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Observation of New Intermediates in the Reaction of Dihydrogen with Iridium, Rhodium, and Mixed Metal A-Frame Complexes with Parahydrogen-Induced Polarization

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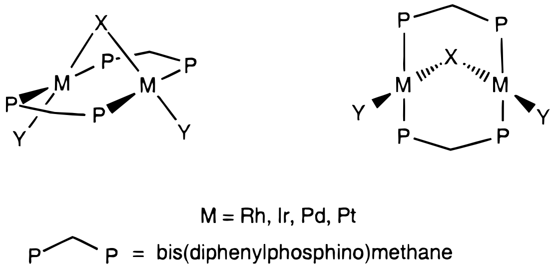
The reaction of hydrogen with iridium and rhodium μ-S A-frame complexes has been investigated using parahydrogen-induced polarization (PHIP) NMR spectroscopy. The reaction of $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ where dppm = bis(diphenylphosphino)methane with hydrogen proceeds by two addition pathways corresponding to oxidative addition inside (endo) and outside (exo) the pocket of the A-frame complex. The exo addition pathway yields a kinetically significant dihydride that has not been previously reported. This species is a key intermediate in the formation of the thermodynamic product of the reaction system. Also present are polarized resonances for the addition of hydrogen to the mixed metal A-frame, $IrRh(\mu\text{-}S)(CO)_2(dppm)_2$, formed as a contaminant from rhodium present in the iridium trichloride starting material. To confirm this observation, $IrRh(\mu\text{-}S)(CO)_2(dppm)_2$ was prepared independently and its reaction with parahydrogen was investigated, leading to results supporting endo addition H_2 as the major pathway and exo addition as a minor reaction channel. The complex $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$, which had not previously been found to react with dihydrogen, generates polarized hydride signals under para-enriched hydrogen, showing that an equilibrium is established between the complex and its H_2 adduct. In all of these cases, PHIP is used to detect species not readily seen by normal NMR spectroscopy and to investigate the mechanism of these reactions.

Introduction

A-frame complexes, **A**, were first synthesized in the late 1970s[1] and have been actively investigated for possible catalytic properties and as models for catalytic systems with more than one metal center.[2−5] In A-frame complexes, the two metal centers possess square-planar or distorted square-planar coordination geometries with the extent of the metal−metal interaction determined by electron count. The coordination geometries include a common bridgehead atom or group X and two bidentate ligands such as bis(diphenylphosphino)methane, dppm, that bridge the two metal ions. Understanding how the two metal ions interact with each other and determining whether transformations occur at one or both metal centers are questions of great importance.



A

One set of initially reported A-frame complexes contained sulfide at the bridgehead position with either Rh(I) or Ir(I) as the metal ions and CO as the remaining terminal ligand (Y). The interaction of A-frame complexes with small molecules has been a source of continuing investigations. The iridium A-frame complex $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ was found to add CO reversibly and react with H_2 to generate a number of different hydride complexes.[3,6] The corresponding rhodium system $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$ was found not to react with H_2 at all.[1,2] The reaction of the iridium A-frame complex with H_2 has been the subject of several reports with products identified by their NMR spectra as described below. In the analysis of this reaction chemistry, hydrogen addition to the iridium A-frame complex was thought to proceed by endo attack, i.e., in the pocket between the two metal centers. While no evidence was

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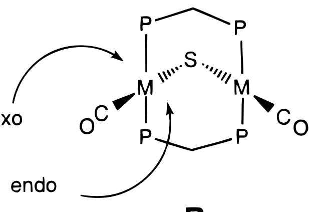
found for exo attack on the opposite sides of the square-planar coordinated metal ions (see **B**), it could not be definitively eliminated. The mixed iridium and rhodium metal system $IrRh(\mu\text{-}S)(CO)_2(dppm)_2$ was also reported to generate a dihydride complex upon reaction with dihydrogen.[7] Although the reactions of these μ-S A-frame complexes with dihydrogen had been investigated previously, we undertook the present study to expand these earlier observations with new experiments employing parahydrogen.



B

Parahydrogen-induced polarization (PHIP) has been used in a number of studies to provide direct evidence of pairwise addition of dihydrogen to metal centers and unsaturated substrates[8−11] and has allowed for the observation of previously undetected species, including low concentration reaction intermediates.[12−16] Parahydrogen is one of two spin isomers of dihydrogen and corresponds to the nuclear spin “singlet”. PHIP can be observed if parahydrogen adds to a metal complex or an organic substrate in a pairwise manner such that spin correlation is maintained between the two transferred protons that originate from the same H_2 molecule. If longitudinal relaxation of these protons is not much greater than the rate of hydrogen addition, then non-Boltzmann populations in the proton spin states can result, leading to enhanced absorption and emission lines in the product NMR spectrum. Signal enhancements of up to 1000-fold have been observed.[14,17] For the observation of PHIP, dihydrogen addition should lead to products in which the transferred protons are magnetically distinct and J coupled to each other, although a somewhat weaker PHIP effect has been reported recently for products having equivalent hydrides.[14,18] Several recent reviews and articles discuss various aspects of parahydrogen-induced polarization in detail including product operator formulations to facilitate analysis of the spin physics of PHIP.[8,10,11,18,19]

Because of the large signal enhancements, normally unobservable, low-concentration species have been observed and characterized using this technique. For example, PHIP has made possible the observation and identification of hydrogen oxidative addition products to $RhX(CO)L_2$ [X = Cl, Br, I] which had not previously been recognized.[13,15,20] Specifically, binuclear μ-X and μ-H species were observed and characterized as reaction products even though they formed in only very minor amounts. Similar species were also identified by PHIP during hydrogenation catalysis using Wilkinson’s catalysis, $RhCl(PPh_3)_3$, and the olefin dihydride catalytic intermediate in this system was observed.[12] In catalysis of styrene hydrogenation promoted by the cationic precatalyst $Rh(COD)(dppb)^+$ (dppb = 1,4-bis(diphenylphosphino)butane), PHIP allowed the observation of an η^6-styrene-coordinated catalytic intermediate by Giernoth et al.[16]

The present study describes the use of PHIP to investigate further the mechanism of hydrogen addition to iridium and rhodium A-frame complexes. It was thought that the signal enhancements of PHIP in 1-D ^1H NMR spectroscopy and in polarization transfer in homonuclear (COSY, NOESY/EXSY) and heteronuclear (HMQC) 2-D NMR spectroscopies would allow for the characterization of new dihydride products and the identification of key kinetic intermediates in the reaction sequence. The results reported below confirm this notion. In fact, the sensitivity of PHIP leads to the unexpected observation of the mixed IrRh A-frame complex in a sample prepared from what was thought to be a pure iridium precursor. The presence of the mixed IrRh system, which would not have been detected by regular NMR spectroscopy, underscores the importance of purity when considering homogeneous catalysis by platinum group element complexes and the value of PHIP in examining such systems.

Results and Discussion

The Iridium A-Frame System. Previous work has shown that reaction of the iridium A-frame complex $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$, **1**, with hydrogen proceeds to generate several hydride complexes.[3,6] As shown in Scheme 1 developed from the results of Vaartstra et al.,[6] H_2 reacts to give initially the dihydride complex **2**, in which reaction has occurred inside the pocket of the A-frame complex, i.e., by endo attack. At room temperature, only one hydride resonance in the ^1H NMR spectrum and one phosphorus resonance in the ^{31}P NMR spectrum were observed, suggesting a symmetrical dihydride complex having a structure **2a** or **2b**. The fluxional nature of **2** was revealed by a variable-temperature NMR investigation. Upon cooling the sample to −90 °C, the hydride resonance was reported to decoalesce into two resonances in the ^1H NMR spectrum, and in the ^{31}P NMR spectrum at this temperature, two phosphorus resonances were observed. The results were consistent with the initial formation of the proposed endo addition product **2** and subsequent equilibration of hydride ligands via **2a** or **2b** as an intermediate or possibly as a transition state for the fluxional process.

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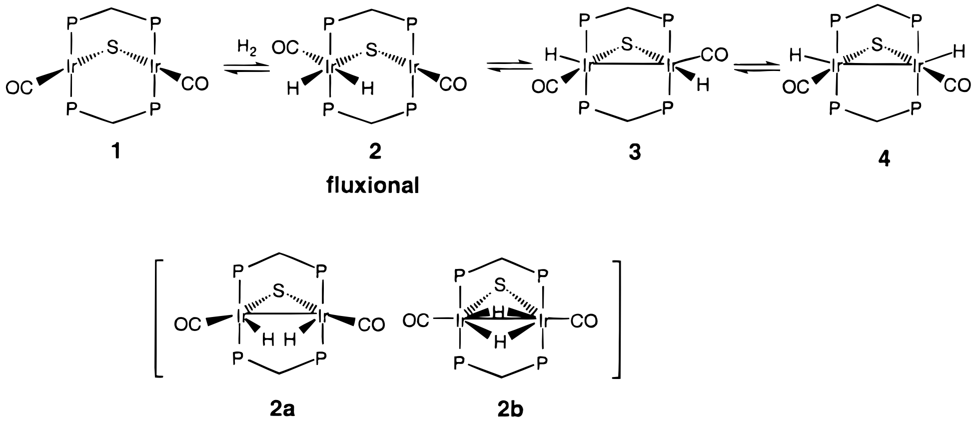
Scheme 1



Further reaction of the system was reported to lead to the formation of complex **3**, an unsymmetrical dihydride complex characterized by two hydride resonances in the ^1H NMR spectrum and two multiplets in the ^{31}P NMR spectrum. Selective decoupling of each phosphorus resonance caused one of the hydride resonances of **3** in the ^1H NMR spectrum to collapse into a singlet, establishing that the two hydride ligands were coordinated to different metal centers. Also formed with **3** was the thermodynamic product, complex **4**, which contains equivalent terminal hydride ligands, in which both hydride ligands reside outside the pocket in a linear arrangement with the metal centers. Complex **4** was characterized by one phosphorus resonance in the ^{31}P NMR spectrum and one hydride resonance in the ^1H NMR spectrum. The ^1H and ^{31}P nuclei in **4** belong to an AA′XX′X″X‴ spin system, as demonstrated by simulation.

The 1-D PHIP experiments were performed as has been described previously.[9,12,21] Frozen samples of **1** or ^{13}CO-labeled **1** were placed under ca. 3 atm of para-enriched H_2. When a series of runs was commenced, a sample was thawed, shaken, and rapidly inserted into the spectrometer with transients of varying numbers of scans collected frequently over a 5−10 min time interval. After polarization had decayed to background, the sample was removed from the spectrometer, re-shaken to reestablish para-enriched H_2 in the reaction solution, and placed back in the spectrometer to reveal new PHIP resonances from species reacting directly with H_2. In Figure 1a, the spectrum is shown of a sample obtained after several shake-and-collect cycles. The products identified previously by Vaartstra et al.[6] are clearly observed. The hydride resonance of the fluxional endo addition product **2**, which appears at −10.6 ppm, is in weak net emission, vide infra. The two triplets at −10.3 and −11.7 ppm are the hydride resonances of the unsymmetrical dihydride complex **3**, while the resonance at −10.1 ppm corresponds to the symmetrical dihydride complex **4**, which is the ultimate thermodynamic product of the system. The most prominent features of the spectrum, however, are two polarized resonances of a previously unobserved product, **5**. Another smaller set of polarized resonances is also present in these spectra, and they too result from a previously unknown product, **8**, described below.

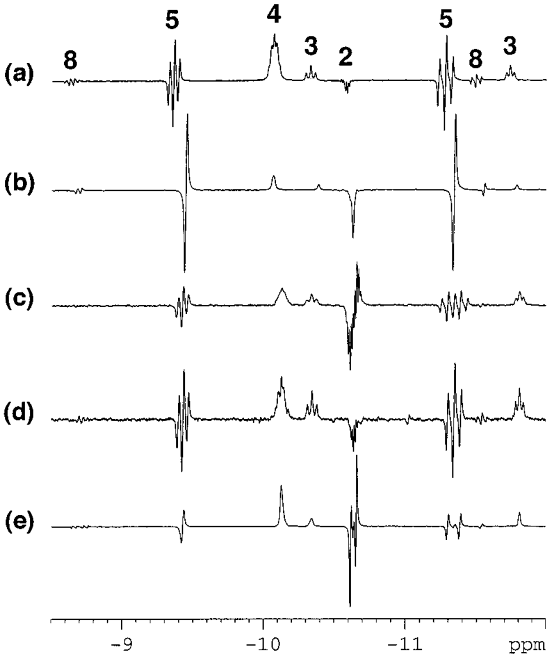


Figure 1. Hydride region of PHIP spectra obtained using a sub-milligram sample of $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$, **1**, and para-enriched hydrogen in 50/50 benzene-d_6/toluene-d_8. (a) ^1H spectrum at 343 K. (b) $^1H\{^{31}P\}$ spectrum at 363 K. (c) ^1H spectrum of ^{13}C-labeled sample at 323 K. (d) $^1H\{^{13}C\}$ spectrum of ^{13}C-labeled sample at 323 K. (e) $^1H\{^{31}P\}$ spectrum of ^{13}C-labeled sample at 323 K.

In the 1-D PHIP spectrum of the reaction system, the two hydride resonances of **5** are observed as triplets of antiphase doublets (−9.36 and −11.27 ppm with $^2J_{HH}$ = 6 Hz). Data for complex **5** are listed in Table 1. The value of $^2J_{HH}$ for **5** was determined directly from the separation between nearest antiphase peaks (a negligible error is introduced by this procedure when the line width is significantly narrower than $^2J_{HH}$, as is the case here; when not, the measured coupling is slightly larger than the actual coupling). The ^{31}P coupling to the two hydride resonances differs ($^2J_{PH}$ = 13 and 19 Hz, respectively), and both resonances simplify to antiphase doublets upon ^{31}P decoupling, Figure 1b. A modified $^1H-^1H\{^{31}P\}$ COSY spectrum,[11,15,22] which is accomplished more easily and rapidly than selective homonuclear decoupling, reveals protons that are *J* coupled

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Table 1. ^1H, ^{31}P, and ^{13}C NMR Data from PHIP Experiments[a]

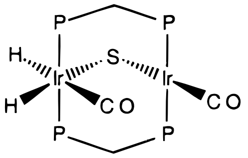
complex	^1H	^{31}P	^{13}C
5	-9.36 (td, $^2J_{PH} = 13$, $^2J_{HH} = 6$, $^2J_{CH} \cong 3$)	3.3	200.8
	-11.27 (td, $^2J_{PH} = 19$, $^2J_{HH} = 6$, $^2J_{CH} = 35$)		
8	-8.64 (dtd, $^1J_{RhH} = 13$, $^2J_{PH} = 12$, $^2J_{HH} = 5$, $^2J_{CH} = 33$)	23.5 ($^1J_{RhP} = 156$)	172.5
	-11.49 (td, $^2J_{PH} = 14$, $^2J_{HH} = 5$, $^2J_{CH} \cong 4$)	-2.6	
9	-10.02 (td, $^2J_{PH} = 19$, $^2J_{HH} = 7$, $^2J_{CH} = 22$)		
	-10.27 (td, $^2J_{PH} = 13$, $^2J_{HH} = 7$, $^2J_{CH} = 13$)		
11	-10.44 (tdd, $^1J_{RhH} = 19$, $^2J_{PH} = 16$, $^2J_{HH} = 9$)	35.2	
	-16.42 (tdd, $^1J_{RhH} = 22$, $^2J_{PH} = 14$, $^2J_{HH} = 9$)		

[a] δ in ppm, J in Hz.

to each other, showing two cross-peaks between the hydride resonances.

To gain more structural information about **5** (as well as the previously reported species **2**−**4**), ^{13}CO-labeled complexes were prepared by placing an NMR tube sample of **1** under an atmosphere of ^{13}CO for 48 h followed by reaction with para-enriched H_2. The PHIP spectrum of ^{13}CO-labeled **5** reveals that the hydride ligand which resonates at δ −9.36 is cis to CO ($^2J_{CH} \cong$ 3 Hz), while the other hydride at δ −11.27 is trans to CO ($^2J_{CH} = 35$ Hz) (see Figure 1c). When the spectrum of ^{13}CO-labeled **5** is ^{13}C-decoupled (Figure 1d), a spectrum similar to that of Figure 1a is obtained. Decoupling of the ^{31}P nuclei in the PHIP spectrum of the ^{13}CO-labeled sample causes the ^1H resonances of **5** to simplify such that only $^2J_{HH}$ and $^2J_{CH}$ couplings are observed, as shown in Figure 1e. The much smaller polarized peak inside the hydride resonance at −11.27 ppm in Figure 1e corresponds to the respective hydride resonance of unlabeled **5**. The phosphorus and carbon resonances that were coupled to the hydride ligands of **5** were detected with modified heteronuclear multiple quantum correlation (HMQC) NMR experiments. In these experiments, the first proton pulse was replaced by a $\pi/4$ pulse, while the rest of the sequence remained as in a standard HMQC experiment.[11,23,24] In this way, the ^{31}P resonance at 3.3 ppm and the ^{13}C resonance at 200.8 ppm were found to be coupled to the hydride resonances of **5**.

The results of all of the spectra of Figure 1 lead to assignment of a coordination sphere for dihydride complex **5**. There are two cis hydride ligands, CO trans to one of the hydride ligands, two mutually trans phosphine donors from dppm, and an anionic ligand X trans to the other hydride ligand. The resonances, however, are different from those seen by low-temperature NMR for the endo H_2 addition product **2**. All of the evidence can be accommodated by assignment of the polarized resonances of **5** to the exo H_2 addition product. Additional 2-D methods described below further support this assignment. In this Ir(III)−Ir(I) binuclear species, the resonances for the Ir(I)-bound ^{31}P nuclei and in the labeled compound the carbonyl ^{13}C nucleus are not observed since they are not coupled to the polarized hydrides of the Ir(III) center.



5

The polarization seen for **5** indicates that it is a kinetically significant species in that it is generated by direct reaction of **1** with H_2. The magnitude of the polarization, which is determined by a number of factors including the rate and reversibility of the H_2 addition reaction, indicates that **5** is kinetically important. For two species with the same concentration and similar structure, it is expected that the one which reacts with or exchanges H_2 more rapidly will have the larger polarization. This does not necessarily mean that the species with the larger polarization will lead directly to the thermodynamically controlled product, but rather that in the initial reaction with H_2 its rate of formation appears to be qualitatively greater. Further studies outlined below indicate that **2** and **5** are indeed the initial hydrides formed in the reaction of $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ (**1**) with H_2 and that **5** does connect to the thermodynamic product of the system **4**. The fact that **5**, as a kinetically important species, is detected readily by PHIP, but was not observed in the earlier studies, attests to the value of PHIP as a means of studying H_2 activation by metal complexes.

We noted above that in the PHIP spectrum the resonance for **2** appears in weak but discernible emission (Figure 1a). Subsequent experiments at different temperatures and in different solvents showed that the magnitude of the polarization for **2** was variable. At 353 K for example, the resonance for **2** was in emission, whereas at 298 K it appears as a possibly enhanced absorption. Quantification of the magnitude of signal enhancement for **2** was not readily feasible on the basis of the variability of polarization observed in runs done under similar conditions. Complex **2**, which forms by endo H_2 addition to the parent iridium A-frame complex **1**, has already been shown to be fluxional with the two hydride ligands exchanging positions in a manner as to equilibrate all four phosphine donors (^{31}P nuclei).[6] In view of the apparent equivalence of the two hydride ligands of **2**, polarization of the corresponding resonance at −10.6 ppm was unexpected. However, recent reports have shown that signal enhancement, possibly weak, can occur in systems having equivalent hydride ligands. For example, Duckett et al.[14] describe a 60-fold enhanced absorption in the single hydride resonance of the trans, cis, cis isomer of $Ru(AsMe_2Ph)_2H_2(CO)_2$, which may be compared with a 1035-fold increase in the resonances for the chemically different hydrides in the corresponding all-cis isomer of $Ru(AsMe_2Ph)_2H_2$-

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$(CO)_2$. In a different report, Aime et. al.[18] report positive enhancement of the single hydride resonance of $Os_3H_2(CO)_{10}$ formed by H_2 addition to $Os_3(MeCN)_2(CO)_{10}$. The signal enhancement in these cases, as explained by Aime et al., arises when the dihydride product (an A_2 system) is formed via the intermediacy of an AX spin system. Through a relaxation mechanism involving cross-correlation between dipolar interaction and chemical shift anisotropy, enhanced magnetization in the $Os_3H_2(CO)_{10}$ hydride resonance was generated. The situation for **2** is complicated by its fluxionality, the second-order nature of its spin system, and possibly the fact that several different hydride species are present in solution, including pairs interconnected by exchange reactions (vide infra). On the basis of the analysis of Aime et al., the weak net emission for **2** may result from the intermediacy of the endo H_2 addition product shown in Scheme 1, which is an AX ^1H spin system, and a relaxation mechanism involving efficient cross-correlation between dipolar interaction and chemical shift anisotropy.[18]

The spin system associated with **2** becomes more complex when a ^{13}CO-labeled precursor is employed. Thus, when ^{13}CO-labeled **1** is used in the reaction system, polarization in the resonance for **2** can be more substantial, as seen in Figure 1c with what appears to be an overall antiphase coupling of 19 Hz as part of a complex resonance pattern. Decoupling of ^{31}P nuclei greatly simplifies this pattern with major absorption and emission lines separated by 19 Hz (Figure 1e), which is too large for $^2J_{HH}$. In fact, the value of 19 Hz nearly equals the average of cis and trans $^2J_{CH}$ found for ^{13}CO-labeled **5**. A possible explanation involves the addition of p-H_2 to yield a complex second-order spin system. Although the hydrides and the two carbonyl ligands in the averaged structure of **2** are chemically equivalent, they are magnetically distinct. Antiphase transitions may thus connect components that include a J_{HH} term. Several examples of this have been reported.[14,23] Another qualitative explanation involves partial polarization transfer from the added ^1H nuclei to the ^{13}C nucleus to which they are coupled, which in turn leads to antiphase lines in the ^1H resonances separated by ca. J_{CH}. Examples of such polarization transfer have been reported as in the ^{31}P resonances of the kinetic isomer of the oxidative addition of p-H_2 to IrX(CO)(dppe) (dppe = bis(diphenylphosphino)ethane).[25]

A more complete analysis of the PHIP spectra of ^{13}CO-labeled **2** will require further work. The averaged structure of ^{13}CO-labeled **2** corresponds to an AA′XX′ system. Recently, Bargon and co-workers have developed a theoretical framework for the analysis of polarization spectra for an AA′X spin system.[26] The treatment based on a complete density approach follows the evolution of zero quantum coherence contained in the parahydrogen density operator. It follows an earlier analysis of the AA′X spin system in PHIP spectra based on populations of the spin system energy levels and how they are influenced by S/T_0 mixing at the catalyst center.[27] While Bargon's work is directed to the analysis of organic hydrogenation products and information that PHIP can provide for reaction intermediates, its extension may well be relevant for the case of fluxional ^{13}CO-labeled **2**.

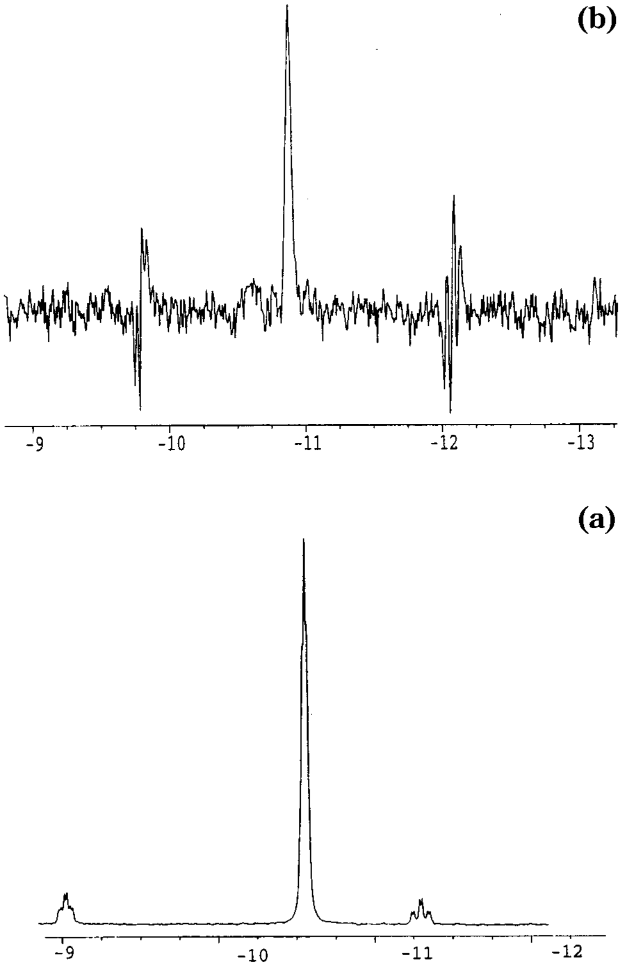

Figure 2. (a) Hydride region of the reaction system **1** + p-H_2 in 50/50 benzene-d_6/toluene-d_8 at 268 K after 20 min of reaction; (b) hydride region of the reaction system **1** + p-H_2 in CD_2Cl_2 at 298 K after 5 min of reaction.

While the experiments leading to the spectra in Figure 1 confirm or characterize the hydrides **2**−**5**, they provide no direct evidence, aside from PHIP, of the time evolution of these hydrides or their kinetic significance. In a different set of experiments, the reaction system of $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ (**1**) + H_2 was examined in different solvents at various temperatures and earliest reaction times. In 1:1 toluene-d_8/benzene-d_6, the first and only hydrides seen at 298 K and lower are **2** and **5**, corresponding respectively to endo and exo addition of H_2 to A-frame complex **1**. The cycling of H_2 by reductive elimination and oxidative addition at 298 K and lower is very slow so that the resonances of **2** and **5** appear with little or no polarization. In these early spectra at lower temperatures, **2** appears initially and is more pronounced in terms of intensity. A spectrum of the system at 268 K taken with 256 scans after 20 min of reaction is shown in Figure 2a. As the temperature is raised above 330 K, the rate of hydrogen cycling increases to the point that significant polarization is seen in the resonances of **5** after para-enriched hydrogen

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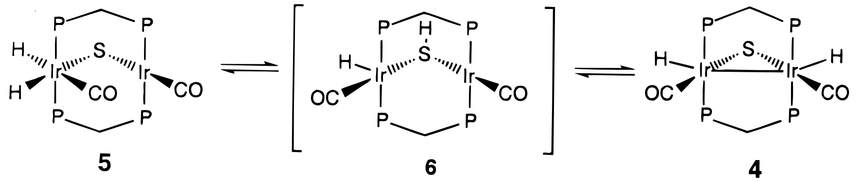
Scheme 2



has been reestablished in solution by shaking of the sample. The extent of polarization in the hydride resonance of **2** at this point is uncertain. The resonance, which is initially more strongly absorbing at 268 K, becomes weakly emissive at 343 K and more strongly emissive at 353 K.

In CD_2Cl_2, a similar result is obtained at 298 K and earliest reaction times, only **2** and **5** are observed, with **2** more intense and **5** weakly polarized. Parenthetically, we note that it is also possible to observe both hydride species at early reaction times in the **1** + H_2 system in CD_2Cl_2 using normal hydrogen. As the reaction is allowed to progress, a very weak resonance for the ultimate thermodynamic product **4** is seen without evidence for **3**. This latter observation has important mechanisitic implication in that it was originally proposed that **3** is an intermediate in the formation of **4**. This is discussed further below. Figure 2b shows the system after 5 min of reaction with **5** polarized, although not greatly enhanced, and the first evidence for the formation of **4**. At 318 K and later reaction times under para-enriched H_2, the resonances for **2**−**5** are all seen, with those of **5** being very weak and little polarized. Because of differences in the nature of the polarization of **2** and **5**, it is not possible to estimate the relative rates for the endo and exo paths of H_2 addition to A-frame complex **1**, but it is evident that **2** and **5** are the initial H_2 oxidative addition products.

A modified 2-D NOESY/EXSY experiment[11,22] was carried out to confirm the close internuclear distances by NOE between the hydride ligands in the different species formed, as well as to explore the possibility of intramolecular structural rearrangement involving the hydride ligands (e.g., rearrangement of **5** to **4**). The 2-D NOESY was modified because in the present case antiphase parahydrogen magnetization must first be refocused. This was achieved by adding the refocusing sequence $d_2-\pi-d_2$ after the initial $\pi/4$ pulse, where $d_2 = 1/4\ J_{HH}$, before the rest of the pulse sequence. Both negative cross-peaks, due to NOE, and positive cross-peaks due to chemical exchange were observed (Figure 3). The two hydride resonances for complex **5** are connected by negative cross-peaks, in support of the close spatial proximity of the hydride ligands. A positive cross-peak is observed that connects the hydride resonances of **5** and the hydride resonance of complex **4**, indicating that **5** converts into **4** on the time scale of the experiment. A mechanism for the conversion of complex **5** into **4** is suggested in Scheme 2, through transfer of one of the hydride ligands across the sulfur bridge to the other iridium metal center. The suggested intermediate in this process, **6**, has been observed at −60 °C previously by McDonald and Cowie.[28] If **5** does convert to **4** through an intermediate such as **6** with an SH bond, the lifetime of this species is too short to allow detection using the present experimental procedures.

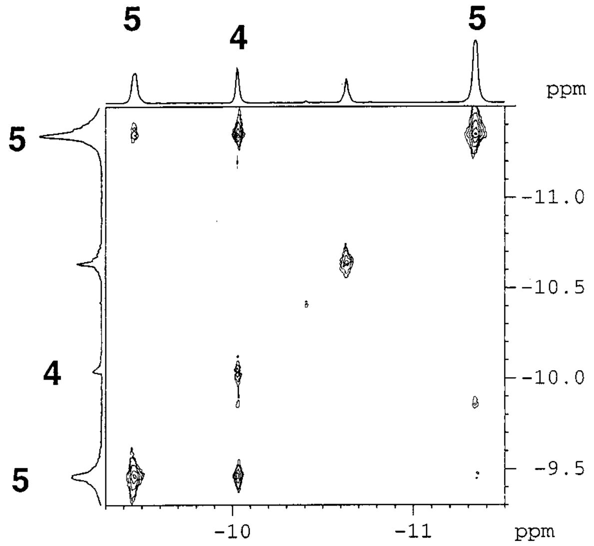


Figure 3. The 2-D NOESY/EXSY NMR spectrum obtained using a sub-milligram sample of **1** and para-enriched hydrogen at 363 K in 50/50 benzene-d_6/toluene-d_8.

The results from the parahydrogen experiments lead to a substantial revision of the proposal for the addition of dihydrogen to the iridium A-frame complex **1** (Scheme 3). A previously undetected dihydride complex **5**, resulting from the exo addition of hydrogen to **1**, has been identified and is kinetically significant, as shown by its PHIP signature. Experiments at 298 K show that only **5** and the endo addition product **2** are seen initially, with the latter favored qualitatively. The early observations also show that the thermodynamic product **4** emerges prior to **3**, in contrast with that proposed previously, while the NOESY/EXSY experiment has demonstrated that **4** forms from the exo H_2 addition product **5**. When hydrogen is removed from the system containing **2**, **3**, and **4**, the disappearance of **2** is noted initially with regeneration of **1**. At longer times and elevated temperatures, the non-PHIP active complexes **3** and **4** decrease in intensity as those of **1** increase in intensity. All of these results are accommodated in the reaction scheme by two independent pathways. One pathway corresponds to endo attack as proposed previously and the other to exo attack leading to the previously unseen kinetic intermediate **5** and ultimately to the thermodynamic product of the system, **4**.

Iridium Rhodium A-Frame. A smaller set of polarized resonances is also seen in the PHIP spectra of H_2 addition to the iridium A-frame complex **1** at −8.64 (a doublet of triplets of antiphase doublets) and −11.49 ppm (a triplet of antiphase doublets) (Figure 1a). The $^1H-^1H\{^{31}P\}$ COSY spectrum gives cross-peaks between these resonances, and the antiphase coupling between these resonances corresponds to $^2J_{HH}$ of 5 Hz. Both

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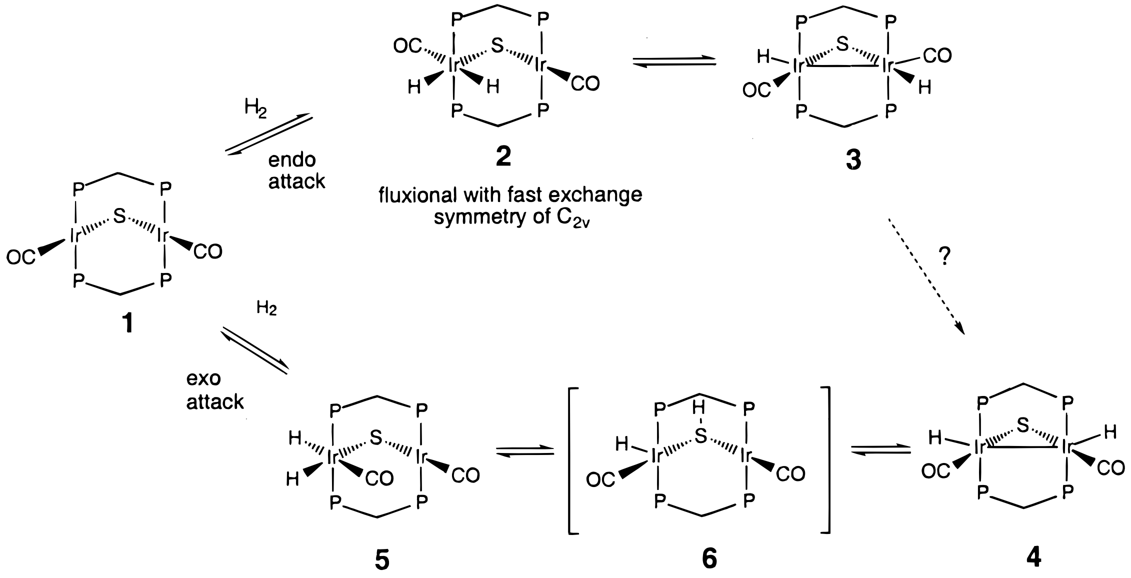
[28] McDonald, R.; Cowie, M. *Inorg. Chem.* **1993**, *32*, 1671−1680.

Scheme 3



hydride resonances are coupled to phosphorus with similar but different coupling constants, $^{2}J_{PH} = 12$ and 14 Hz. The $^{1}H\{^{31}P\}$ NMR spectrum (Figure 1b) removes the coupling to ^{31}P, simplifying the resonances, but an extra coupling of 13 Hz remains in the −8.64 ppm resonance. The ^{31}P NMR spectrum of the sample exhibits two resonances at −2.6 and 5.1 ppm, the latter of which has a large doublet coupling of 156 Hz. A modified $^{1}H-^{31}P$ HMQC shows that both hydrides couple to the phosphorus resonance at −2.6 ppm. The ^{13}CO-labeled sample reveals that the hydride ligand at −8.64 ppm has a relatively large doublet coupling of 35 Hz, while a modified $^{1}H-^{13}C$ HMQC experiment[11,23,24] yields a carbonyl resonance at 172.5 ppm that is coupled to the hydride at −8.64 ppm.

The formulation of this product was initially puzzling because of the extra coupling observed in the −8.64 ppm resonance as seen in Figure 1a. On the basis of the magnitude of the polarization of the hydride resonances, it was evident that this species was a relatively minor component of the reaction system. The existence of the extra coupling, which was definitively ruled out as due to ^{31}P or ^{13}C, led to the suggestion of ^{103}Rh in the product despite the fact that only iridium precursors were apparently used in the preparation of **1**. The existence of extra $^{1}H-^{103}Rh$ couplings had been of vital importance in assigning hydride bridges in PHIP studies of H_2 addition to $RhX(CO)(PMe_3)_2$ [X = Cl, Br, I].[13,15,20] The key to the assignment of this minor product was obtained from the work of Vaartstra and Cowie on the mixed metal A-frame complex $IrRh(\mu\text{-}S)(CO)_2(dppm)_2$, **7**.[7] Specifically, **7** was found to react with H_2 to generate an endo addition product **8** with spectroscopic characteristics nearly the same as observed by us in the minor product. In **8**, both hydride ligands are bound to the iridium metal center, but one of them possesses an additional coupling to the rhodium metal center with $^{1}J_{RhH} = 13$ Hz. This hydride ligand is in an unsymmetrical bridge because no additional coupling to the phosphine ligands bound to rhodium is observed, and the magnitude of $^{1}J_{RhH}$ is smaller than that previously reported for bridging hydride ligands between 20 and 25 Hz.[29,30] Table 1 includes spectroscopic data for **8**.

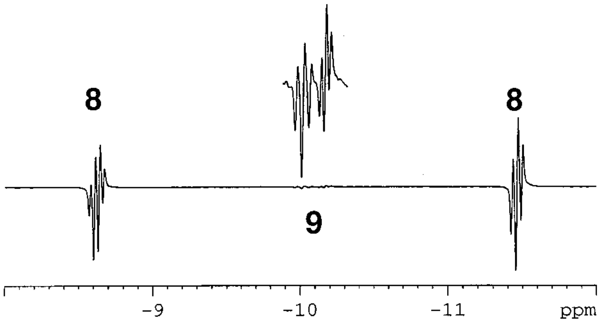


Figure 4. Hydride region of PHIP spectra obtained using a sub-milligram sample of $IrRh(\mu\text{-}S)(CO)_2(dppm)_2$, **7**, and para-enriched hydrogen at 328 K in benzene-d_6. The central hydride resonances are enlarged above the original trace.

The unexpected generation of PHIP signals due to **8** can only be explained by the presence of small amounts of $IrRh(\mu\text{-}S)(CO)_2(dppm)_2$, **7**, in the sample of **1** employed in these studies. This in turn means that there was minor contamination of iridium starting materials by the corresponding rhodium analogues. In the absence of the PHIP result, no spectroscopic or analytical evidence suggested the rhodium impurity. To prove that these resonances were in fact due to the mixed metal dihydride species, **8**, the IrRh A-frame precursor **7** was prepared independently. Reaction of parahydrogen with the authentic IrRh A-frame complex **7** results in polarized resonances shown in Figure 4 that are identical, except for their intensity, with those seen from the contaminant in the iridium A-frame sample. A PHIP spectrum of a ^{13}CO-labeled sample of **7** showed single ^{13}C couplings of 33 and 4 Hz to the two hydride resonances at −8.64 and −11.49 ppm, respectively, while a parahydrogen-modified $^{1}H-^{31}P$ HMQC experiment confirmed that both hydrides couple to the same ^{31}P nuclei that are bound to iridium. The results strongly support the view that the additional coupling

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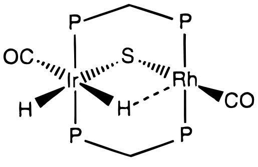
(29) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 4207−4211.

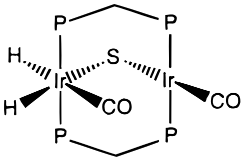
(30) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 1290−1297.

initially seen in the −8.64 ppm resonance is due to ^{103}Rh. Thus, the dominant resonances in Figure 4 correspond to the direct endo addition of H_2 to the mixed metal complex **7**.

The sensitivity of PHIP in Figure 4 also reveals the presence of much smaller polarized hydride resonances in addition to those of **8**. The resonances have similar chemical shifts (δ −10.02 and −10.27 ppm), and each exhibits coupling to two equivalent ^{31}P nuclei ($^2J_{PH}$ = 19 and 13 Hz, respectively) as well as the antiphase $^2J_{HH}$ of 7 Hz characteristic of polarized dihydride products. No rhodium coupling is observed in these resonances. The species responsible for these signals was not detected in the original iridium A-frame sample leading to Figure 1 because its resonances are much less intense than those of **8**. The absence of coupling to ^{103}Rh indicates that this product has both hydride ligands coordinated to iridium. In addition, the PHIP spectrum of the ^{13}CO-labeled sample revealed ^{13}C couplings of 22 and 13 Hz to the two hydride resonances. The most logical formulation for this previously unobserved species is that of the exo addition product **9**. Spectroscopic data for **9** are listed in Table 1.



8



9

The detection of the mixed metal complex in the iridium sample provides *an important caveat*. While much research deals with iridium systems as catalysts, it is possible that trace amounts of rhodium present in such systems could be partially, or even totally, responsible for the system's catalytic activity. If these rhodium impurities are present in very low concentration, they may under normal conditions be spectroscopically unobservable and therefore go unnoticed.

Rhodium A-Frame. It was previously reported that the rhodium A-frame complex $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$, **10**, does not react with dihydrogen.[2] However, in light of successes with PHIP to observe previously unseen H_2 addition products to $RhX(CO)(PR_3)_2$ [X = Cl, Br, I], it was deemed worthy to reexamine the reaction of **10** with H_2. If the rhodium A-frame complex **10** + H_2 is in equilibrium with a small amount of a dihydride complex **11** in low concentration, the use of PHIP could lead to its detection and characterization. In fact when the reaction is carried out using parahydrogen, two hydride resonances are observed as triplets of doublets of antiphase doublets, which resonate at −10.44 and −16.42 ppm with $^2J_{HH}$ = 9 Hz, $^2J_{PH}$ = 16 and 14 Hz, respectively (Figure 5a). Both resonances reveal phosphorus coupling, which is removed upon ^{31}P decoupling (Figure 5b). The $^1H\{^{31}P\}$ NMR spectrum shows the resonances as antiphase doublets of doublets due to proton and rhodium coupling, ($^1J_{RhH}$ = 19 and 22 Hz, respectively). The $^1H-^1H\{^{31}P\}$ COSY spectrum shows cross-peaks between the two resonances. Additionally, a phosphorus resonance at 35.2 ppm couples to the hydride resonances of this complex, as detected with the modified HMQC NMR experiment.[11,23,24] Spectroscopic data for **11** are listed in Table 1.

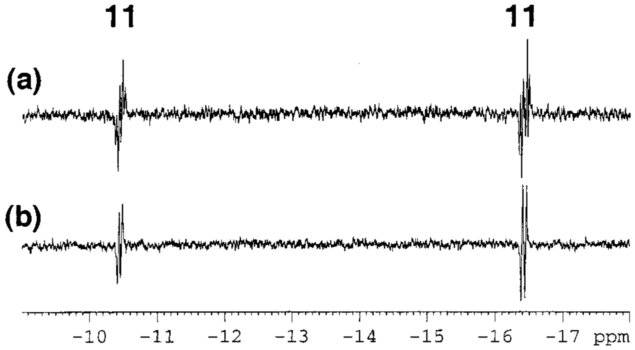
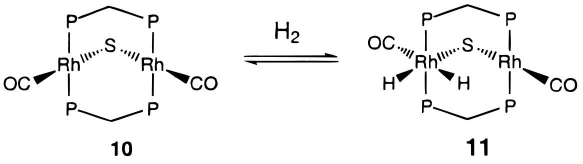


Figure 5. Hydride region of PHIP spectra obtained using a sub-milligram sample of $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$, **10**, and para-enriched hydrogen at 300 K in 50/50 benzene-d_6/toluene-d_8. (a) ^{1}H spectrum. (b) $^1H\{^{31}P\}$ spectrum.

The results clearly indicate H_2 addition to the original rhodium A-frame complex **10**. The coupling to ^{103}Rh indicates that the two hydride ligands are terminally bound to one metal center and not involved in bridging between the two rhodium atoms. Because the polarized signals are much less intense than those of the iridium analogue, less data were collected for **11** than for **5**. The experiments carried out do, however, prove that the rhodium A-frame complex does react reversibly with dihydrogen. The polarized resonances observed are a result of the dihydride complex **11**, which is in equilibrium with the starting rhodium A-frame complex, eq 1.



(1)

At this point, it is not possible to discern whether the dihydride product corresponds to endo addition or exo addition, but on the basis of the greater tendency of both **1** and **7** to undergo endo addition in the pocket of the A-frame, it seems probable that H_2 addition to **10** also proceeds preferentially via the endo pathway. While the equilibrium for eq 1 lies to the left and the dihydride complex **11** is present in only small concentration, parahydrogen-induced polarization makes possible its observation.

Conclusions

The present study provides additional evidence that parahydrogen-induced polarization (PHIP) can make possible the detection of species not otherwise observed in H_2 addition reactions using normal hydrogen. By reinvestigation of H_2 addition to the Ir A-frame complex **1** using PHIP, it was found that both endo and exo pathways of addition exist, leading to **2** and **5**, respectively, as the initial oxidative addition products. The exo addition product **5** had not been observed previously. On the basis of a modified 2-D NOESY/EXSY experiment linking **5** to the thermodynamic product **4** and the emergence of **4** relative to another intermediate **3**, a reanalysis of the mechanism for the **1** + H_2 reaction system is developed that differs considerably from that proposed previously. Also present in the sample of the Ir A-frame complex **1** was the mixed metal A-frame complex IrRh(μ-S)(CO)$_2$(dppm)$_2$ in low concentration, a result of starting material apparently contaminated with trace amounts of rhodium. Such a contamination would not normally be detected. The iridium rhodium A-frame complex, synthesized independently, is found using PHIP to react with H_2 by both endo and exo pathways of addition, the latter being seen for the first time. Finally, the rhodium A-frame complex Rh$_2$(μ-S)(CO)$_2$(dppm)$_2$ does react with H_2, yielding small equilibrium amounts of the dihydride product, a result only observable when the reaction is carried out using parahydrogen. These results reported here add to the data already available on A-frame hydrides and give a more comprehensive view for H_2 addition to A-frame complexes. Equally important, the results provide support for PHIP as an essential tool for studying the reactions of dihydrogen with metal complexes and in homogeneous hydrogenation reactions.

Experimental Section

General Methods. All complexes were prepared using standard inert-atmosphere Schlenk, vacuum line, and drybox techniques. Solvents were distilled under nitrogen immediately prior to use with toluene and benzene distilled from sodium benzophenone ketyl, and methylene chloride distilled from CaH$_2$. Anhydrous diethyl ether, 2-propanol, and methanol (Aldrich Chemical Co.), ethanol (Pharmca Prod.), and water were degassed with nitrogen prior to use. NMR solvents benzene-d_6, toluene-d_8, and methylene chloride-d_2 were purchased from Cambridge Isotopes and dried over sodium benzophenone ketyl or CaH$_2$ (methylene chloride-d_2). Bis(diphenylphosphino)methane (dppm), cyclooctene (COE), 1,5-cyclooctadiene (COD), and sodium sulfide were purchased from Aldrich Chemical Co. and used as received. Iridium trichloride hydrate and rhodium trichloride hydrate were used as received from the Johnson-Mathey Aesar/Alfa Company. Hydrogen and carbon monoxide were obtained from Air Products. ^{13}C-labeled carbon monoxide was obtained from Cambridge Isotopes. Ir$_2$(μ-S)(CO)$_2$(dppm)$_2$,[3,31] IrRh(μ-S)(CO)$_2$(dppm)$_2$,[7,32−34] and Rh$_2$(μ-S)(CO)$_2$(dppm)$_2$[1,2,35,36] were prepared following published procedures. ^{13}C-labeled Ir$_2$(μ-S)(CO)$_2$(dppm)$_2$ was prepared by putting a NMR tube sample of Ir$_2$(μ-S)(CO)$_2$(dppm)$_2$ in 50/50 benzene-d_6/toluene-d_8 under ^{13}CO overnight.

The 1-D ^{1}H, ^{1}H{^{31}P}, and ^{1}H{^{13}C} NMR spectra and 2-D ^{1}H−^{1}H COSY, ^{1}H−X {X = ^{31}P or ^{13}C } HMQC, and NOESY/EXSY NMR spectra were recorded on Bruker AMX-400 or Bruker DRX-400 spectrometers. The 2-D ^{1}H−X {X = ^{31}P or ^{13}C } spectra were acquired using a modified (HMQC) pulse sequence. The first proton pulse was replaced by a $\pi/4$ pulse, while the rest of the sequence remained as in a standard HMQC experiment.[11,23,24] The 2-D NOESY/EXSY experiment was modified with a $d_2-\pi-d_2$ sequence after the initial $\pi/4$ pulse, where $d_2 = 1/4\ J_{HH}$, before the rest of the pulse sequence.[11,22] ^{1}H NMR chemical shifts were referenced relative to the residual proton peak(s) of deuterated solvents, while ^{31}P NMR shifts were referenced relative to 85% H_3PO_4 at 0.0 ppm. Actual NMR probe temperatures were determined using the measured difference in chemical shifts of the methyl and OH protons in methanol and of the CH$_2$ and OH protons in ethylene glycol.[37] All ^{1}H PHIP spectra were acquired using a 45° pulse angle. Typically, NMR samples (1 mg or less for PHIP studies) were prepared in a 5 mm tube fitted with a high-vacuum valve (J. Young) into which deuterated solvent was added by vacuum transfer.

For the reaction of **1** with parahydrogen the optimal temperatures are shown in the Figure 1. Although a 50/50 mixture of benzene-d_6/toluene-d_8 was used, antiphase signals were also observed in benzene-d_6. For the reaction of **7** with parahydrogen, the optimal temperature is shown in the Figure 3. Although benzene-d_6 was the solvent, antiphase signals were also observed in toluene-d_8. For the reaction of **10** with parahydrogen, the optimal temperature is shown in the Figure 4. Although a 50/50 mixture of benzene-d_6/toluene-d_8 was used, antiphase signals were also observed in methylene chloride-d_2, but their decay was much faster.

Preparation of Para-Enriched Hydrogen (para-H$_2$). Hydrogen was enriched in the para spin state by immersion in liquid N$_2$ of a 1 L flask containing hydrogen gas over a catalyst of yellow ferric(III) chloride adsorbed on silica. The extent of parahydrogen enrichment was estimated by comparing the relative intensities of the ^{1}H NMR resonance of orthohydrogen (parahydrogen is NMR silent) in a normal hydrogen sample and in a para-enriched H_2 sample relative to residual ^{1}H in toluene-d_8. The equation $f = 1/3(4\chi_p - 1)$, where χ_p is the mole fraction of parahydrogen,[8] can be used to estimate the extent of parahydrogen enrichment relative to the high-temperature limit for normal H_2 for which $f = 0$. For pure parahydrogen $f = 1$, and for an equilibrium sample of H_2 at 77 K where $\chi_p = 0.504$, $f = 0.34$. For the system employed in the present study, f was found to be 0.2 after 2 h ($\chi_p = 0.4$). The stability of parahydrogen enrichment was monitored by following the change in the intensity of the orthohydrogen resonance over time. Slow conversion to the equilibrium distribution at 298 K was observed over 2 weeks.

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