a classical or nonclassical trihydride (Figure 3).



1-(H)(H_2) **1-(H)$_3$**

Figure 3. Possible structures for **1-H_3**.

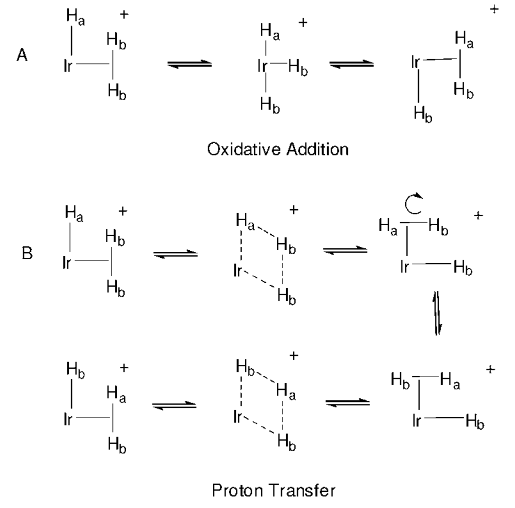
The three hydrogen atoms in **1-H_3** undergo rapid intramolecular scrambling, leading to a single broad resonance at ambient temperature. At low temperature, the ^1H NMR spectrum decoalesces to two resonances with intensity ratios of 2:1 at 0.3 and −41.9 ppm. The very high field signal at −41.9 ppm is consistent with a hydride ligand trans to a vacant site. Low-temperature ^2H NMR spectra of deuterium-labeled samples reveals $^1J_{H\text{-}D}$ = 33 Hz in the low field resonance, consistent with the presence of a dihydrogen ligand.

To access a temperature cold enough to restrict hydrogen site exchange and the resulting relaxation averaging, it was necessary to employ a Freon solvent ($CDCl_2F$). At the lowest accessible temperature (150 K, 500 MHz) the extremely short value of T_1 = 14 ms supports the assignment of the downfield resonance at 0.3 ppm as a dihydrogen ligand. The value of T_1 = 175 ms for the upfield resonance at −41.9 ppm is in the expected range for a hydride ligand. Though a direct calculation of the HH distance is not possible without a minimum T_1, the estimated values are consistent with formulation of **1-H_3** as a cationic dihydrogen/hydride complex.

The exchange rate for the dihydrogen/hydride complex was measured for both **1-D_3** and **1-H_3** complexes employing line-broadening techniques. For **1-D_3**, the line-width of the η^2-D_2 resonance was measured in the temperature range of 184−208 K. In the case of **1-H_3**, the rate was calculated by measuring the line-broadening of the hydride signal from 175 to 197 K. The rate of exchange in the triproteo-complex corresponded to $\Delta G^\ddagger$ = 9.1 kcal/mol, while the rate in the trideuterated-complex corresponded to $\Delta G^\ddagger$ = 9.8 kcal/mol (see Supporting Information). Based on these data, an isotope effect of $k_H/k_D \approx 6$ was estimated. The existence of an isotope effect, in which the energy barrier for the deuterated-complex is higher than the triproteo-complex, was expected since the breaking of the H−H (or D−D) bond in the η^2-H_2 (η^2-D_2) is probably involved in the transition state for site exchange.

Two possible mechanisms for this hydrogen exchange are depicted in Scheme 2. In the first mechanism, A, the dihydrogen oxidatively adds to the iridium center forming a trihydride intermediate or transition state (formally Ir^V). Subsequent reductive coupling of H_2 can lead to the starting complex, where no site exchange has occurred, or the complex in which H_a, originally the terminal hydride, has been incorporated into the η^2-H_2 site. Mechanism B involves a proton transfer from the dihydrogen to the hydride through a transition state in which there is partial and symmetrical bonding of the migrating hydrogen to both remaining hydrogens.[21] No trihydride intermediate is required. Both of these mechanisms require breaking of the H−H bond, so would be expected to lead to a KIE. It is interesting to note that the activation energy for H atom site exchange in complex **1-H_3** is significantly greater than in $[TpIr(PMe_3)(H_2)(H)]^+$, which is a closely related *cis*-dihydrogen/hydride complex of iridium.[18]

Scheme 2



*(b). (POCOP)Rh(H_2) (**2-H_2**).* Rather surprisingly, given the important role that rhodium hydrides play in homogeneous catalysis, relatively few rhodium dihydrogen complexes have been documented.[15,22] In contrast to the iridium POCOP complex, $(POCOP)IrH_2$, the rhodium complex **2-H_2** displays both T_1(min) and $^1J_{H\text{-}D}$ coupling values consistent with a dihydrogen structure. Using the analysis of Halpern,[13] the minimum relaxation time of 23 ms corresponds to an H−H distance of 0.87 Å assuming fast rotation of the bound dihydrogen ligand. Further confirmation of the dihydrogen formulation of complex **2-H_2** was provided by the presence of a $^1J_{H\text{-}D}$ coupling in the HD isotopomer of 32 Hz. Using the previously developed correlation between $^1J_{H\text{-}D}$ and H−H distance, the H−H distance is calculated to be 0.88 Å.[14] This observation confirms the assumption that the H_2 ligand is rotating rapidly compared to the rate of molecular tumbling. These observations suggest that the structure of **2-H_2** is likely very similar to the previously reported dihydrogen complex $(PCP)Rh(H_2)$.[15]

PONOP Complexes. *(a). $[(PONOP)Ir(H)_2][BAr^f_4]$ (**3-H_2**).* As stated previously, the majority of late transition metal dihydrogen complexes are cationic. Thus, we chose to explore cationic iridium centers (see **1-H_3** and discussion thereof) in the hopes of suppressing oxidative addition of hydrogen at the group 9 element center. Utilizing the neutral PONOP ligand, we prepared in a two-step procedure the cationic iridium complex **3-H_2**. This complex was subjected to analogous NMR studies as described above. The T_1(min) as determined by ^1H NMR spectroscopy was found to be 873 ms (264 K) and no $^1J_{H\text{-}D}$ coupling could be detected when HD gas was used in place of dihydrogen in the hydrogenation of **3-C_2H_4**. These observations lead us to conclude that, even with a formal positive charge, the iridium center undergoes oxidation to the +3 state and a classical dihydride complex results.

*(b). $[(PONOP)Rh(H_2)][BAr^f_4]$ (**4-H_2**).* Based upon the η^2-binding of dihydrogen in the neutral **2-H_2**, we assumed that a similar η^2-binding motif would be observed in the cationic **4-H_2** complex. On the basis of both T_1(min) and $^1J_{H\text{-}D}$ coupling values, we attribute the hydride signals in **4-H_2** to an η^2-dihydrogen ligand in a formally Rh(I) metal complex. The T_1(min) of **4-H_2** was determined to be 33 ms (264K) and the $^1J_{H\text{-}D}$ coupling

value 30.1 Hz, which correspond to H−H bond lengths of 0.93 and 0.91 Å, respectively. Despite the formal positive charge at the rhodium center of **4-H_2** an elongation, rather than the expected shortening, of the calculated H−H bond in the dihydrogen ligand is observed in comparison with neutral **2-H_2**. This likely arises due to the trans-influence of the nitrogen of the tightly bound pyridine of the PONOP ligand. Complexes **2-H_2** and **4-H_2** are novel, as very few rhodium dihydrogen complexes are known, especially in a four-coordinate geometry. **4-H_2** is distinguished again by its T_1(min) value which indicates fast rotation of the η^2-H_2 ligand.

■ CONCLUSION

A series of iridium and rhodium hydride complexes, supported by both anionic and neutral tridentate pincer ligands, have been developed as a platform for the examination of the reaction of dihydrogen with d^8 Ir(I) and Rh(I) complexes. The character of the metal-bound hydrides (classical vs η^2-ligation) was established using T_1(min) and $^1J_{\text{H-D}}$ coupling values. Preparation of the cationic $[(\text{POCOP})\text{Ir}(\text{H})(\text{H}_2)][\text{BAr}^f_4]$ (**1-H_3**), which was found to exhibit a dihydrogen-hydride structure, affirmed the important role electron density plays in the rupture of the H−H bond in a coordinated dihydrogen ligand. As expected, based upon the stability of the Rh(I) oxidation state, (POCOP)Rh(H_2) (**2-H_2**) is an η^2-dihydrogen complex, as determined by NMR spectroscopy. Surprisingly, given the important role of rhodium in homogeneous catalysis, complex **2-H_2** represents a rare example of a neutral rhodium dihydrogen complex.

Cationic iridium (**3-H_2**) and rhodium (**4-H_2**) complexes of the neutral PONOP ligand were prepared to examine the effect of electron density on the oxidative addition of dihydrogen. Our results are consistent with our previous studies of related iridium[12a] and rhodium[12b] PONOP complexes. Thus, the iridium complex (**3-H_2**) was found to undergo oxidative addition where the rhodium congener (**4-H_2**) did not. We attribute this behavior to the greater ease of reduction of rhodium relative to iridium.

It is tempting to compare the dihydrogen σ-complex **4-H_2** with the recently reported methane σ-complex $[\text{PONOP-Rh}(\text{CH}_4)][\text{BAr}^f_4]$.[12b] The strong, nonpolar, C−H σ bond is a weak donor and steric interactions between an alkyl group and the metal center also hamper efforts to isolate metal−alkane complexes. Thus, dihydrogen σ-complexes are significantly more well-studied.[1,2,20,23] An indication of the strength of interaction of the dihydrogen and methane moieties may be garnered by examination of the relative extent of Rh−H coupling in these complexes. The observed $^1J_{\text{Rh−H}}$ coupling constant is 27.6 and 6.3 Hz in **4-H_2** and $[\text{PONOP-Rh}(\text{CH}_4)][\text{BAr}^f_4]$, respectively. However, the $^1J_{\text{Rh−H}}$ observed in the methane complex is an average of coupling to the "coordinated" H and the remaining "terminal" H's since methane tumbles rapidly in the coordination sphere. If the 3 terminal H's show weak coupling (ca. 0) then the coupling of the coordinated H is 4 × 6.3, or about 25 Hz, close to the value of 28 Hz in **4-H_2**. A closely related PNP-Rh(H-SiR$_3$) has been reported by Ozerov and co-workers (PNP = bis(*o*-diisopropylphosphinophenyl)amide).[24] The $^1J_{\text{Rh−H}}$ coupling constant in this silane σ-complex was found to be 24 Hz (room temperature in C_6D_6) and is consistent with the values of both **4-H_2** and $[\text{PONOP-Rh}(\text{CH}_4)][\text{BAr}^f_4]$, indicating similar σ-interactions are present in all three σ-complexes.

■ EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Argon was purified by passage through columns of BASF R3-11 (chemalog) and 4 Å molecular sieves. Pentane and methylene chloride were passed through columns of activated alumina and deoxygenated by purging with N_2. Benzene was dried over 4 Å molecular sieves and degassed to remove both oxygen and nitrogen. NMR spectra were recorded on Bruker DRX 400, AMX 300 and 500 MHz instruments and are referenced to residual protio solvent peaks. ^{31}P chemical shifts are referenced to an external H_3PO_4 standard. Since there is a strong ^{31}P−^{31}P coupling in the pincer complexes, many of the ^{1}H and ^{13}C signals exhibit virtual coupling and appear as triplets. These are specified as vt with the *apparent* coupling simply noted as *J*. All reagents, unless otherwise noted, were purchased from Sigma-Aldrich and used without further purification. Propylene was used as received from National Specialty Gases of Durham, NC. Ethylene was purchased from Matheson. The syntheses of the phosphinite complexes, (POCOP)Ir(H)(Cl), (POCOP)Rh(H)(Cl), $[(\text{POCOP})\text{Ir}(\text{H})(\text{C}_3\text{H}_6)][\text{BAr}^f_4]$, (PONOP)Ir(Cl), and (PONOP)Rh(Cl) have been previously described in the literature. The abbreviation of BAr^f_4 is used to represent the counterion tetrakis(3,5-trifluoromethylphenyl)borate. The ^{1}H and ^{13}C spectral data for BAr^f_4 in CD_2Cl_2 are the same for all complexes listed and therefore not reported in the characterizations below. **BAr^f_4**: ^{1}H NMR (CD_2Cl_2): δ 7.72 (s, 8H, H_o), 7.56 (s, 4H, H_p). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.2 (q, $J_{\text{C−B}}$ = 37.4 Hz, C_{ipso}), 135.2 (C_o), 129.3 (q, $J_{\text{C−F}}$ = 31.3 Hz, C_m), 125.0 (q, $J_{\text{C−F}}$ = 272.5, CF_3), 117.9 (C_p). Elemental analyses were performed by Robertson Microlit Laboratories Inc. in Madison, NJ or Atlantic Microlab Inc. in Norcross, GA.[25]

In Situ Generation. ***$[(\text{POCOP})\text{IrH}(\text{H}_2)][\text{BAr}^f_4]$ (1-H_3).*** A solution of $[(\text{POCOP})\text{Ir}(\text{H})(\text{C}_3\text{H}_6)][\text{BAr}^f_4]$ (10 mg, 0.0066 mmol) in methylene chloride-d_2 (0.5 mL) was added to a medium-walled screw cap NMR tube. H_2 was purged through solution at −78 °C, shaking the tube occasionally for 2 min. ^{1}H NMR (500 MHz, CD_2Cl_2, 173 K): δ 7.16 (bs, 1H, 1-H), 6.82 (d, $^3J_{\text{H−H}}$ = 6.0 Hz, 2H, 2-H), 1.17 (m, 36H, P(tBu)$_2$), 0.3 (b, 2H, H_2), −41.88 (t, $J_{\text{P−H}}$ = 12.1 Hz, 1H, IrH). At 295 K, the hydride resonance is a broad singlet at −14 ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 173 K): δ 194.7.

$[(\text{POCOP})\text{Ir}(\text{D})(\text{D}_2)][\text{BAr}^f_4]$ 1-D_3. $[(\text{POCOP})\text{Ir}(\text{D})(\text{D}_2)]$ $[\text{BAr}^f_4]$ was generated using the same procedure as **1-H_3** with the addition of deuterium gas instead of hydrogen gas.

$[(\text{POCOP})\text{Ir}(\text{H/D})(\text{H}_2/\text{HD}/\text{D}_2)][\text{BAr}^f_4]$. The partially deuterated sample was generated as above, with appropriate mixtures of H_2 and D_2.

*(POCOP)Rh(H_2) **(2-H_2)**.* The dihydride can be generated directly from the hydrido-chloride[16] by reaction with (Et_2O)Li−N(SiMe$_3$)$_2$ under an atmosphere of hydrogen. ^{1}H NMR (500 MHz, C_6D_{12}): δ 6.65 (t, $^3J_{\text{H−H}}$ = 8.0 Hz, 1H, 1-H), 6.35 (d, $^3J_{\text{H−H}}$ = 8.0 Hz, 2H, 2-H), 1.21 (vt, J = 6.8 Hz, 36H, P(tBu)$_2$), −3.27 (br d, $J_{\text{Rh−H}}$ = 18.5 Hz, 2H, Rh(H_2)). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 219.10 (d, $J_{\text{Rh−P}}$ = 167 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_{12}): δ 168.80 (Ar), 126.34 (Ar), 104.6 (Ar), 39.10 (C(CH$_3$)$_3$), 29.05 (C(CH$_3$)$_3$). One Ar−C resonance not detected.

*$[(\text{PONOP})\text{Ir}(\text{C}_2\text{H}_4)][\text{BAr}^f_4]$ **(3-C_2H_4)**.* A heavy-walled glass reaction vessel was charged with 0.020 g (0.032 mmol) of (PONOP)Ir−Cl, 0.026 g (0.029 mmol) of NaBAr^f_4, and 10 mL of methylene chloride. On a vacuum line, 1 atm of ethylene was added at ambient temperature, and the orange solution was stirred for 3 days. The volatiles were removed in vacuo, the residue was extracted in a minimal amount of methylene chloride (*ca.* 1 mL), filtered through Celite, and layered with pentane at −35 °C to afford 0.031 g (66%) of **3-C_2H_4** as orange needles. Calcd for $C_{55}H_{55}IrNP_2O_2BF_{24}$: C, 44.55; H, 3.74; N, 0.94. Found: C, 44.28; H, 3.60; N, 0.90. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.98 (t, $^3J_{\text{H−H}}$ = 8 Hz, 1H), 6.97 (d, $^3J_{\text{H−H}}$ = 8.0 Hz, 2H), 3.42 (vt, J = 4 Hz, 4H, C_2H_4), 1.38 (vt, 36H, J = 6.5 Hz, P(tBu)$_2$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 188.8. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ 28.1 (vt, 3.3 Hz, P−C(CH$_3$)$_3$), 39.1 (C_2H_4), 42.9 (vt, 9.0 Hz, P-C(CH$_3$)$_3$), 103.1, 146.2, 161.5 (C_6H_3N).

[(PONOP)Ir(H)$_2$][BAr$^f_4$] (3-H$_2$). A heavy-walled glass reaction vessel was charged with 0.050 g (0.034 mmol) of **3-C$_2$H$_4$** and 10 mL of methylene chloride. On a vacuum line, the solution was frozen at −196 °C and 1 atm of dihydrogen was admitted to the vessel. The solution was warmed to ambient temperature and stirred for 8 h. The volatiles were removed in vacuo, the residue extracted in a minimal amount of methylene chloride (ca. 1 mL), filtered through Celite, and layered with pentane at −35 °C to afford 0.035 g (71%) of **3-H$_2$** as orange blocks. ^{1}H NMR (400 MHz, C_6D_5Cl): δ 8.00 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.09 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 1.34 (vt, 36H, J = 8 Hz, P(tBu)$_2$), −25.07 (vt, J = 12 Hz, 2H, IrH). ^{31}P{^{1}H} NMR (162 MHz, C_6D_5Cl): δ 206.8. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_5Cl): δ 26.8 (vt, 3.1 Hz, P−C(CH_3)$_3$), 41.2 (vt, 10.7 Hz, P-C(CH_3)$_3$), 103.3, 146.1, 163.3 (C_6H_3N).

[(PONOP)Rh(C$_2$H$_4$)][BAr$^f_4$] (4-C$_2$H$_4$). A heavy-walled glass reaction vessel was charged with 0.050 g (0.093 mmol) of (PONOP)Rh−Cl, 0.083 g (0.093 mmol) of NaBAr$^f_4$, and 10 mL of methylene chloride. On a vacuum line, 1 atm of ethylene was added at ambient temperature, and the yellow solution was stirred for 8 h. The volatiles were removed in vacuo, the residue was extracted in a minimal amount of methylene chloride (ca. 1 mL), filtered through Celite, and layered with pentane at −35 °C to afford 0.059 g (45%) of **4-C$_2$H$_4$** as yellow needles. Calcd for $C_{55}H_{55}RhNP_2O_2BF_{24}$: C, 47.40; H, 3.98; N, 1.01. Found: C, 47.17; H, 3.75; N, 1.01. ^{1}H NMR (23 °C, CD_2Cl_2): δ 1.36 (vt, 7.6 Hz, 36H, P−C(CH_3)$_3$), 3.71 (m, 4H, C_2H_4), 6.88 (d, 8.4 Hz, 2H, m-C_6H_3N), 7.88 (t, 8.4 Hz, 1H, p-C_6H_3N). ^{31}P{^{1}H} NMR (23 °C, CD_2Cl_2): δ 211.8 (d, 124 Hz). ^{13}C{^{1}H} NMR (23 °C, CD_2Cl_2): δ 27.9 (vt, 4.0 Hz, P−C(CH_3)$_3$), 42.0 (m, P-C(CH_3)$_3$), 52.2 (C_2H_4), 103.4, 145.6, 163.9 (C_6H_3N).

[(PONOP)Rh(H$_2$)][BAr$^f_4$] (4-H$_2$). **4-H$_2$** was prepared in a fashion similar to **3-H$_2$** in 65% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.90 (t, $^3J_{H-H}$ = 8 Hz, 1H), 6.91 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 1.32 (vt, 36H, J = 8 Hz, P(tBu)$_2$), −8.26 (dt, J_{Rh-H} = 27.6 Hz, J_{P-H} = 4.4 Hz, 2H, RhH). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 224.6 (d, J_{Rh-P} = 126.4 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ 27.8 (vt, 4.0 Hz, P−C(CH_3)$_3$), 40.4 (m, P-C(CH_3)$_3$), 103.9, 146.5 (C_6H_3N), one C_6H_3N signal not located.

■ ASSOCIATED CONTENT

Supporting Information

Calculations of exchange rates of D and H in **1-H$_3$** and k_H/k_D. Detailed calculation of H−H distances in dihydrogen complexes. Sample NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

The authors declare no competing financial interest.

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