

# Synthesis and Reactivity of [IrH<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>P)CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu<sub>2</sub>)], a Dynamic Iridium Polyhydride Complex

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The iridium complex [IrH<sub>4</sub>(<sup>t</sup>Bu<sub>2</sub>P)CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu<sub>2</sub>)] (**2**) is formed by treating [IrHCl(<sup>t</sup>Bu<sub>2</sub>P)CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu<sub>2</sub>)] (**1**) with LiBEt<sub>3</sub>H in a hydrogen atmosphere. Subsequent sublimation of [IrH<sub>4</sub>(<sup>t</sup>Bu<sub>2</sub>P)CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu<sub>2</sub>)] (**2**) causes the loss of hydrogen to give [IrH<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>P)CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu<sub>2</sub>)] (**3**). The metal-bound hydrogen atoms of **3** show a broad resonance at  $\delta -23.5$  with a  $T_{1\text{min}} = 79$  ms, ( $-70$  °C, 250 MHz), which suggests a classical hydride-type bonding. A dynamic motion of the metalated CH bond and/or exchange of the "agostic" hydrogen atom is reflected in the <sup>13</sup>C NMR equivalence of the tertiary butyl group quaternary carbon atoms.

## Introduction

Organometallic polyhydride complexes are important in catalysis,<sup>1</sup> hydrogen storage,<sup>2</sup> protection to reactive metal centers,<sup>3</sup> and bond fluxionality.<sup>4</sup> Interpretations of hydrogen fluxionality in polyhydrides has led to the development of new bonding modes besides the common two-electron two-center bond.<sup>5</sup> X-ray molecular structure determinations<sup>6</sup> are particularly informative in this regard. In addition <sup>1</sup>H, <sup>13</sup>C NMR,<sup>6</sup> and infrared data<sup>6</sup> point to bonding modes with transannular  $\mu$ -hydrogen bridges between a metal and carbon, C–H–M. These special interactions have been called agostic bonds.<sup>6</sup> They are of interest because they are thought to be important links in the understanding of C–H metalation processes of hydrocarbons.<sup>7</sup> In addition, they can

be considered as part of a general class of compounds that include  $\mu$ -hydrogen bridges between metals, M–H–M, and nonmetals, C–H–C.

An example of the latter case is the bicyclic tetradecyl cation.<sup>8</sup> Spectroscopic evidence suggests that the  $\mu$ -hydrogen atom in the 10-membered bicyclic carbon ring is an intrabridgehead system with a three-center bond.

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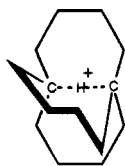
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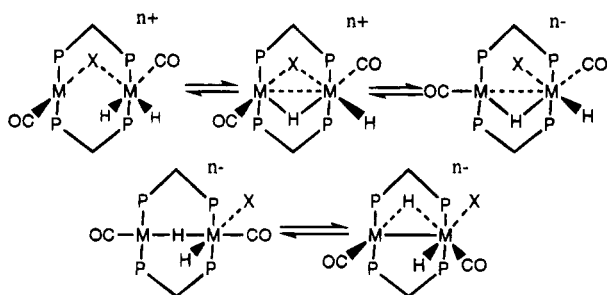
The low chemical shift of the bridged hydrogen atoms is due to charge delocalization over both bridgehead carbon atoms.



Another example is the A-frame complex in Scheme 1 described by Cowie.<sup>9</sup> The bridged hydrogen atom tunnels between two metal atoms in a bicyclic eight-membered ring system. Equivalence in the ligand with small energy differences between the bent  $\mu$ -hydrogen bond and linear form demands a facile movement of the hydrogen atom between the metal atoms. Rosenberg<sup>10</sup> has suggested that the fluxionality of the hydrogen atom in metal hydride clusters can exist as an alternative to agostic interactions in organometallic compounds.

This paper describes the synthesis of a bicyclic eight-membered iridium phosphine polyhydrogen complex. The bulky groups on the phosphine with their hindered rotation around the donor atoms facilitate C-H metalation, an agostic C-H-M interaction, and activate the molecule toward a loss of dihydrogen. This interaction exhibits a dynamic exchange process in the molecule.

Scheme 1



## Results

$[\text{IrH}_2(\text{tBu}_2\text{P})\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{P}(\text{tBu}_2)]$  (**3**). The X-ray molecular structure of  $[\text{IrHCl}(\text{tBu}_2\text{P})\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{P}(\text{tBu}_2)]$  (**1**) as a precursor to **3** shows a rather hindered iridium atom with a metal hydrogen bond that is trans to the metal-carbon C-H bond.<sup>11</sup>

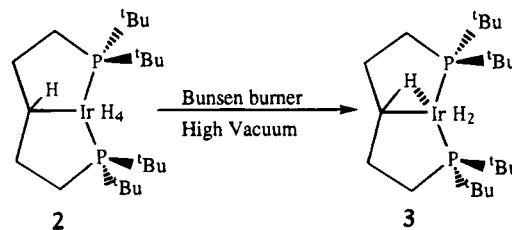
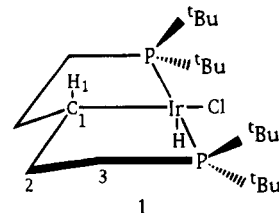
Treatment of this sterically hindered complex with the reactive hydriding agent  $\text{LiBEt}_3\text{H}$  was expected to yield the corresponding dihydride. Instead, a mixture of products forms which is difficult to separate. However,  $[\text{IrH}_4(\text{tBu}_2\text{P})\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{P}(\text{tBu}_2)]$  (**2**)<sup>12</sup> is obtained quantitatively as a white solid by titrimetrically treating an orange pentane solution of **1** with

$\text{LiBEt}_3\text{H}$  under  $\text{H}_2$  gas at atmospheric pressure until the solution is colorless. Compound **2** is not stable under reduced pressure at room temperature and slowly loses hydrogen to give an orange material **3**. When the

white solid **2** is spread evenly on the walls of the flask and gently heated with a Bunsen burner under dynamic vacuum, there is a loss of  $\text{H}_2$  and **3** sublimes in the flask as a red solid.

**NMR Spectra of 2.** The  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data for **2** and **3** are shown in Table 1. Complex **2** was briefly described by Shaw who showed that four hydrogen atoms are equally coupled to both phosphorus nuclei. We also observed that the off resonance decoupled  $^{31}\text{P}$  NMR at  $-5^\circ\text{C}$  gives a quintet which is in agreement with four hydrogen atoms bound to iridium. The hydride resonance in the  $^1\text{H}$  NMR spectrum at room temperature is a triplet at  $\delta -10$  due to coupling of the mutually trans phosphorus atoms with the four hydrogen atoms on the iridium,  $^2J_{\text{PH}} = 10$  Hz.

When the temperature is lowered the triplet metal hydrogen resonance becomes broad until at  $-100^\circ\text{C}$  a new triplet at the low field side of a broad singlet appears. Since the temperature-limited spectrum could not be obtained, no assignment of the hydride multiplet can be made. The  $T_{1\text{min}}$  of 90 ms ( $-70^\circ\text{C}$  at 250 MHz) is at the borderline of the classical and nonclassical hydride determination.<sup>13</sup> Thus, we are not able to distinguish whether a seven-coordinate hydride complex (**2a**) or a six-coordinate  $\eta^2\text{-H}_2$  (**2b-d**) dihydrogen dihydride complex is present as shown in Scheme 2. Since a fast fluxional process is observed as low as  $-100^\circ\text{C}$ , there could also be an exchange of both tautomeric forms (**2a-d**).



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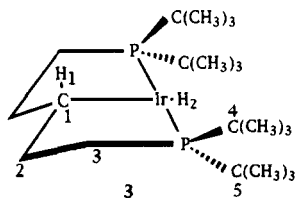
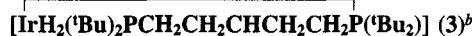
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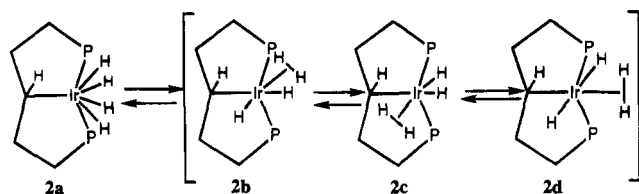
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Table 1.  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}$  NMR<sup>a</sup> Peak Assignments for  $[\text{IrH}_4(\text{tBu})_2\text{PCH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{P}(\text{tBu})_2]$  (2) and

complex	$^{13}\text{C}\{^1\text{H}\}$						$^{31}\text{P}\{^1\text{H}\}$ <sup>b</sup>
	C-1	C-2	C-3	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	
2	28.1, $J_{\text{CH}} = 127.5$	45.0, (vt), $^2J_{\text{PC}} = 12.6^e$	30.6 (vt), $J_{\text{PC}} = 25.10^e$	32.6 (vt), 32.0 (vt), $J_{\text{PC}} = 23.26^e$ , $J_{\text{PC}} = 24.78^e$	29.8 (s), 29.6 (s), $^2J_{\text{PC}} = 4.98^e$ , $^2J_{\text{PC}} = 4.98^e$	83.6 <sup>c</sup>	
3	78.6 (s), $J_{\text{CH}} = 104$	40.7 (vt), $^2J_{\text{PC}} = 18.2^e$	29.4 (vt), $J_{\text{PC}} = 11.0^e$	34.7 (vt), $J_{\text{PC}} = 11.3^e$	29.7 (s)	99.7 <sup>d</sup>	

<sup>a</sup> GE (500 MHz) and Bruker (250 MHz) spectrometers were used. <sup>b</sup> Abbreviations used are as follows: b = broad, s = singlet, d = doublet, t = triplet, vt = virtual triplet.  $\delta$  in ppm, toluene-*d*<sub>8</sub>.  $J$  values are given in Hz. <sup>c</sup> Quintet, off resonance decoupled at  $-5^\circ\text{C}$ ,  $J_{\text{PH}} = 8.04$ . <sup>d</sup> Triplet, off resonance decoupled at  $-30^\circ\text{C}$ ,  $J_{\text{PH}} = 8.0$  Hz. <sup>e</sup>  $J_{\text{PC}} = |J_{\text{PC}} + J_{\text{PC}}|$ .

Scheme 2



The room temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** shows seven resonances. When coupling to phosphorus is observed, the carbon signals are split into virtual triplets. An important resonance is C-1 at  $\delta$  28.1 ( $J_{\text{CH}} = 127.5$  Hz), which has a similar chemical shift when compared to the corresponding carbon atom in **1** ( $\delta$  28.4, ( $J_{\text{CH}} = 129.5$  Hz)). This is indicative of a  $\text{sp}^3$  hybrid carbon atom. In addition, the quaternary carbon atoms of the *tert*-butyl groups  $\text{C}(\text{CH}_3)_3$  can be distinguished as two sets of virtual triplets because there is no horizontal mirror plane in the molecule. The primary carbon atoms  $\text{C}(\text{CH}_3)_3$  show just two single peaks not coupled to phosphorus. A similar observation can be made for **1**.

**NMR Spectra of 3.** Complex **3** is extremely soluble in all aromatic and aliphatic solvents and interacts rapidly with chlorinated and fluorinated hydrocarbons. With chlorinated hydrocarbons, **1** is re-formed. A slow reaction occurs with benzene and toluene at room temperature. The NMR data are invariant if the solutions are kept cool, however. At higher temperatures a reaction occurs over a period of time with pentane and cyclohexane.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum displays a singlet at  $\delta$  99.7 which is invariant to changes in temperature to  $-90^\circ\text{C}$ . Off resonance decoupling at  $-40^\circ\text{C}$  gives a triplet in the phosphorus NMR spectrum. This is a result of two hydrogen atoms on the iridium which couple to the phosphorus nuclei ( $^2J_{\text{PH}} = 8.0$  Hz). The phosphorus triplet resonance follows the same low-temperature dependence as the resonance for the iridium-bound hydrogen atoms in the  $^1\text{H}$  NMR spectra (see Figure 1 below).

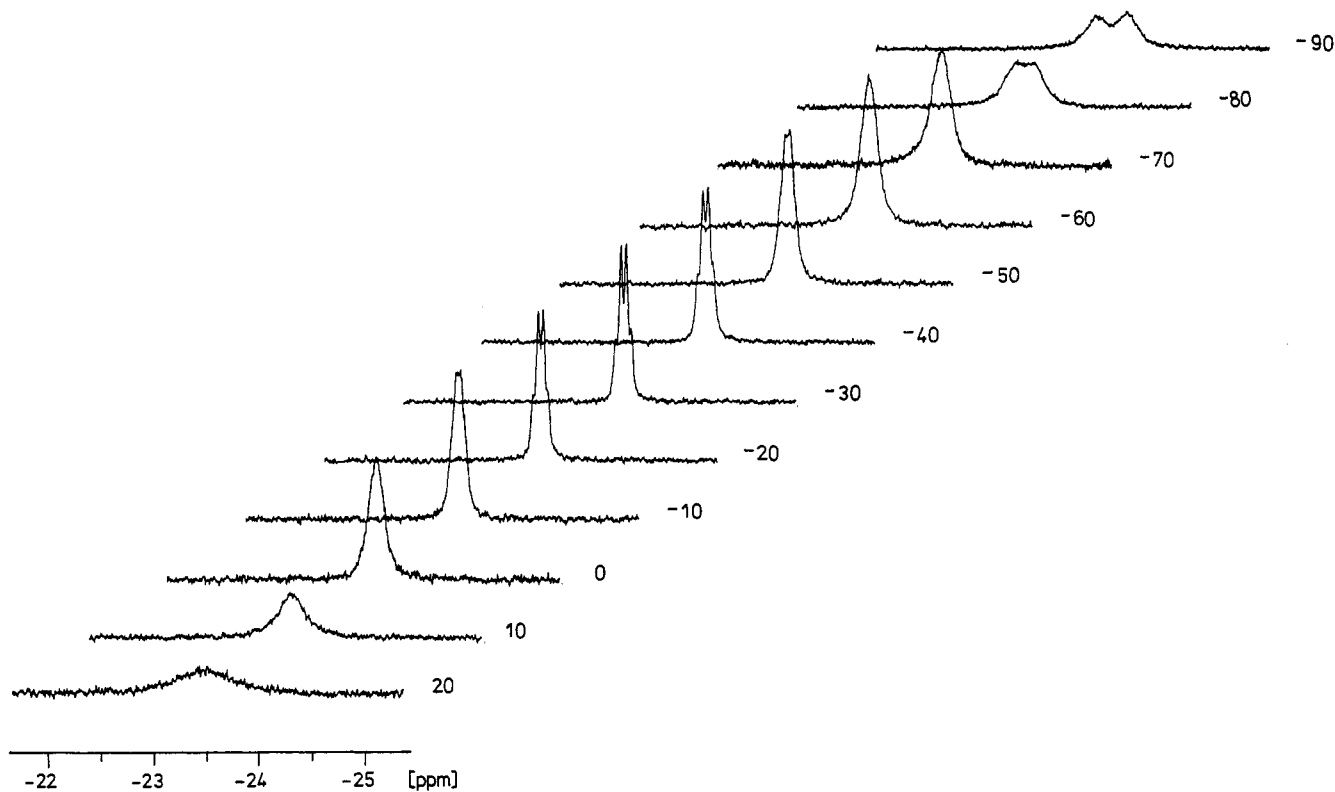
At room temperature the major features in the  $^1\text{H}$  NMR spectrum are a single virtual triplet at  $\delta$  1.33 due to the *tert*-butyl groups and a broad resonance at  $\delta$

$-23.5$  with no resolvable coupling for both metal-bonded hydrogen atoms. This broad peak is resolved into a doublet of triplets in the temperature range of  $-20$  to  $-40^\circ\text{C}$  (Figure 1) demonstrating that the dynamic process responsible for the line broadening is slowed down. Further cooling of the sample again results in a broadening of the line shape which is consistent with a second exchange process. At the lowest accessible temperature ( $-90^\circ\text{C}$ ), the splitting of the resonance into two broad peaks indicates the existence of two inequivalent hydrides in the ground state structure.

A two-dimensional carbon-proton correlated spectrum showed that C-1 is bonded to proton H-1 at  $\delta$  1.33. This single proton resonance is obscured by the strong *tert*-butyl group multiplets of the complex. Proton homonuclear decoupling at  $\delta$  1.33 simplified the metal hydride pattern to a triplet ( $^2J_{\text{PH}} = 8.0$  Hz) which shows that there is a scalar interaction of the hydrogen atoms on the iridium with H-1 in the temperature range of  $-20$  to  $-40^\circ\text{C}$ . In **1** and **2**, H-1 resonates at  $\delta$  2.40 and  $\delta$  3.35, respectively, and can be readily observed. This progressive shift to higher fields is somewhat indicative of an "agostic" hydrogen atom<sup>7</sup> for H-1 in **3**, although other molecular systems show that such hydrogen atoms can have variable chemical shifts.<sup>7i</sup> Better evidence is the carbon-hydrogen coupling constant (cf. vide infra).

Spin saturation experiments were performed in the temperature range of  $-13$  to  $-25^\circ\text{C}$  in order to elucidate the dynamic behavior of the iridium complex **3**. Irradiation at the resonance  $\delta$  1.33 showed a clear decrease in the intensity of the iridium hydrogen resonance at  $\delta$   $-23$ . This suggests that the carbon-bound hydrogen H-1 undergoes an exchange with the iridium bound hydride atoms and thus is responsible for the line broadening of the hydride signal above  $-20^\circ\text{C}$ . Below  $-25^\circ\text{C}$  no exchange process could be observed by the spin saturation method.

Variable temperature  $T_1$   $^1\text{H}$  NMR studies show that the  $T_1$  of the two hydrides goes through a minimum  $T_{1\text{min}} = 79$  ms ( $-70^\circ\text{C}$ , 250 MHz) as predicted by theory if a dipole-dipole mechanism is responsible for relaxation of the two nuclei. This supports the assumption that at temperatures below  $-40^\circ\text{C}$  each hydride is relaxed by only one neighboring proton. By further assuming an isotropic motion of the molecule, one is able



**Figure 1.** The 400-MHz  $^1\text{H}$  NMR spectrum in toluene- $d_8$  of the metal-bonded hydrogen atoms in **3** from 20 to  $-90$  °C. Note inequivalent hydrides at  $-90$  °C.

to calculate a H–H distance of 1.54 Å. Because this model ignores relaxation from other sources the distance calculated above is a lower limit and thus a reasonable value for a classical dihydride.<sup>14</sup>

The room temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows five instead of seven resonances at  $\delta$  29.4(C-3), 29.7 C(CH<sub>3</sub>)<sub>3</sub>, 34.8 C(CH<sub>3</sub>)<sub>3</sub>, 40.7(C-2), and 78.4(C-1). In the case of C-2, -3, -4, the carbon signals are split into virtual triplets caused by coupling to the two chemically equivalent phosphorus atoms. From a proton-coupled  $^{13}\text{C}$  NMR spectrum at  $-30$  °C, a coupling constant of 104 Hz for C-1 is observed. This reduced C–H interaction is further evidence which suggests the presence of an “agostic” hydrogen atom.<sup>7</sup>

Another important feature of the  $^{13}\text{C}$  NMR spectrum are the quaternary carbon atoms C(CH<sub>3</sub>)<sub>3</sub> and the methyl carbon atoms C(CH<sub>3</sub>)<sub>3</sub>. Figure 2 shows the variable temperature spectra of the *tert*-butyl quaternary carbon atoms at  $\delta$  34.98 which exhibit a single virtual triplet at room temperature but split into two virtual triplets at  $-35$  °C and below. The methyl carbon atoms show a single resonance at room temperature, but separate into two resonances at lower temperature. Thus, in contrast to **1** and **2** there is a temperature dependent exchange mechanism which allows for a symmetry that makes the pendent *tert*-butyl groups in **3** equivalent at room temperature.

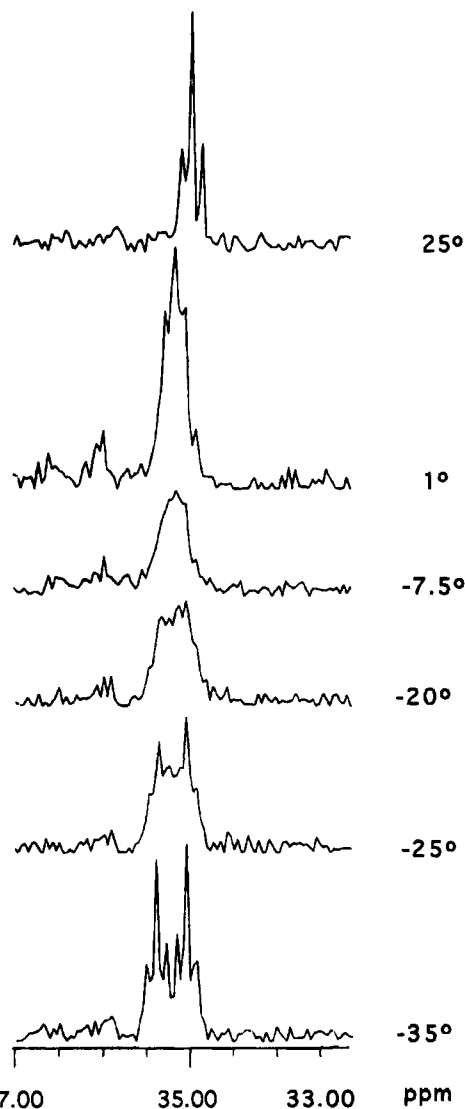
We attempted to detect this exchange process by isotopic labeling. The C-1 position was conveniently

deuterated by treating **1** with LiBEt<sub>3</sub>D/D<sub>2</sub> to form **2-d<sub>n</sub>**. When treated with these reagents the  $^2\text{H}$  NMR spectrum of **2-d<sub>n</sub>** shows a small amount of deuterium incorporation at C-1 ( $\delta$  3.35) and the *tert*-butyl groups CH<sub>2</sub>D ( $\delta$  1.67). Most of the deuterons are bonded to the iridium atom, Ir H<sub>*n*</sub>D<sub>4-*n*</sub>, at  $\delta$   $-10$ . Pyrolysis of this white complex under vacuum gives **3-d<sub>n</sub>** ( $n > 1$ ) with a greater concentration of deuterium atoms on C-1 and the *tert*-butyl groups. Surprisingly, the  $^2\text{H}$  NMR spectrum of **3-d<sub>n</sub>** shows no deuterium on the iridium atom. The  $^{13}\text{C}$  NMR spectrum confirms the presence of deuterium at C-1 because there are two  $^{13}\text{C}$  resonances one at  $\delta$  78.84 and another at  $\delta$  78.74 for  $^{13}\text{C}$ -1–H<sup>15</sup> and  $^{13}\text{C}$ -1–D, respectively. The  $^{13}\text{C}$ -1–D species can be identified by its broader line shape with respect to the  $^{13}\text{C}$ -1–H species. No coupling of the deuterium nucleus to the carbon atom can be observed. When D<sub>2</sub> gas is then added to a solution of **3-d<sub>n</sub>** in pentane, the red solution discolors to form **2-d<sub>n</sub>** ( $n > 1$ ). Resublimation of **2-d<sub>n</sub>** a second time gives **3-d<sub>n</sub>** with more deuterium atoms at C-1 and the *tert*-butyl groups. When pentane is condensed onto freshly sublimed solid **3-d<sub>n</sub>** and the  $^2\text{H}$  NMR spectrum is observed at  $-80$ ,  $-45$ , and  $25$  °C (successively higher temperatures), there is no evidence for the presence of Ir–D.

The gas phase synthesis of **2**, the incorporation of deuterons, and the absence of deuterons on the iridium atom can be explained in Scheme 3. When the tetrahydride (deuteride) is sublimed, C–H metalation must readily occur so that deuterons are introduced via cyclometalation into the *tert*-butyl groups. This can be accomplished by species **4** in the gas phase which is a 14 e system that can internally metalate the C–H bond

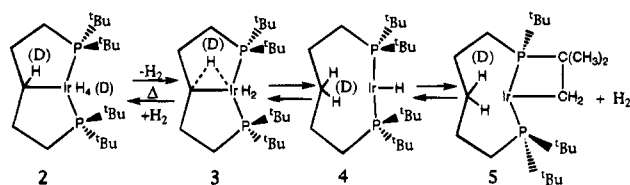
(14) (a) Hamilton, D. G. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Crabtree, R. H.; Lavin, M. L.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (c) Morris, R. H. et al. *J. Am. Chem. Soc.* **1988**, *110*, 7031. (d) Luo, X.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788. (e) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027. (f) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 97. (g) Crabtree, R. H. Personal communication. (h) Brane, E. G.; Wasylshen, R. E. In *NMR Spectroscopy Techniques*; Dybowski, C.; Lichter, R. L., Practical Spectroscopy Series; Marcel Dekker, Inc.: New York, 1987; Vol. 5, p 45.

(15) Nakashima, Y.; Nakane, H.; Ban, S.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2025 and references cited therein. See also: Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc.* **1981**, 506.



**Figure 2.** The 500-MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum toluene- $d_8$  of  $\text{C}(\text{CH}_3)_3$  in **3** from 25 °C to -35 °C.

**Scheme 3**



or "ortho"-metalate with a *tert*-butyl group when the sample is hot. Structure **4** is not important in solution in the temperature range of 20 to -95 °C because on the NMR time scale the resonance position of C-1 is invariant to -95 °C. The solution absence of Ir-D resonances in **3** at various low temperatures is puzzling. We can only explain this by the preference of deuterium to be bonded to C-1 rather than the terminal metal-hydride position for thermodynamic reasons,<sup>16</sup> cf. vide infra.

**Infrared Spectra.** Infrared evidence was gathered under a variety of conditions to obtain evidence for  $\eta^2$ -

(16) (a) Siehl, H. U. In *Advances in Physical Organic Chemistry*; Bethell, D., Ed.; Academic Press: New York, 1987; Vol. 23, 63. (b) Watt, C. I. F. *Advances in Physical Organic Chemistry*; Bethell, D., Ed.; Academic Press: New York, 1988; Vol. 24, p 57. The tendency for deuterium to bind to carbon could overwhelm the migration of hydrogen.

$\text{H}_2$  bonding in **2** and **3**. The results do not clearly point to the presence of this bonding type. The five prominent  $\nu(\text{M}-\text{H})$  stretching bands for **2** are 2045 (m), 1961 (m), 1909 (vs), 1862 (m), 1798 (w)  $\text{cm}^{-1}$ . This is more absorptions than the two required by symmetry for the complex. Jensen<sup>17</sup> reports three bands for the tetrahydride complex  $\text{IrClH}_2(\text{PPr}^i_3)_2(\text{H}_2)$  at 2207 (w), 2183 (vw), and 2152 (m)  $\text{cm}^{-1}$  and discards infrared evidence for H-H.

Support for the presence of **3** as a dihydride complex comes from the presence of two  $\nu(\text{M}-\text{H})$  stretches at 2280 (vw) and 1974 (mb)  $\text{cm}^{-1}$  in a KBr pellet. In Nujol the same absorptions are observed at 2063 and 1965  $\text{cm}^{-1}$ , respectively. The dihydride  $\text{IrClH}_2(\text{PBu}^t_3)_2$ <sup>17</sup> has  $\nu(\text{M}-\text{H})$  at 2334 and 2324  $\text{cm}^{-1}$ . A dihydride similar to **3** which was synthesized by Fryzuk<sup>18</sup> et al. shows one band at 2200 (m)  $\text{cm}^{-1}$ ,  $\text{IrH}_2(\text{Ph}_2\text{PCH}_2\text{Me}_2\text{SiNSiMe}_2\text{CH}_2\text{PPh}_2)$ . The infrared spectrum of  $[\text{IrHCl}(\text{C}_6\text{H}_5)(\text{PPr}^i_3)_2]$  shows an absorption at 2273  $\text{cm}^{-1}$ .<sup>17b</sup>

The deuterated complex **3-d<sub>n</sub>** shows the same peaks as **3** except for  $\nu(\text{C}-\text{D})$  at 2200 and 2154  $\text{cm}^{-1}$  which are stretching vibrations from the presence of deuterium in the *tert*-butyl groups [ $\nu(\text{C}-\text{H})/\nu(\text{C}-\text{D})$ ] = 1.4-1.36<sup>19</sup> and possibly C-1-D.

Infrared spectral preparation of **3** was often hampered by the presence of **2** even though there was no evidence of **2** in the  $^1\text{H}$  NMR spectrum of the sample to be used. This was especially evident when spectra of **3** were taken in liquid xenon (see Experimental Section). There are no low-frequency stretching vibrations reduced by a factor of 1.4 [ $\nu(\text{Ir}-\text{H})/\nu(\text{Ir}-\text{D})$ ] which would indicate the presence of  $\nu(\text{Ir}-\text{D})$ . Recall that the  $^2\text{H}$  NMR spectrum of **3-d<sub>n</sub>** did not show the presence of Ir-D resonances either.

## Discussion

**NMR Spectra of 3.** The two features of major interest in complex **3** are the unusual NMR parameters and the effects of temperature on the molecular structure. The unusual parameters include the low chemical shift of C-1, the low coupling constant for  $J_{\text{C}1-\text{H}1}$ , and the upfield  $^1\text{H}$  NMR shift of the "agostic" hydrogen H-1 atom. The effects of temperature can be seen in the quaternary and methyl carbon atoms of the *tert*-butyl groups which are equivalent from room temperature down to -30 °C. After that they change to two virtual triplets as shown in Figure 2. In addition, the broad iridium hydride resonance at room temperature changes to a doublet of triplets at -30 °C whereupon it becomes broad again and then gives broad doublet at -95 °C as shown in Figure 1 (250 MHz).

There are two temperature regimes that need to be discussed with regard to the NMR dynamics of **3**: The

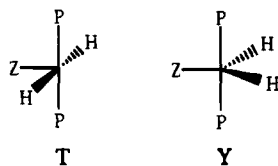
(17) (a) Mediati, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1992**, *31*, 1827. (b) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090.

(18) (a) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803. (c) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2939.

(19) (a) Bullock, R. M.; Lemke, F. R.; Szalda, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 3244. (b) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415. (c) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (d) Anson, C. E.; Sheppard, N.; Powell, D. B.; Norton, J. R.; Fischer, W.; Keiter, R. L.; Johnson, B. F. G.; Lewis, J.; Bhattacharya, A. K.; Knox, S. A. R.; Turner, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 3058.

first is from about  $-35$  to  $-95$  °C. The second is from about  $-30$  °C to room temperature.

One interpretation of the two hydride resonances at  $-95$  °C is that they simply occupy two different positions in the complex. Another interpretation can be drawn from the work of Eisenstein<sup>20</sup> with regard to the structure of  $d^6\text{ML}_5$  complexes. The nature of Z is important in orienting the structure toward T or Y geometries. Thus, when Z is a  $\sigma$ -acceptor and/or a

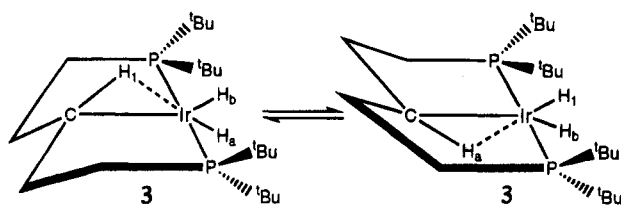


$\pi$ -donor Y is preferred, but if Z is a  $\sigma$  donor and/or a  $\pi$ -acceptor T is preferred. When Z is a  $\text{sp}^3$  carbon atom, a borderline case can exist where both T and Y forms can be observed at low temperature. At room temperature both forms are in rapid equilibrium.

The second temperature regime from  $-35$  °C to room temperature in Figure 1 shows that the metal-bound hydrogen atoms change from a doublet of triplets at  $-35$  °C to a broad single peak at room temperature. In addition, Figure 2 shows the  $^{13}\text{C}\{^1\text{H}\}$  NMR of the *tert*-butylphosphine group quaternary carbon atoms at  $\delta$  34.98 in **3** change to a single set of virtually coupled triplets at room temperature. This is contrary to expectations if one assumes there is no rotation about the phosphorus–iridium bond because of the closed ring and the sterically restrained *tert*-butyl groups. The C–H–Ir atoms should be contained in a vertical plane as in **3**. Moreover, there is no horizontal plane of symmetry which includes the phosphorus, iridium, and C-1–H atoms.

Equivalence of the quaternary carbon atoms in **3** can be best explained by spin saturation transfer experiments which were performed at various temperatures between IrH<sub>2</sub> and H1.<sup>21</sup> The decrease in the intensity of the iridium hydrogen resonance at  $\delta$   $-23$  shows that an exchange occurs. Scheme 4 illustrates the proposed

Scheme 4



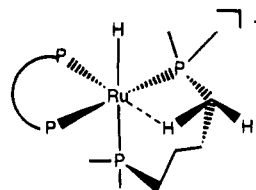
slow exchange that H1 undergoes with the iridium atom even though both infrared spectra and  $^2\text{H}$  NMR data do not indicate the presence of Ir–D bonds. In this scheme the “agostic” H-1 moves to the iridium atom while one of the iridium hydrogen atoms moves to C-1.<sup>22</sup> The slow exchange is not observed below  $-25$  °C. Our

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(21) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1987.

(22) A similar slow exchange was observed in a rhodium complex: Mayer, H. A.; Kaska, W. C. *Chem Ber.* **1990**, *123*, 1827.

observations are similar to the following ruthenium complex reported by Saburi.<sup>23</sup> As in the case of **3** this



complex shows an exchange of the agostic hydrogen atom with Ru–H although the  $^{13}\text{C}$  NMR chemical shift and coupling constant  $\delta$  27.9 ( $J_{\text{CH}} = 119$  Hz) are not as pronounced as they are in **3**. The driving force for the exchange which includes the formation of a carbon–ruthenium bond, and C–H bond activation is presumably the formation of an  $\eta^2\text{-H}_2$  complex. In contrast, **3** keeps the carbon iridium bond intact and includes C–H exchange as well.

Some useful comparisons can be made with  $\text{PdCH}_3$ –

$[\text{tBu}_2\text{P}(\text{CH}_2)_2\text{CH}(\text{CH}_2)_2\text{P}(\text{tBu}_2)]$  which has been synthesized by Trogler.<sup>24</sup> The X-ray molecular structure of the diphospha-7-pallada[3.3.0]bicyclooctane ring is similar to the structure reported by Shaw for **1**. The ring adopts a double bent conformation with methylene groups that are displaced from a pseudo mirror plane which bisects the molecule. This has two effects: (1) It promotes a difference in the positioning of the *tert*-butyl groups which persists even in solution and causes separate  $^{13}\text{C}\{^1\text{H}\}$  resonances for the quaternary carbon atoms, and (2) it forces ligands in the square plane downward and prevents their optimal bonding to the metal, but in the case of **3** it could include more interaction of H-1 with the iridium bound hydrogen atoms. In spite of this Trogler reports  $J_{\text{CH}} = 120$  Hz for H-1 in his complex which is normal for a  $\text{sp}^3$  aliphatic C–H bond and there is no temperature dependence for the palladium hydrogen bond in the Trogler complex  $\text{PdH}[\text{tBu}_2\text{P}(\text{CH}_2)_2\text{CH}(\text{CH}_2)_2\text{P}(\text{tBu}_2)]$  or the iridium hydrogen bonds in the complex synthesized by Fryzuk,<sup>18</sup>  $\text{IrH}_2(\text{Ph}_2\text{PCH}_2\text{Me}_2\text{SiNSiMe}_2\text{CH}_2\text{PPh}_2)$ .

It is noteworthy that C-1 in complex **3** is shifted to lower field by more than 50 ppm than the corresponding carbon atoms in the complexes **1** and **2**. The chemical shift for C-1,  $\delta$  78.6, in complex **3** is lower than the chemical shift for C-1 in the Trogler<sup>24</sup> complex,  $\text{PdCH}_3$ – $[\text{tBu}_2\text{P}(\text{CH}_2)_2\text{CH}(\text{CH}_2)_2\text{P}(\text{tBu}_2)]$  ( $\delta$  57.53), and the carbene complex prepared by Shaw,<sup>25</sup>  $\text{IrCl}[\text{tBu}_2\text{P}(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{P}(\text{tBu}_2)]$ .

(23) (a) Ogasawara, M.; Aoyagi, K.; Saburi, M. *Organometallics* **1993**, *12*, 3393. (b) Ogasawara, M.; Saburi, M. *Organometallics* **1994**, *13*, 1911. (c) A static  $\alpha\text{-CH-M}$  interaction observable by NMR: Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

(24) Seligson, S. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738. (25) (a) Emsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (b) Crocker, C.; Emsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217.

Bu<sub>2</sub>], which has a shift of  $\delta$  66.3. Although it is still possible that a form of paramagnetic anisotropy lowers the chemical shift of C-1 the resonance position of **3** suggests a highly deshielded ylidic carbon atom.

There are two additional models that might explain the quaternary carbon atom equivalence in the complex. One possibility is the intermolecular transfer of a hydrogen atom from the C-1-H bond to another molecule. This would show up as a concentration effect on the <sup>13</sup>C{<sup>1</sup>H} NMR of the quaternary carbon atoms and C-1 at various temperatures which has not been observed.

In another model the H-1 atom could be moving rapidly above and below the plane to account for the equivalence of the *tert*-butyl carbon atoms, at room temperature.<sup>26</sup> This may involve a "positional" tunneling component which often occurs when the ground-state geometry of the reactant closely resembles that of the product. This effect could be small and still account for the equivalence. The driving force for such an effect and that described in Scheme 4 may come from the very low  $J_{CH}$  value for C-1 and the low chemical shift for C-1. If the C-1-Ir bond is very polar and weak, because of a change in the hybridization of C-1 from sp<sup>3</sup> to sp<sup>2</sup> the entire C-H bond could flex in an unusual way which would encompass an exchange process that allows for symmetry in **3** at room temperature. This could be influenced by severe *tert*-butyl group crowding which prevents effective bonding of the hydrogen atoms to the metal, thus changing the classical oxidation state from (III) to something which approaches (I).

Trogler suggests a similar effect to explain the short carbon-palladium bond, 2.056 Å, in the diphospha-7-pallada[3.3.0]bicyclooctane complex.

## Experimental Section

**Reagents.** Benzene, pentane, and hexane (HPLC grade) and etheral solvents were distilled from benzophenone-ketyl. Methylene chloride was distilled from LiAlH<sub>4</sub>. Deuterated solvents were stored in the glovebox (Vacuum Atmospheres) after being dried, degassed, and distilled from LiAlD<sub>4</sub>.

**Elemental Analyses.** Elemental analyses were performed by Desert Analytics, Tucson, AZ.

The <sup>1</sup>H chemical shifts are referenced to the residual proton peak of C<sub>6</sub>H<sub>6</sub> at  $\delta$  7.15 (vs TMS), the residual proton peak of toluene-*d*<sub>8</sub> at  $\delta$  2.09 (vs TMS), and the residual proton peak of cyclohexane-*d*<sub>12</sub> at  $\delta$  1.38 (vs TMS). The <sup>13</sup>C resonances are referenced to benzene,  $\delta$  128.0, toluene, 20.4, and cyclohexane, 26.4, relative to TMS. <sup>31</sup>P NMR shifts are given relative to external H<sub>3</sub>PO<sub>4</sub>. The spin saturation transfer experiments were performed with a Varian Gemini-200 MHz instrument at -25, -17.5, -15, and -13.0 by irradiating the region at  $\delta$  -1.33. There was a variable temperature decrease in intensity of the iridium hydride resonance. The liquid xenon spectra were taken in a specially constructed cell and recorded on a

PE 1700 IR spectrometer with 2 cm<sup>-1</sup> nominal resolution, with a cell path of 1.43 cm at -70 °C and 80 psi. The samples were prepared by first syringing a pentane sample of the complex into the infrared cell, vacuum removal of the pentane, and then addition of liquid xenon to dissolve the sample in the cell. This procedure may have caused the vacuum sensitive **3** to disproportionate to give some of complex **2**, thus contaminating the sample. Grinding of the samples for KBr or Nujol preparation could cause the same effects. Desorption CI mass spectra were obtained on a BG 70-250HF double-focusing conventional geometry mass spectrometer.

**General Procedures.** All reactions and manipulations were carried out on a double-manifold high vacuum line, a Vacuum Atmospheres glovebox under argon, or in Schlenk-type glassware according to previously described procedures.<sup>27</sup> NMR tubes with J-Young sealed Teflon caps were used throughout.

### Synthesis of IrH<sub>4</sub>(<sup>t</sup>Bu)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu)<sub>2</sub> (**2**).

An arbitrary amount of **1** was placed in a flask under hydrogen gas, and sufficient pentane was added so that an orange-red solution was formed. The solution was then saturated with H<sub>2</sub> gas. A solution of LiBEt<sub>3</sub>H in THF was added slowly at room temperature until the orange-red solution became just a pale orange. After 5 min additional drops of the hydride were added so that the solution was completely colorless. The maintenance of the H<sub>2</sub> gas atmosphere was important. There was a slight turbidity from the formation of LiCl. The colorless solution was filtered under hydrogen, and the pentane was removed to give a white solid which slowly became pale orange as hydrogen was lost.

### Synthesis of [IrH<sub>2</sub>(<sup>t</sup>Bu)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>P(<sup>t</sup>Bu)<sub>2</sub>]

(**3**). In a typical experiment 100 mgs (0.18 mmol) of white **2** was placed in a round-bottom sublimation flask and dissolved in pentane. The pentane solution was swirled as it was evaporated so that a thin film of **2** was left in the flask. Evaporation under a stream of H<sub>2</sub> was quite satisfactory. While the flask was still under dynamic vacuum the film was heated gently and rapidly with a Bunsen burner (heating in an oil bath gave lower yields because the compound could not be heated quickly). When the film was thin and the heating rapid, the red complex could be collected onto a liquid nitrogen-cooled finger in the sublimator. It could be moved throughout the flask as a red solid under vacuum. In this way all of complex **2** was converted into **3**. The final product could be obtained by washing the red solid from the cold finger in the glove box since it is extremely sensitive to oxygen. Yield: 98 mg (98%). Anal. Calcd for C<sub>21</sub>H<sub>47</sub> P<sub>2</sub>Ir: C, 45.55; H, 8.55. Found: C, 45.10, H, 8.53.

**Acknowledgment.** We greatly appreciate the financial support for this research from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Naval Research. We are indebted to Dr. Nancy Keder for many attempts to find suitable crystals of complex **3**, to Dr. Joseph Ziller, Department of Chemistry, University of California, Irvine for also trying to find a suitable crystal of **3**, to Dr. Hugh Webb for the mass spectra, and to Professor E. Rosenberg for many discussions. We are especially grateful to Professor Robert Bergman and Dr. Kevin Kyle for the infrared spectra in liquid xenon. W.C.K. is also grateful to the Anorganische Chemie Institut, Universität Tübingen, and to Professor E. Lindner for the use of facilities in the completion of this work. The authors are also appreciative for the helpful comments and suggestions of the reviewers of this paper.

OM9308194

(27) Kaska, W. C.; Nemeš, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13.

(26) (a) Cowie has proposed a similar situation between two metal atoms: Vaartstra, B. A.; Cowie, M. *Inorg. Chem.* **1989**, *28*, 3138. (b) See also: Azam, K. A.; Puddephat, R. J. *Organometallics* **1983**, *2*, 1396. (c) Long has proposed a "tunneling" of the H<sup>-</sup> ligand in HFe(CO)<sub>4</sub><sup>-</sup> to explain dynamic motion in the ion: Long, G. J.; Granjean, F.; Whitmire, K. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 884. (d) A similar intramolecular "tunnel" process is present in {[N(CH<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>)<sub>3</sub>NiH]BPh<sub>4</sub>}; Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini A. *Inorg. Chem.* **1984**, *23*, 922. (e) We tried to replace H1 with deuterium and then determine the magnitude of the  $kH/kD$  for the two species. However, incomplete deuteration did not allow us to accurately complete the analysis with DNMR5 to determine the effects of barrier tunneling. In addition, the narrow temperature range of the spin saturation transfer experiments did not allow accurate calculation of rate constants from NMR data.