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Article

Dynamics of a *cis*-Dihydrogen/Hydride Complex of Iridium

H. V. Nanishankar, Saikat Dutta, Munirathinam Nethaji, and Balaji R. Jagirdar*

Department of Inorganic & Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India

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Insertion of CS_2 into one of the Ir–H bonds of $[Ir(H)_5(PCy_3)_2]$ takes place to afford the dihydrido dithioformate complex *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ accompanied by the elimination of H_2. Protonation of the dithioformate complex using $HBF_4{\cdot}Et_2O$ gives *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ wherein the H atom undergoes site exchange between the dihydrogen and the hydride ligands. The dynamics was found to be so extremely rapid with respect to the NMR time scale that the barrier to exchange could not be measured. Partial deuteration of the hydride ligands resulted in a $J(H,D)$ of 6.5 and 7.7 Hz for the H_2D and the HD_2 isotopomers of *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$, respectively. The H–H distance (d_{HH}) for this complex has been calculated to be 1.05 Å, which can be categorized under the class of *elongated* dihydrogen complexes. The *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ complex undergoes substitution of the bound H_2 moiety with CH_3CN and CO resulting in new hydride derivatives, *cis*-$[Ir(H)(L)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (L = CH_3CN, CO). Reaction of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ with electrophilic reagents such as MeOTf and Me_3SiOTf afforded a new hydride aquo complex *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ via the elimination of CH_4 and Me_3SiH, respectively, followed by the binding of a water molecule (present in trace quantities in the solvent) to the iridium center. The X-ray crystal structures of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ and *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ have been determined.

Introduction

Ever since the first transition metal dihydrogen complex was reported,[1] intensive research activity has taken place to unravel the possibility of the existence of dihydrogen complexes as intermediates in the fluxional processes involving polyhydride complexes.[2] The study of the dynamic processes in complexes containing a hydride and a dihydrogen ligand has also attracted enormous attention since such complexes can be viewed as prototypical examples of polyhydrides. There have been a large number of reports on the dynamics of trans[3] and the cis dihydrogen hydride complexes.[4] Most of the cis complexes exhibit interesting dynamics of the H atom site exchange between the dihydrogen and the hydride ligands involving significant rearrangements of the coligands resulting in relatively higher activation barriers for the processes, typically 9−10 kcal/mol. Heinekey et al. reported that highly symmetric cis dihydrogen hydride complexes involving no heavy atom rearrangement show dynamics with much smaller barriers.[5a−d] Systems exhibiting such low barriers have been much less

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* To whom correspondence should be addressed. E-mail: jagirdar@ipc.iisc.ernet.in.

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studied.[5e,f] The factors that determine the structure and dynamics of these types of molecules are subtle and not clearly understood.

We have been interested in realizing *cis*-dihydride complexes wherein the hydride ligands are related by a mirror plane and study the protonation of such complexes in an effort to understand the factors that determine their structures and dynamics. During the course of our studies on the insertion reactions of heterocumulenes such as CO_2, CS_2, and COS into M−H bonds,[6] we found that CS_2 inserts into one of the Ir−H bonds of $[Ir(H)_5(PCy_3)_2]$[7] to afford a dihydrido dithioformate derivative *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**). The two hydride ligands in this complex are in cis conformation. The protonation of **1** using $HBF_4{\cdot}Et_2O$ resulted in the *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) derivative, which shows rapid dynamics for the H atom site exchange between the dihydrogen and the hydride ligands. In this paper, we report these studies along with the reactivity of **1** with certain electrophilic reagents.

Experimental Section

General Procedures. All reactions were carried out under a N_2 or Ar atmosphere at room temperature using standard Schlenk[8] and inert-atmosphere techniques unless otherwise stated. Solvents used for the preparation of the dihydrogen complexes were thoroughly saturated with either H_2 or Ar just before use. The ^1H and ^{31}P NMR spectral data were acquired using an Avance Bruker 400 and 500 MHz spectrometers. Variable-temperature proton T_1 measurements were carried out at 400 MHz using the inversion recovery method.[9] The T_1 data have been deposited in the Supporting Information. ^{31}P NMR chemical shifts have been measured relative to 85% H_3PO_4 (aqueous solution) as an external standard. Elemental analysis for **1** was carried out at the Department of Organic Chemistry, IISc (Thermo Finnigan Flash EA1112 instrument), and for the other complexes at the Regional Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow, India. The $[Ir(H)_5(PCy_3)_2]$ complex and $CDF_2Cl/CDFCl_2$ were prepared by literature methods.[7,10]

Preparation of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (1). To a toluene solution (10 mL) of $[Ir(H)_5(PCy_3)_2]$ (50 mg, 0.06 mmol) under an atmosphere of Ar was added CS_2 (20 equiv, 80 μL) using a syringe. The reaction mixture was stirred overnight after which time the volatiles were stripped leaving behind a yellow solid. The product of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ was crystallized from a toluene solution via slow evaporation of solvent at room temperature. Yellow crystals of **1** were obtained in a yield of 42 mg (76%). Anal. Calcd for $C_{37}H_{69}IrP_2S_2$: C, 53.39; H, 8.35. Found: C, 53.94; H, 8.23. ^1H NMR (C_6D_6): δ −21.64 (t, 2H, Ir−*H*, J(H,P) = 17.0 Hz), 1.30−2.28 (m, 66H, $P(C_6H_{11})_3$), 13.89 (br s, 1H, $(\eta^2\text{-}S_2CH)$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.1 (s, $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.1−38.5 (m, $P(C_6H_{11})_3$), 231.5 (s, $(\eta^2\text{-}S_2CH)$). ^1H NMR (CD_2Cl_2): δ −22.24 (t, 2H, Ir−*H*, J(H,P) = 17.0 Hz), 1.21−2.03 (m, 66H, $P(C_6H_{11})_3$), 13.48 (br s, 1H, $(\eta^2\text{-}S_2CH)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 27.6 (s, $P(C_6H_{11})_3$).

Protonation Reaction of $[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ 1 Using $HBF_4{\cdot}Et_2O$. A 5 mm NMR tube charged with *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (15 mg) was evacuated and filled with H_2 in three cycles. The dihydride complex was then dissolved in CD_2Cl_2 (0.6 mL), and to this solution was added $HBF_4{\cdot}Et_2O$ (5 equiv, 12 μL). The ^1H and ^{31}P NMR spectra revealed the complete conversion of the dihydride into the *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) complex (excess acid is not required for the complete conversion of **1** to **2**; even with 1 equiv of acid, complete conversion can be achieved). ^1H NMR (CD_2Cl_2, rt (room temperature)): δ −11.63 (br t (br s in the $^1H\{^{31}P\}$ NMR), 3H, Ir−H_3, $J(H_3,P)$ = 5.9 Hz), 1.36−2.08 (m, 66H, $P(C_6H_{11})_3$), 13.38 (br s, 1H, $(\eta^2\text{-}S_2CH)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ 18.4 (s, $P(C_6H_{11})_3$). For the variable-temperature NMR spectroscopic studies, the protonation was carried out in a similar manner in $CDF_2Cl/CDFCl_2$ solvent mixture at 273 K and the tube was inserted into the NMR probe, precooled to 273 K.

Observation of the H−D Isotopomers of *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$. The dihydrogen hydride complex *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) was prepared as described above. Through this solution HD gas (generated from NaH and D_2O) was purged at a steady rate for ca. 10 min. The HD isotopomers formed were observed by ^1H NMR spectroscopy (room temperature). By this method, the extent of deuteration was found to be very low.

To obtain higher degree of deuteration, freshly prepared dihydrogen hydride samples were purged with D_2 gas for 30 min and then they were analyzed by NMR spectroscopy. By this method, in addition to the achievement of a greater degree of deuteration, the corresponding H_2D and the HD_2 isotopomers were also observed.

Preparation of *cis*-$[Ir(H)(CH_3CN)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (3). The dihydrogen hydride complex *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) was prepared as described above by starting from $[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (50 mg, 0.06 mmol) and $HBF_4{\cdot}Et_2O$ (5 equiv, 40 μL) in CH_2Cl_2 (10 mL). Without isolation of the dihydrogen complex, CH_3CN (10 equiv, 30 μL) was added and the reaction mixture was stirred for 2 h. The volatiles were removed in vacuo resulting in a sticky residue that was washed several times with petroleum ether. The reddish-brown product of *cis*-$[Ir(H)(CH_3CN)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**3**) was obtained in a yield of 41 mg (71%). Anal. Calcd for $C_{39}H_{71}BF_4IrNP_2S_2{\cdot}0.5C_7H_8$: C, 50.78; H, 7.42. Found: C, 50.40; H, 6.80 (the presence of toluene was confirmed using ^1H NMR spectroscopy). ^1H NMR ($CDCl_3$): δ −19.83 (t, 1H, Ir−*H*, J(H,P) = 13.0 Hz), 1.20−2.21 (m, 66H, $P(C_6H_{11})_3$), 2.72 (s, 3H, CH_3CN), 12.88 (br s, 1H, $(\eta^2\text{-}S_2CH)$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.9 (s, $P(C_6H_{11})_3$). ES-MS: m/z = 832 $[M^+ - (CH_3CN + BF_4^-)]$.

Preparation of *cis*-$[Ir(H)(CO)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (4). The dihydrogen hydride complex *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) was prepared as described above starting from $[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (100 mg, 0.12 mmol) and $HBF_4{\cdot}Et_2O$ (4 equiv, 65 μL) in CH_2Cl_2 (10 mL). Without isolation of the dihydrogen complex, CO gas (1 atm) was purged through this solution for 5 min during which time the color of the solution turned from reddish yellow to brown. The reaction mixture was stirred for an additional 1 h, and then the solvent was stripped under vacuum and the reddish-brown solid of *cis*-$[Ir(H)(CO)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**4**) was dried under vacuum. Yield: 90 mg (85%). ^1H NMR (CD_2-

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Cl_2): δ −18.70 (t, 1H, Ir−*H*, *J*(H,P) = 12.0 Hz), 1.20−2.20 (m, 66H, $P(C_6H_{11})_3$), 12.40 (br s, 1H, (η^2-S_2CH)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.5 (s, $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.10−29.60 (m, P*Cy*$_3$), 164.00 (t, Ir−*C*O, *J*(C,P) = 26.8 Hz), 238.09 (s, (η^2-S_2CH)). IR (KBr): ν(CO) 2026 cm^{-1}. ES-MS: *m*/*z* = 860 [$M^+ - BF_4^-$]. (Satisfactory elemental analysis data for this compound could not be obtained because of the formation of noncombustible metal fluorides during combustion.)

Reaction of [Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] with MeOTf/Isolation of *cis*-[Ir(H)(H_2O)(η^2-S_2CH)(PCy_3)$_2$][OTf] (5). To a toluene solution (10 mL) of [Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (50 mg, 0.06 mmol) was added MeOTf (3 equiv, 20 μL, 0.18 mmol) using a syringe, and the reaction mixture was stirred for 1 h. Upon stripping of the volatiles under vacuo, a thick red sticky residue was obtained which was washed several times with petroleum ether. The product was crystallized from its concentrated toluene solution via slow evaporation of the solvent at room temperature. Yield: 30 mg (50%). The product was identified as *cis*-[Ir(H)(H_2O)(η^2-S_2CH)(PCy_3)$_2$][OTf] (**5**) by NMR spectroscopy. Anal. Calcd for $C_{38}H_{70}F_3IrO_4P_2S_2$: C, 45.67; H, 7.06. Found: C, 46.02; H, 6.59. ^1H NMR (C_6D_6): δ −19.03 (t, 1H, Ir−*H*, *J*(H,P) = 13.9 Hz), 1.11−2.21 (m, 66H, $P(C_6H_{11})_3$), 3.40 (s, 2H, H_2O), 11.92 (br s, 1H, (η^2-S_2CH)). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.5 (s, $P(C_6H_{11})_3$).

The reaction of [Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] with Me_3SiOTf under similar reaction conditions as the above reaction with MeOTf also afforded *cis*-[Ir(H)(H_2O)(η^2-S_2CH)(PCy_3)$_2$][OTf] (**5**). Yield: 53%.

Determination of the pK_a of *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (2). A 20 mg (0.02 mmol) sample of [Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] was dissolved in 0.5 mL of CD_2Cl_2. The solution was freeze−pump−thaw degassed in three cycles and then saturated with argon. Then $HBF_4 \cdot Et_2O$ (4 μL, 1 equiv) was added to convert the starting dihydride into the dihydrogen/hydride complex, *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (**2**). To this solution, distilled water (saturated with argon) (0.4 μL, 1 equiv) was added at room temperature. Within minutes, an equilibrium was established as shown in eq 6. The concentrations of *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (**2**), [Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (**1**), and H_3O^+ were obtained by integration of the respective signals in the hydride region (for the iridium complexes) and the signal due to H_3O^+ (δ 6.64) in the ^1H NMR spectrum. The concentration of H_2O which is needed to compute the K_{eq} of reaction 6 was back-calculated by subtracting the concentration of H_3O^+ (formed due to protonation of H_2O, observable in the ^1H NMR spectrum) from the initial concentration of H_2O (known quantity) and multiplying it by the ratio of molecular weight of H_3O^+ and H_2O. This was done since the signal due to H_2O could not be observed in the presence of H_3O^+ in the ^1H NMR spectrum. The pK_a value of **2** was calculated from the equilibrium depicted in eq 6 using the expression given in eq 7.

X-ray Structure Determinations of *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (1) and *cis*-[Ir(H)(H_2O)(η^2-S_2CH)(PCy_3)$_2$][OTf] (5). Suitable crystals of **1** and **5** were chosen after examination under a microscope. The unit cell parameters and the intensity data were collected on a Bruker SMART APEX CCD diffractometer equipped with a fine-focus Mo Kα X-ray source. The SMART software was used for data acquisition and the SAINT software for data reduction.[11a] Absorption corrections were made using SADABS program[11b] and Multiscan method[11c] for **1** and **5**, respectively. The structures were solved and refined using the SHELX programs.[11d] The iridium atom position in both the complexes was observed by the Patterson method, and the non-hydrogen atoms were located by successive difference Fourier maps and were refined anisotropically. The two toluene molecules observed in the unit cell of **5** were refined isotropically. The hydride ligands in **1** were located from the difference Fourier map and refined isotropically. All the other hydrogen atoms in **1** and **5** were generated in idealized positions and refined in a riding model. The crystallographic data are summarized in Table 1.

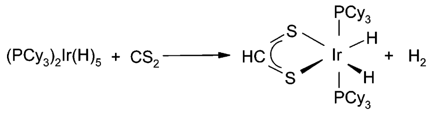
Table 1. Crystallographic Data for *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (**1**) and *cis*-[Ir(H)(H_2O)(η^2-S_2CH)(PCy_3)$_2$][OTf] (**5**)

param	1	5
formula	$C_{37}H_{69}IrP_2S_2$	$C_{52}H_{86}F_3IrO_4P_2S_3$
fw	832.18	1182.53
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	12.534(9)	14.486(7)
b, Å	16.756(11)	14.576(7)
c, Å	19.027(13)	16.653(9)
α, deg	90.00	84.049(8)
β, deg	107.660(11)	67.300(7)
γ, deg	90.00	61.362(7)
V, Å^3	3808(4)	2832(3)
Z	4	2
D_{calcd}, g/cm^3	1.452	1.385
T, K	293(2)	293(2)
λ, Å	0.710 73	0.710 73
μ, mm^{-1}	3.724	2.574
R^a	0.0206	0.0359
$R_w{}^a$	0.0480	0.0848

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ (based on reflections with $I > 2\sigma(I)$).

Results and Discussion

Synthesis and Characterization of *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (1). The insertion of CS_2 into the Ir−H bond of [Ir(H)$_5$(PCy_3)$_2$] afforded the *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] complex accompanied by the elimination of H_2 (eq 1). Upon workup and crystallization, yellow crystals of the complex were obtained in 76% yield.



1

(1)

The ^1H NMR spectrum of **1** shows a triplet for the two hydrides at δ −21.64 due to coupling with the two equivalent cis phosphorus nuclei with a *J*(H,P_{cis}) of 17.0 Hz and a broad singlet at δ 13.89 for the dithioformate hydrogen. The PPh_3 analogue, *cis*-[Ir(H)$_2$(η^2-S_2CH)(PPh_3)$_2$], reported by Robinson and Sahajpal[12] has very similar NMR spectral features. The $^{31}P\{^1H\}$ NMR spectrum is composed of only one singlet at δ 28.1, indicating the trans disposition of the two phosphines. The $^{13}C\{^1H\}$ NMR spectrum shows a singlet at δ 231.5 for the dithioformate carbon.

An X-ray crystallographic study of *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (**1**) has been carried out, and the ORTEP diagram is shown in Figure 1. The structure consists of a severely

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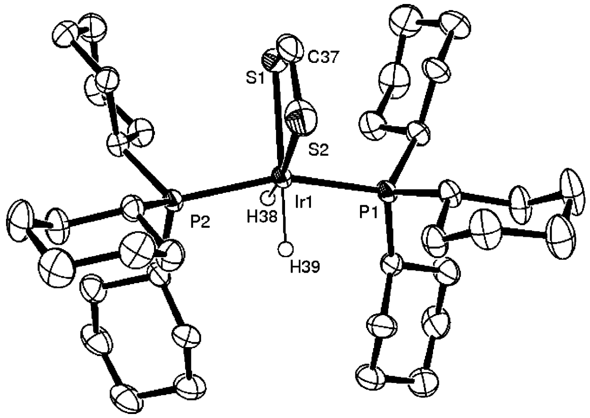


Figure 1. ORTEP view of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**) at the 50% probability level.

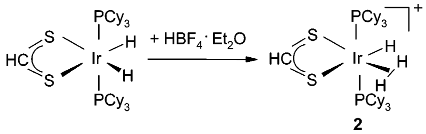
Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**) and *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ (**5**)

	1	**5**
Ir(1)−H(38)	1.5528(315)	
Ir(1)−H(39)	1.5460(237)	
Ir(1)−P(1)	2.3218(12)	2.3903(12)
Ir(1)−P(2)	2.3217(16)	2.3731(11)
Ir(1)−S(1)	2.4677(14)	2.3032(12)
Ir(1)−S(2)	2.4510(16)	2.4789(15)
Ir(1)−O(4)		2.144(2)
C(37)−S(1)	1.657(3)	1.689(4)
C(37)−S(2)	1.671(3)	1.661(3)
O(3)−O(4)[a]		2.592(4)
O(1)−O(4)[b]		2.712(3)
P(1)−Ir(1)−P(2)	157.76(2)	158.96(2)
P(1)−Ir(1)−S(1)	98.79(5)	94.30(5)
P(1)−Ir(1)−S(2)	98.51(4)	98.81(3)
P(2)−Ir(1)−S(1)	99.21(4)	92.47(5)
P(2)−Ir(1)−S(2)	99.84(3)	102.23(4)
S(1)−Ir(1)−S(2)	70.02(4)	71.34(3)
S(1)−C(37)−S(2)	116.01(16)	112.9(2)
P(1)−Ir(1)−O(4)		88.78(8)
P(2)−Ir(1)−O(4)		88.90(8)

[a] Intramolecular hydrogen bond. [b] Intermolecular hydrogen bond.

distorted octahedron. The two PCy_3 phosphines are trans to one another, and the dithioformate moiety is bound to the metal in an η^2-fashion. The two hydride ligands approximately trans to the dithioformate ligand were located from the successive difference Fourier maps. The geometry around the carbon of the S_2CH moiety is slightly deviated from an ideal sp^2 carbon atom (116.01(16)°). The two C−S distances (S(1)−C(37) and S(2)−C(37)) are 1.657(3) and 1.671(3) Å, respectively. These intermediate distances between C−S single and double bonds, which signify delocalization of electron density over the S−CH−S fragment, have been observed previously in certain ruthenium complexes by us[6b] and others.[13] The dithioformate bite angle S(1)−Ir(1)−S(2) is 70.02(4)°. Pertinent bond lengths and angles have been summarized in Table 2.

Preparation and Characterization of *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (2). It is interesting to note that *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**) has five available sites for protonation: two sulfurs and one carbon of the dithioformate moiety and the two hydride ligands. Upon protonation of **1** using $HBF_4{\cdot}Et_2O$, we obtained the corresponding dihydrogen hydride complex which we believe is *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) (eq 2). We found no evidence of protonation on any other site even in the presence of excess acid. Recent work in our laboratories showed that the site of protonation in a ruthenium hydride dithioformate complex of the type *trans*-$[Ru(H)(SC(S)H)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) is the sulfur resulting in a hydride dithioformic acid derivative.[6a] On the other hand, the protonation of $[Os(H)(CO)(S_2CH)(P^iPr_3)_2]$ complex in CD_2Cl_2 gave the corresponding dihydrogen complex and, in Et_2O solvent, the site of protonation was the dithioformate resulting in a methane dithiolate derivative.[14] Use of HOTf ($pK_a = -14$ estimated by the Hammett H_0 method; in pure water, its acidity is leveled to that of H_3O^+, $pK_a = -1.75$),[15] a stronger acid than $HBF_4{\cdot}Et_2O$, also afforded only the dihydrogen hydride complex. Our attempts to isolate **2** in the solid state failed, and we could only recover certain unidentifiable species as confirmed by NMR spectroscopy; therefore, we characterized **2** using only NMR spectroscopy. The ^1H NMR spectrum of **2** at room temperature shows only one broad triplet at δ −11.63 which appears as a broad singlet in the hydride region of the $^1H\{^{31}P\}$ NMR spectrum. The triplet pattern is a result of coupling of the two cis P atoms with the three equivalent hydride ligands, and the broadness of the signals is suggestive of a rearrangement process that is rapid on the NMR time scale. The $^{31}P\{^1H\}$ NMR spectrum is composed of only one singlet at δ 18.4, suggesting that the trans disposition of the phosphine ligands is retained upon protonation. In an attempt to get an insight into the dynamic processes of the hydride ligands, we studied the low-temperature NMR behavior of **2** down to 185 K in toluene-d_8. While extensive line broadening of the hydride signal took place at 185 K, no limiting spectrum was apparent. Even at 158 K in $CDF_2Cl/CDFCl_2$ solvent, only a single hydride signal was observed in the ^1H NMR spectra, which could be due to a highly fluxional trihydride or a rapidly exchanging dihydrogen/hydride structure. The variable-temperature $^{31}P\{^1H\}$ NMR spectrum showed no change in the spectral characteristics except that the phosphine resonances underwent an upfield shift and broadened with decrease in the temperature.



2

(2)

To unequivocally establish the presence of both hydride and dihydrogen ligands, we reacted *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) with CH_3CN and CO to obtain the products of displacement of H_2, *cis*-$[Ir(H)(L)(\eta^2\text{-}S_2CH)$-

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(13) (a) Gervasio, G.; Vastag, S.; Szalontai, G.; Markó, L. *J. Organomet. Chem.* **1997**, *533*, 187−191 and references therein. (b) Gao, Y.; Holah, D. G.; Hughes, A. N.; Spivak, G. J.; Havighurst, M. D.; Magnuson, V. R.; Polyakov, V. *Polyhedron* **1997**, *16*, 2797−2807. (c) Gopinathan, S.; Unni, I. R.; Gopinathan, C.; Puranik, V. G.; Tavele, S. S.; Guru Row, T. N. *Polyhedron* **1987**, *6*, 1859−1861.

(14) Albeniz, M. J.; Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 3746−3748.

(15) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

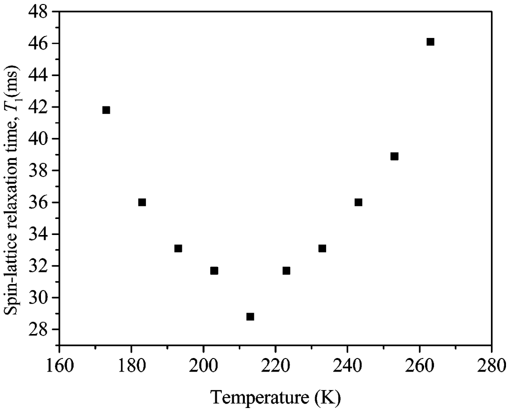
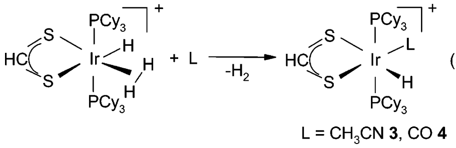


Figure 2. Plot of T_1 (400 MHz) versus temperature for *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (**2**).

(PCy_3)$_2$][BF_4] (L = CH_3CN (**3**), CO (**4**)) (eq 3). The free H_2 liberated was detected using ^{1}H NMR spectroscopy (singlet at δ 4.60). The ^{1}H NMR spectrum of *cis*-[Ir(H)(CH_3CN)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (**3**) shows a triplet at δ −19.83 for the hydride coupled to the two cis P nuclei and a singlet at δ 2.72 for the bound nitrile moiety. The ^{31}P{^{1}H} NMR spectrum is composed of only one singlet which is suggestive of the trans disposition of the two phosphine ligands. The ^{1}H and the ^{31}P NMR spectral characteristics of *cis*-[Ir(H)(CO)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (**4**) are similar to those of the nitrile complex. ν(CO) of this complex is 2026 cm^{-1}.



(3)

To determine the existence of either a fluxional trihydride or a fluxional dihydrogen/hydride species, we carried out the variable-temperature spin−lattice relaxation time (T_1) measurements in CDF_2Cl/$CDFCl_2$. Figure 2 shows a plot of T_1 (400 MHz) versus temperature for **2**. The data presented in Figure 2 for complex **2** are the population-weighted average values since we could not obtain the frozen out spectra. The short T_1 values observed for **2** qualitatively indicate the presence of a bound H_2 ligand in a dihydrogen/hydride structure. We also determined the variable-temperature spin−lattice relaxation times for the terminal hydride ligands of the starting dihydride complex **1**, and the data are graphically shown in Figure 3. To obtain the H−H distances in the fast and the slow rotation regimes of the dihydrogen ligand in **2**, we treated the data presented in Figures 2 and 3 as has been done by Heinekey and co-workers for certain rhodium and iridium complexes earlier.[5b] The details of the calculations can be found in the Supporting Information. From the analysis, we obtained a T_1(min) (400 MHz) of 20 ms. Thus, H−H distances of 0.88 and 1.11 Å have been obtained from these calculations for the fast and the slow spinning regimes, respectively, of the bound H_2 ligand in **2**. Solutions containing **2** purged with HD gas resulted in the partial conversion of H_3 to the H_2D isotopomers. The H_2D isotopomers appear as approximately

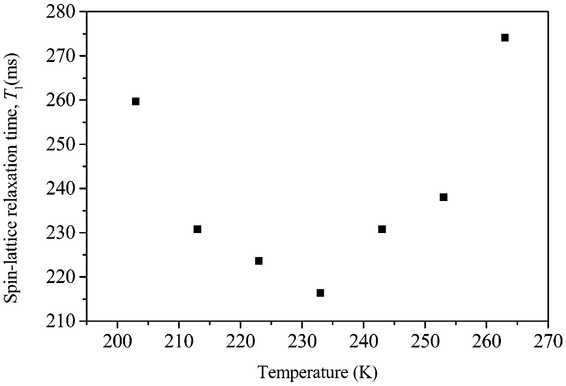


Figure 3. Plot of T_1 (400 MHz) versus temperature for *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (**1**).

1:1:1 triplets in the ^{1}H{^{31}P} NMR spectrum and exhibit small downfield isotope shifts of ca. 40 ppb. Several other complexes reported in the literature show downfield isotope shifts.[5b,16] Highly deuterated samples of **2** were obtained by purging the solution containing the corresponding dihydrogen complex with D_2 gas for a considerable period of time. The resulting samples contained H_3, H_2D, and HD_2 isotopomers. The resonances due to H_2D and HD_2 isotopomers are downfield shifted with respect to **2** by $\Delta\delta$ = 97 and 49 ppb (273 K) and 153 and 71 ppb (193 K), respectively, suggesting the operation of isotopic perturbation arising from nonstatistical distribution of deuterium. In addition, the three resonances show temperature-dependent chemical shifts: upon lowering of the temperature, the signals moved more downfield. The chemical shifts of H_3, H_2D, and the HD_2 isotopomers have been plotted as a function of the observation temperature, and the figure showing the plot has been deposited in the Supporting Information. However, in the observed temperature region, decoalescence of the signals into separate resonances for the H_2 and the hydride moieties could not be achieved.

Figure 4 shows the hydride region of the ^{1}H NMR spectrum of complex **2** at 263 K (500 MHz) with deuterium incorporated in the hydride ligands. The signal due to H_2D is approximately a 1:1:1 triplet with *J*(H,D) = 6.5 Hz

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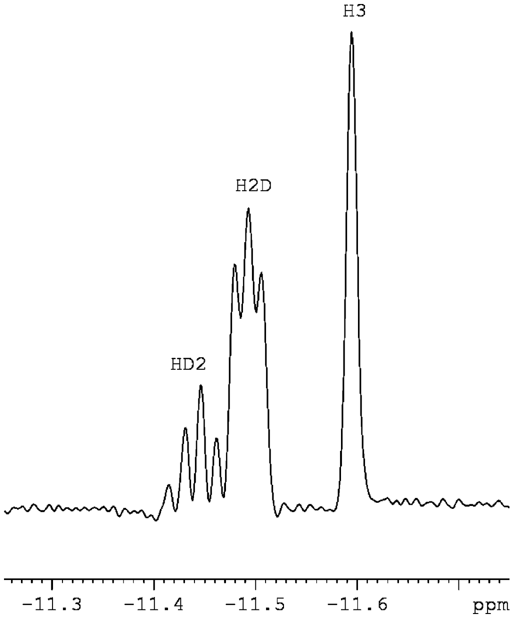
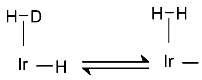


Figure 4. Hydride region of the ^1H NMR spectrum of *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][BF_4]$ (**2**) in $CDF_2Cl/CDFCl_2$ at 263 K (500 MHz) with deuterium incorporation.

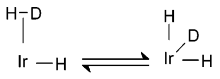
whereas the resonance due to HD_2 species exhibits a quintet with $J(H,D) = 7.7$ Hz. The observed HD couplings of the hydride resonance varies from ca. 6.4 to 5.0 Hz for the H_2D and from ca. 7.7 to 7.1 Hz for the HD_2 isotopomers over the temperature range studied, and this observation has been graphically shown in a figure deposited in the Supporting Information.

Isotopic Perturbation of Equilibrium. The H_3, H_2D, and the HD_2 isotopomers experience large temperature-dependent downfield chemical shifts signaling the isotopic perturbation of equilibrium.[17] The observed isotope shifts may result from perturbation of an equilibrium within a single dihydrogen/hydride ground-state structure wherein the deuterium gets incorporated in a particular site (eq 4).



$$\begin{array}{c}\text{H–D}\\ | \\ \text{Ir}-\text{H}\end{array} \rightleftharpoons \begin{array}{c}\text{H–H}\\ | \\ \text{Ir}-\text{D}\end{array} \qquad (4)$$

The spectrum in Figure 4 which shows downfield shifts for the H_2D and HD_2 isotopomers confirms the hydride site preference for deuterium in a single dihydrogen/hydride structure. A second possibility (eq 5) wherein perturbation of an equilibrium between a dihydrogen/hydride complex and a trihydride complex may be ruled out on the basis of the T_1 and the HD coupling data.



$$\begin{array}{c}\text{H–D}\\ | \\ \text{Ir}-\text{H}\end{array} \rightleftharpoons \begin{array}{c}\text{H}\\ |\;\text{D}\\ \text{Ir}\overset{/}{}-\text{H}\end{array} \qquad (5)$$

Heinekey and co-workers analyzed the chemical shifts and the J(H,D) data for hydrotris(pyrazolyl)borate dihydrogen/hydride complexes of Rh and Ir to obtain the limiting chemical shifts of the H_2 and the hydride ligands as well as the J(H,D) in the bound dihydrogen ligand.[5b] Their method was based on the procedure used by Calvert and Shapley[18] for studying fluxional agostic methyl groups. We also carried out similar analysis of our data using Heinekey's method[5b] and obtained the limiting chemical shifts of the dihydrogen and the terminal hydride ligands and the energy difference between deuterium substitution of the H_2 site versus the hydride site. The details of the analysis have been deposited in the Supporting Information. Thus, $\delta H_2 = -10.58$ ppm, $\delta H = -13.61$ ppm, $J(H,D) = 21.6$ Hz, $\Delta E_1 = -0.151$ kcal/mol, and $\Delta E_2 = -0.118$ kcal/mol.[19] For a somewhat related iridium complex, $[Ir(H)Tp(\eta^2\text{-}H_2)(PMe_3)]^+$ (Tp = hydrotris(1-pyrazolyl)borate), Heinekey et al.[5b] found these differences in energy to be -0.130 and -0.107 kcal/mol, respectively. Consistent with Heinekey's analysis, the deuterium concentrates in the terminal hydride position in **2**.

H−H Distance. The T_1 data analysis (see Supporting Information) gave a T_1 (min) (400 MHz, $CDF_2Cl/CDFCl_2$) of 20 ms for complex **2** which is consistent with an H−H distance (d_{HH}) of 0.88 Å (fast spinning) or 1.11 Å (slow spinning). The J(H,D) values for H_2D and the HD_2 isotopomers were found to be 6.5 and 7.7 Hz, respectively. Thus, the H−H distance (d_{HH}) calculated from the inverse relationship between d_{HH} and J(H,D) (21.6 Hz; vide infra) is 1.05 Å.[20,21] Complexes of this type belong to the class of *elongated* dihydrogen complexes which show H−H distances intermediate between those of dihydrogen complexes (≤ 1 Å) and dihydride complexes (≥ 1.5 Å). Such structures represent arrested intermediate states in the very important process of oxidative addition of H_2 to a metal center. There have been only a few examples of elongated dihydrogen complexes of iridium reported in the literature.[4i,5b,e,22]

Hydride Dynamics. Since static low-temperature-limiting ^1H NMR spectra could not be obtained even at 158 K, we presume that the activation energy for the H atom site exchange, $\Delta G^\ddagger$, must be less than 5 kcal/mol. A similar observation was made earlier by Heinekey and co-workers[5b] for an iridium complex; however, the limiting chemical shifts for the hydride and the dihydrogen ligands were estimated using the isotope perturbation of resonance effect and the $\Delta G^\ddagger$ was calculated to be ≤ 5 kcal/mol. Two distinct dynamic processes can be considered: (a) rotation of the H_2 ligand around the $M-H_2$ bond axis since barriers to hydrogen rotation are quite low, except in d^2 systems;[23] (b) H atom

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(17) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070−8071.

(18) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726−7727.

(19) ΔE_1 is the energy difference between Ir(HD)H and $Ir(H_2)D$.; ΔE_2 is the energy difference between $Ir(D_2)H$ and Ir(HD)D.

(20) (a) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396−4399. (b) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396−5407. (c) King, W. A.; Luo, X.-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782−6783.

(21) d_{HH} (Å) $= -0.0167[J(H, D)\ (Hz)] + 1.42$.

(22) (a) Heinekey, D. M.; Lledós, A.; Lluch, J. M. *Chem. Soc. Rev.* **2004**, *33*, 175−182. (b) Pons, V.; Heinekey, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 8428−8429.

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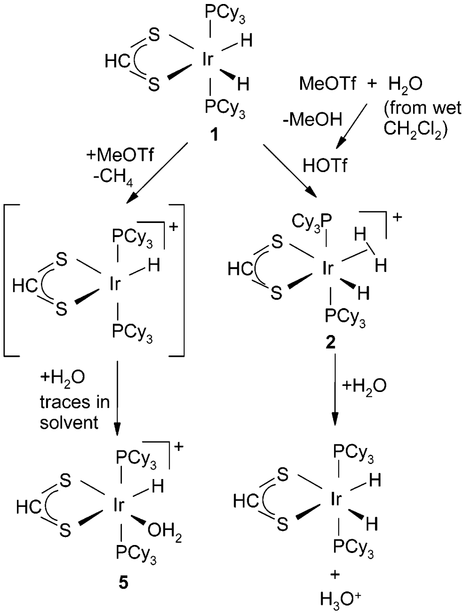
exchange between the dihydrogen and the hydride ligands. The combination of overall positive charge and the presence of phosphine coligands in complex **2** could be expected to result in the heterolytic cleavage of the bound H_2 followed by a proton transfer to the hydride moiety rendering the three hydride ligands equivalent with respect to the NMR time scale. The pK_a of the bound H_2 ligand in **2** has been estimated to be ~ -1.0 (see later). We also cannot rule out a second possible mechanism: since the H−H bond in **2** is elongated, a substantial degree of bond formation (between the elongated H_2 moiety and the hydride) involving an *associative* type of mechanism to generate a trihydrogen intermediate or transition state could take place in a highly concerted manner rendering the three hydrogens equivalent.[1b] Such a stretching of the H_2 toward an adjacent hydride has been calculated to be a low-energy process that leads to a transition state with trihydrogen character in $[M(H)_4(Cp)(\eta^2\text{-}H_2)(PR_3)]^+$ (M = Mo; W) complexes.[24] The presumed barrier for the exchange process in our system (≤5 kcal/mol), in agreement with the inability to decoalesce the ^{1}H NMR signals in the hydride region even at 158 K, is consistent with the proposed trihydrogen species. Heinekey and co-workers were able to measure the H_2/H exchange rate in a ruthenium dihydrogen/hydride complex $[Ru(\eta^2\text{-}H_2)(L_2)(PCy_3)_2]^+$ and found an approximate free energy of activation, $\Delta G^{\ddagger}_{120} = 5.5$ kcal/mol.[5d] A mechanism that is consistent with a highly concerted exchange process involving a ruthenium−trihydrogen-like transition state has been suggested. A combination of experimental and theoretical studies on $[IrX(H)_2(\eta^2\text{-}H_2)(PR_3)_2]$ revealed exchange barriers of 1.9 (1.5(2) kcal/mol from inelastic neutron scattering studies), 1.8, and 1.7 kcal/mol for X = Cl, Br, and I, respectively.[5e,f] A mechanism involving oxidative addition/reductive elimination pathway through a tetrahydride intermediate has been suggested on the basis of theoretical calculations.

Reactivity of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ toward Electrophilic Reagents. We examined the reactivity behavior of **1** with electrophilic reagents such as MeOTf and Me_3SiOTf. In both the reactions, the electrophile presumably attacks one of the hydride ligand to generate the alkane/silane that is eliminated. The CH_4 and the Me_3SiH generated were observed spectroscopically. The residual water present in the solvent then binds to the metal in the vacant site thus created to afford *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ (**5**). An even trace amount of moisture in rigorously dried solvents is enough for the formation of the aquo complex. In addition to the aquo complex, another unidentifiable iridium hydride species was also obtained. When these reactions were carried out in slightly wet solvents, the only product obtained was *cis*-$[Ir(H)(\eta^2\text{-}H_2)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$. The electrophilic reagent in this case reacts first with the water present in the solvent to generate HOTf (a broad singlet at δ 13.80 in the ^{1}H NMR spectrum), which causes the protonation of the dihydride. In addition to HOTf, a signal due to MeOH formed was also observed in the ^{1}H NMR spectrum. Addition of a slight excess water to **2** resulted in its protonation to form H_3O^+ (detected using ^{1}H NMR spectroscopy, br s at δ 6.64) and the recovery of the starting dihydride complex $[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**), indicating that the complex **2** is quite acidic. It is rather intriguing to note that **5** cannot be made by any other independent route. These reactions have been summarized in Scheme 1. It is rather interesting to note that the dithioformate moiety acts as a *spectator* under these reaction conditions. In contrast, we found that the electrophilic reagents such as the ones employed in the present work actually functionalize the dithioformate moiety of certain ruthenium hydride dithioformate complexes, whereas the hydride ligand is unaffected.[6a]

Scheme 1. Reaction of *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**) with MeOTf



We have been able to crystallize the aquo complex *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ (**5**) and determine its structure by X-ray crystallography. The molecular structure of *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ complex is shown in Figure 5. The structure consists of a severely distorted octahedral cation. In addition, the structure solution revealed the presence of two toluene molecules. The Ir(1)−O(4) bond distance was found to be 2.144(2) Å; all the other bond lengths are comparable to those in *cis*-$[Ir(H)_2(\eta^2\text{-}S_2CH)(PCy_3)_2]$ (**1**). The geometry around the carbon of the

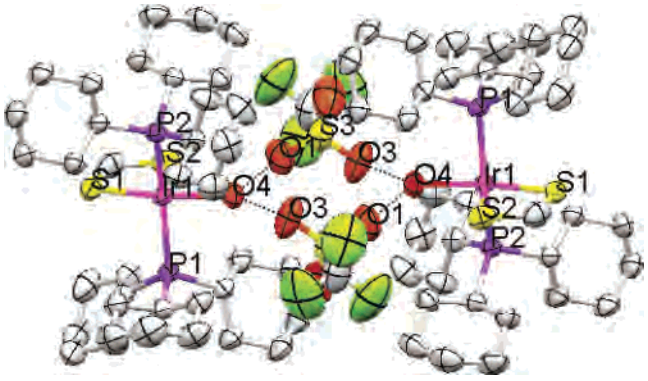


Figure 5. Molecular structure of *cis*-$[Ir(H)(H_2O)(\eta^2\text{-}S_2CH)(PCy_3)_2][OTf]$ (**5**) showing the intra- and the intermolecular H-bonds between the iridium-bound aquo ligand and the OTf counterion.

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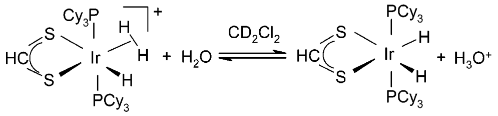
[24] Bayse, C. A.; Hall, M. B.; Pleune, B.; Poli, R. *Organometallics* **1998**, *17*, 4309−4315.

dithioformate moiety (S(1)−C(37)−S(2) angle of 112.9(2)°) is quite strained from an ideal sp^2 carbon. The water coordinated to the iridium atom forms one intra- and one intermolecular hydrogen bonds with the OTf counterion making a dimer at the inversion center. The intramolecular O(3)−O(4) distance was found to be 2.592(4) Å, shorter in comparison to the 2.712(3) Å for the corresponding intermolecular O(1)−O(4) distance. The important bond lengths and angles have been summarized in Table 2.

Acidity Measurement. The acidities of the dihydrogen complexes reported in the literature have been measured on the pseudoaqueous pK_a scale.[20b,25] The equilibrium constant K_{eq} of reaction 6



(6)

has been obtained from the ^{1}H NMR spectral integrations (converted into concentrations; see Experimental Section) of the hydride signals of the iridium complexes and the H_3O^+ species and the calculated concentration of H_2O. As suggested earlier by Kristjánsdóttir and Norton,[26] the pK_a value (in CD_2Cl_2) of the dihydrogen/hydride complex **2** has been estimated from the equilibrium constant K_{eq} and the pK_a of H_3O^+ (−1.74, aqueous)[15] using eq 7.

$$\mathrm{p}K_a\{[\mathrm{Ir(H)}(\eta^2\text{-}\mathrm{H_2})(\eta^2\text{-}\mathrm{S_2CH})(\mathrm{PCy_3})_2]^+\} = \mathrm{p}K_a\{[\mathrm{H_3O}]^+\} + \mathrm{p}K_{eq} \quad (7)$$

A K_{eq} of 0.194 was obtained for the reaction 6. Thus, using the above expression, a pK_a of −1.0 was obtained for complex **2** indicating that it is quite acidic. The high acidity of complex **2** supports our proposed mechanism involving the heterolytic cleavage of the bound H_2 ligand followed by the proton transfer to the hydride rendering the three hydrogens equivalent.

Protonation Reactions of *cis*-[Ir(H)(CH_3CN)(η^2-S_2CH)(PCy_3)$_2$][BF_4]. The attempted protonation of *cis*-[Ir(H)(CH_3CN)(η^2-S_2CH)(PCy_3)$_2$][BF_4] using HBF_4·Et_2O (up to 70 equiv) or HOTf (up to 50 equiv) did not afford the corresponding dihydrogen complex *cis*-[Ir(η^2-H_2)(CH_3CN)(η^2-S_2CH)(PCy_3)$_2$]$^{2+}$, a dicationic species that could be expected to be quite acidic compared to a monocationic dihydrogen complex. Similar observations were made in the attempted protonation reactions of *cis*-[Ir(H)(CO)(η^2-S_2CH)(PCy_3)$_2$][BF_4]. In both the cases, we recovered the starting hydride complexes.

Conclusions

The protonation reactions of the dihydride complex *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] with HBF_4·Et_2O resulted in a highly dynamic dihydrogen hydride derivative *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4]. Even low-temperature NMR spectroscopy did not yield limiting spectra with separate resonances due to the dihydrogen and the hydride moieties indicating that the $\Delta G^\ddagger$ for the H atom site exchange process must be quite small (≤5 kcal/mol). It can be concluded that the dynamic process involves minimal movement of the coligands rendering the three hydrogens equivalent. The J(H,D) for the partially deuterated isotopomers of *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4] complex is 21.6 Hz, which corresponds to a d_{HH} of 1.05 Å. Such species belong to the category of *elongated* dihydrogen complexes.

The protonation of the monocationic hydride complexes *cis*-[Ir(H)(L)(η^2-S_2CH)(PCy_3)$_2$]$^+$ (L = CH_3CN, CO) using either excess HBF_4·Et_2O or excess HOTf did not afford the corresponding dicationic dihydrogen complexes suggesting that a much stronger acid is required and that such derivatives, if realized, could be expected to be highly acidic and extremely unstable.

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Supporting Information Available: X-ray crystallographic data for *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (**1**) and *cis*-[Ir(H)(H_2O)(η^2-S_2CH)(PCy_3)$_2$][OTf] (**5**) in CIF format, a structure of complex **5** showing the hydrogen bonds and a list of hydrogen bonds in complex **5**, T_1 data (400 MHz) for *cis*-[Ir(H)$_2$(η^2-S_2CH)(PCy_3)$_2$] (**1**) and *cis*-[Ir(H)(η^2-H_2)(η^2-S_2CH)(PCy_3)$_2$][BF_4] (**2**), plots of the ^{1}H NMR chemical shifts versus temperature and the H, D coupling constants versus temperature for the HD isotopomers, and details of the analysis of NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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