Synthesis and Reactivity of the Labile Dihydrogen Complex $[\{MeC(CH_2PPh_2)_3\}Ir(H_2)(H)_2]BPh_4$

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The novel Ir(III) nonclassical tetrahydrido complex $[(triphos)Ir(H_2)(H)_2]BPh_4$ (**4**BPh_4) has been prepared by hydrogenation of the ethene dihydride complex $[(triphos)Ir(C_2H_4)(H)_2]BPh_4$ in either the solid state ($P_{H_2} \geq 1$ atm) or CH_2Cl_2 solution ($P_{H_2} \geq 3$ atm) [triphos = $MeC(CH_2PPh_2)_3$]. Complex **4**BPh_4 is very labile in solution and can be isolated in the solid state exclusively from solid−gas reactions. Characterization of **4**BPh_4 in solution can be achieved by high-pressure NMR and IR spectroscopies, however. Various deuterated isotopomers of $[(triphos)Ir(H_2)(H)_2]^+$ have been obtained in CD_2Cl_2 solution at low temperature by treatment of the trihydride $[(triphos)IrH_3]$ with $DOSO_2CF_3$. On the basis of a variety of NMR experiments, the complex cation $[(triphos)Ir(H_2)(H)_2]^+$ is assigned an octahedral structure where two terminal hydride ligands and a dihydrogen molecule are *trans* to the phosphorus atoms of a facial triphos ligand. Complex **4**BPh_4 dissolves in THF at room temperature yielding $[(triphos)IrH_3]$, BPh_3, and benzene; a similar reaction occurs in acetone, whereas in CH_2Cl_2 the complex loses H_2 converting to the dimers *cis*- and *trans*-$[(triphos)IrH(\mu\text{-}H)_2HIr(triphos)](BPh_4)_2$.

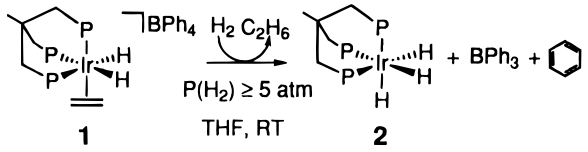
Introduction

In a number of homogeneous hydrogenation reactions assisted by monocationic metal complexes, we have observed the degradation of the tetraphenylborate counteranion to BPh_3 and benzene with concomitant formation of a neutral complex with a new M−H bond.[1,2] In the example considered in this work, the ethene dihydride complex $[(triphos)Ir(C_2H_4)(H)_2]BPh_4$ (**1**) reacts with H_2 (>5 atm) in THF producing, already at room temperature, the trihydride $[(triphos)IrH_3]$ (**2**), ethane, BPh_3 and benzene (Scheme 1).[2]

The reaction shown in Scheme 1 is not surprising *per se* as one considers that hydrido metal complexes may act as Brønsted acids[3] and that the BPh_4^- anion is susceptible to attack by acids.[4] Since the protonolysis of BPh_4^- requires the action of strong acids, we soon started hypothesizing the formation of transient nonclassical H_2 complexes in the course of the hydrogenolysis reactions of BPh_4^-. Indeed, unlike classical polyhydride complexes, η^2-H_2 coordination compounds may be very acidic with pK_a values below 0.[5,6]

After many efforts, we have now been able to unambiguously show that the nonclassical dihydrogen dihydride cation $[(triphos)Ir(H_2)(H)_2]^+$ (**4**$^+$) is indeed formed when **1** is reacted with H_2 in either the solid state or solution. Nonconventional experiments such as high-pressure NMR spectroscopy and solid−gas organometallic reactions have been of crucial importance in solving the chemical puzzle that is described here.

Scheme 1. Hydrogenation of $[(triphos)Ir(C_2H_4)(H)_2]BPh_4$ in THF



Experimental Section

General Procedures. The ligand 1,1,1-tris[(diphenylphosphino)-methyl]ethane (triphos)[7] and the complexes $[(triphos)IrH_2(C_2H_4)]BPh_4$ (**1**)[8] and $[(triphos)IrH_3]$ (**2**)[9] were prepared as described in the literature. $CFCl_3$ was purchased from Aldrich and used as received. Deuterated solvents for NMR measurements (Merck) were dried over activated molecular sieves (4 Å) and freeze−pump−thaw degassed three times each before dissolving solid samples. ^{1}H NMR spectra were recorded on Bruker Avance DRX 500, Varian VXR 300, or Bruker AC200 spectrometers operating at 500.13, 299.94, or 200.13 MHz, respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance ($\delta_{CD_2Cl_2}$ 5.32, δ_{THF-d_8} 3.70 and 1.80, $\delta_{acetone-d_6}$ 2.20, δ_{DMF-d_7} 2.92). ^{31}P{^{1}H} NMR spectra were recorded on the same instruments operating at 202.46, 121.42, and 81.01 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. The spin−lattice relaxation time (T_1) measurements were carried out in $CD_2Cl_2/CFCl_3$ at 300 MHz by the inversion−recovery method using standard 180°−τ−90° pulse sequences with calibration of the 90° pulse at all reported temperatures. ^{1}H{^{31}P} NMR spectra were recorded on the Avance DRX 500 instrument using the wide-band phosphorus decoupling sequence GARP.[10] The high-pressure NMR (HPNMR) experiments were carried in 10-mm sapphire tubes (Saphikon Inc., NH) assembled with an in-house-built Ti-alloy pressure head. The HPNMR spectra were recorded by using a standard 10-mm probe tuned to ^{31}P and ^{1}H on the Bruker AC200 spectrometer. The ^{31}P{^{1}H} HPNMR measurements were acquired with composite pulse proton decoupling (WALTZ16).[10]

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Infrared spectra were generally recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates. Variable-pressure solution spectra were recorded on a Perkin-Elmer 1760 FT-IR spectrometer using a NaCl cell capable of withstanding high pressures (up to 200 atm). The IR solution experiments were made in a stainless-steel vessel (125 mL) having a pressure gauge and two stopcocks. Air was evacuated from the vessel by a vacuum pump, and then a CH_2Cl_2 solution of the complex under examination was introduced by suction. The required pressure of H_2 was obtained using a high-pressure cylinder. Reactions under controlled pressure were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. GC analyses were performed on a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector and with a 4.5-m 60/80 Carboxen-1000 stainless-steel column (3.2-mm o.d./2.1-mm i.d.; Supelco Inc.). Elemental analyses were performed using a Carlo Erba model 1106 elemental analyzer. **CAUTION**: All manipulations involving high pressures are potentially hazardous. Safety precautions must be taken at all stages of NMR studies involving high-pressure NMR tubes.[11]

Synthesis of the Complex [(triphos)IrD$_3$] (2-*d*$_3$). The trideuteride complex [(triphos)IrD$_3$] (**2**-*d*$_3$) was prepared from the protiated complex **2** by H/D exchange at room temperature with CH_3OD in CH_2Cl_2. The isotopic purity (>90%) of the isolated product was determined by ^{1}H NMR integration of the residual proton resonances in the hydride region against the resonances of the phosphine protons. IR (KBr): ν(Ir−D) 1450 cm^{-1} (br, m).

Synthesis of [(triphos)Ir(H_2)(H)$_2$]BPh_4 (4BPh_4). (A) Solid-Gas Reaction. A solid sample of **1** (0.200 g, 0.17 mmol) was placed in a Teflon vessel inside the Parr reactor, which, after three vacuum−nitrogen cycles, was pressurized with 5−10 atm of dihydrogen. The reactor was heated to 60 °C for 3 h. After this time, the reactor was cooled to room temperature and slowly depressurized. The volatile contents of the reactor were analyzed by GC (which showed the presence of ethane) while the pale yellow solid in the Teflon vial was transferred into a Schlenk flask which was filled with nitrogen and stored in the refrigerator at −5 °C. ^{31}P{^{1}H} and ^{1}H NMR spectra of the crude product dissolved in cold (−50 °C) CD_2Cl_2 (0.7 mL) in a 5-mm NMR tube showed the almost quantitative formation of **4**BPh_4 (>97%). $C_{65}H_{63}BIrP_3$ (1140.2): calcd C 68.47, H 5.57; found C 68.45, H 5.51. IR: ν(Ir−H) 2068 (m) and 2013 cm^{-1} (w), ν(B−C) 610 cm^{-1} (m). ^{31}P{^{1}H} NMR (CD_2Cl_2/$CFCl_3$, 1:1 v/v, 121.42 MHz): at −20 °C, δ −11.15 (br s); at −80 °C, δ −9.15 (br s, 1P), δ −12.63 (br s, 2P). ^{1}H NMR (CD_2Cl_2/$CFCl_3$, 200.13 MHz): at −10 °C, δ_{Ir-H} −9.01 (br, $\omega_{1/2} \approx$ 176 Hz, 4H); at −90 °C, δ_{Ir-H} −8.40 (br q, ^2J(H,P) ≈ 22 Hz, 2H), −10.70 (br d, ^2J(H,P$_{trans}$) ≈ 113 Hz, 2H).

(B) HPNMR Experiment. A 10-mm sapphire HPNMR tube was charged with a CD_2Cl_2 (2.2 mL) solution of **1** (0.050 g, 4.29 × 10^{-2} mmol) prepared under nitrogen and then was sequentially pressurized with hydrogen to 3, 10, and 20 atm at room temperature. ^{1}H and ^{31}P-{^{1}H} NMR spectra recorded at room temperature revealed the quantitative formation of **4**BPh_4 already at the P_{H_2} of 3 atm. The proton NMR spectrum confirmed also the stoichiometric formation of ethane (singlet at 0.81 ppm).

Synthesis of the Complex [(triphos)Ir(D_2)(D)$_2$]BPh_4 (4BPh_4-*d*$_4$). The perdeuterated isotopomer **4**BPh_4-*d*$_4$ was prepared in quantitative yield by replacing H_2 with D_2 in the procedures A and B described above. Alternatively, the perdeuterated isotopomer can be prepared *in situ* with isotopic purity higher than 90% (^{1}H NMR) by treating **2**-*d*$_3$ with $DOSO_2CF_3$ in CD_2Cl_2 under D_2 (1 atm).

Synthesis of [(triphos)Ir(H_2)(H)$_2$]BF_4 (4BF_4). (A) Solid−Gas Reaction. Substitution of [(triphos)IrH_2(C_2H_4)]BF_4 for **1** in the solid−gas preparation of **4**BPh_4 gives **4**BF_4 as a pale yellow powder. $C_{41}H_{43}BF_4IrP_3$ (907.7): calcd C 54.20, H 4.77; found C 54.06, H 4.63. IR: ν(Ir−H) 2070 (m) and 2016 cm^{-1} (w), ν(B−F) 1054 cm^{-1} (br, s).

(B) Reaction of [(triphos)IrH_3] (2) with HBF_4·OMe_2 at Low-Temperature. A 5-mm NMR tube was placed in a dry ice/acetone bath and charged with 30 mg of **2** (3.66 × 10^{-2} mmol) and with a solution of HBF_4·OMe_2 (5.0 μL, 4.11 × 10^{-2} mmol) in 0.7 mL of CD_2Cl_2 cooled to −78 °C. The tube was cautiously shaken until complete dissolution of **2** occurred to give a colorless solution. The tube was inserted into the NMR probehead precooled to −40 °C; ^{1}H and ^{31}P{^{1}H} NMR spectra, immediately recorded, showed the quantitative transformation of **2** into **4**$^+$.

Reaction of 4BPh_4 (or 4BF_4) with NEt_3. A Schlenk tube was charged under nitrogen with a magnetic bar, 0.7 mL of CD_2Cl_2, and NEt_3 (8.0 μL, 5.73 mmol) and cooled to −78 °C with a dry ice/acetone bath. Solid **4**BPh_4 (50 mg, 4.39 × 10^{-2} mmol) was then added with stirring. The pale yellow solution turned immediately colorless and was transferred via syringe into a 5-mm NMR tube. ^{31}P{^{1}H} and ^{1}H NMR analysis of the solution revealed the quantitative formation of the trihydride **2** and (NEt_3H)$^+$. In a similar way, the addition of NEt_3 to a cold solution of **4**BF_4 in CD_2Cl_2 gave **2**.

Behavior of 4BPh_4 in CD_2Cl_2 under Nitrogen. A 5-mm NMR tube containing a solution of **4**BPh_4 (0.025 g, 2.20 × 10^{-2} mmol) in CD_2Cl_2 (0.7 mL) was saturated with nitrogen at room temperature and then inserted into the NMR probe. ^{31}P{^{1}H} and ^{1}H NMR analysis of the solution showed the quantitative transformation of **4**BPh_4 into the tetrahydrido dimer *cis*-[(triphos)IrH(μ-H)$_2$HIr(triphos)](BPh_4)$_2$ (*cis*-**3**).[8] On standing at room temperature, the solution slowly became orange in color, while orange crystals of the stereoisomer *trans*-[(triphos)IrH-(μ-H)$_2$HIr(triphos)](BPh_4)$_2$ (*trans*-**3**) began to separate. After 1 week at room temperature, *ca.* 85% of the initial dihydrogen dihydride complex had converted to the orange isomer, which is practically unsoluble in CH_2Cl_2 and in most common organic solvents. Dimethylformamide (DMF) is the only solvent in which *trans*-**3** is sufficiently soluble for NMR characterization.

***cis*-3.** ^{31}P{^{1}H} NMR (CD_2Cl_2/$CFCl_3$, 1:1 v/v, 121.42 MHz): at 20 °C, δ −20.04 (s), the A_3 pattern is temperature invariant down to −120 °C. ^{1}H NMR (CD_2Cl_2, 81.01 MHz, 20 °C): δ −13.31 (sept, J(H,P) = 17.0 Hz, 4H). IR (Nujol): ν(Ir−H) 2127 (s), 2104 cm^{-1} (shoulder); ν(Ir−H−Ir) not observed.[8]

***trans*-3.** ^{31}P{^{1}H} NMR (DMF-*d*$_7$, 81.01 MHz): at 24 °C, $\delta \approx$ −1.2 (br s, $\omega_{1/2} \approx$ 173 Hz); at −55 °C, δ 15.69 (br s, J(P,P) not resolved, 1P, in the proton-coupled spectrum transforms into a broad doublet with J(H,P$_{trans}$) ≈ 160 Hz), δ −8.57 (br s, 2P); ^{1}H NMR (DMF-*d*$_7$, 200.13 MHz): at 24 °C, δ −7.74 (br s, $\omega_{1/2} \approx$ 170 Hz); at −55 °C, δ −2.99 (br d, J(H,P$_{trans}$) = 163 Hz, 2H), δ −12.39 (br quintet, J(H,P) = 36.2 Hz, 2H). IR (Nujol): ν(Ir−H) 2105 (ms) and 2057 (ms) cm^{-1}; ν(Ir−H−Ir) not observed.

Behavior of 4BPh_4 in THF-*d*$_8$. A 5-mm NMR tube containing a solution of **4**BPh_4 (0.025 g, 2.20 × 10^{-2} mmol) in THF-*d*$_8$ (0.7 mL) was saturated with nitrogen at −20 °C and then inserted into the NMR probe precooled at the same temperature. Appreciable transformation of **4** into **2** occurred already at 10 °C. After 15 min at 20 °C, ^{31}P{^{1}H} and ^{1}H NMR analysis of the solution showed the complete disappearence of **4**$^+$ with formation of a mixture of **2** (≥90%) and of the THF adduct [(triphos)Ir(H_2)(THF)]$^+$.[12] Occasionally, some *cis*-**3** is also formed. When **4**BPh_4 was dissolved in THF saturated with H_2, **2** was selectively produced. GC−MS analysis showed the concomitant formation of *ca.* 1 equiv of benzene. In a reaction carried out in a Schlenk tube with 500 mg of **4**BPh_4, after the solvent was removed *in vacuo* at room temperature, a white crystalline product sublimed from the residue at 70 °C (at 0.5 Torr). This air-sensitive product was identified as triphenylboron from its elemental analysis and IR spectrum.[13] When a sample of **4**BPh_4-*d*$_4$ was dissolved in THF-*d*$_8$, GC−MS analysis revealed the formation of benzene-*d*$_1$.

Behavior of 4BPh_4 in Acetone-*d*$_6$. Under similar conditions but in acetone-*d*$_6$, NMR spectroscopy showed the disappearence of **4**BPh_4 with formation of a *ca.* 1:1 mixture of **2** and of the solvento complex [(triphos)Ir(H_2)($OCMe_2$)]$^+$. Benzene and BPh_3 were also formed. NMR data for [(triphos)Ir(H_2)($OCMe_2$)]$^+$: ^{31}P{^{1}H} NMR (acetone-*d*$_6$, 121.42 MHz, 20 °C) δ −0.69 (t, J(P,P) = 13.5 Hz), δ −8.74 (d); ^{1}H NMR (acetone-*d*$_6$, 200.13 MHz, 20 °C) δ −10.43 (AA′XX′Y spin system, J(H,P$_{trans}$) ≈ 99 Hz, 2H).[8,12]

Behavior of 4BF_4 in THF-*d*$_8$. The dissolution of **4**BF_4 in THF-*d*$_8$ (NMR experiment) at room temperature under nitrogen gave mixtures of the THF adduct [(triphos)Ir(H_2)(THF)]BF_4 (>90%) and *cis*-**3**.

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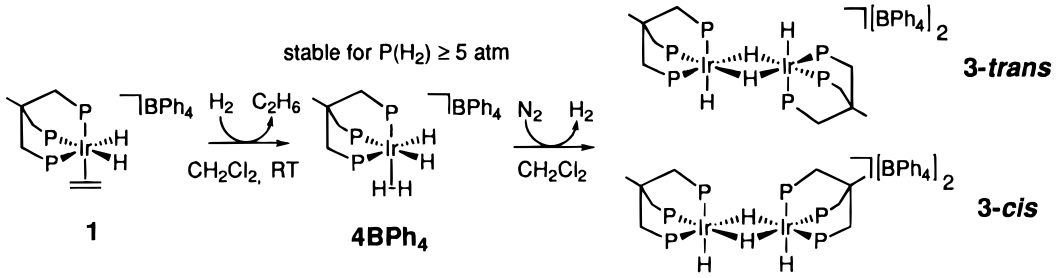
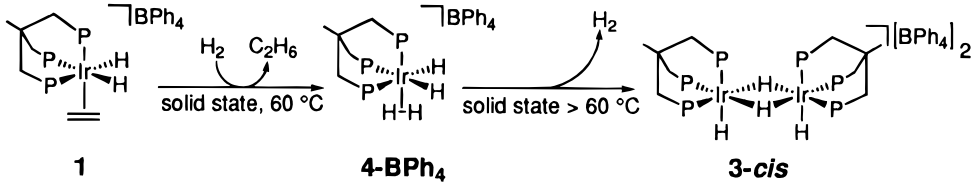
Scheme 2. Hydrogenation of $[(triphos)Ir(C_2H_4)(H)_2]BPh_4$ in Dichloromethane



Scheme 3. Solid-State Hydrogenation of $[(triphos)Ir(C_2H_4)(H)_2]BPh_4$



Reaction of $4BPh_4$ with Ethene in CD_2Cl_2. A 5-mm NMR tube containing a solution of **4**BPh_4 (0.025 g, 2.20×10^{-2} mmol) in CD_2Cl_2 (0.7 mL) was saturated with ethene at −20 °C and then inserted into the NMR probe. $^{31}P\{^1H\}$ NMR analysis of the solution showed the quantitative transformation of **4**BPh_4 into **1**.

Reaction of $4BPh_4$ with Carbon Monoxide in CD_2Cl_2. A 5-mm NMR tube containing a solution of **4** (0.025 g, 2.20×10^{-2} mmol) in CD_2Cl_2 (1.0 mL) was saturated with CO at −20 °C and then inserted into the NMR probe. $^{31}P\{^1H\}$ NMR analysis of the solution revealed the quantitative transformation of **4**BPh_4 into the known carbonyl dihydride complex $[(triphos)IrH_2(CO)]BPh_4$.[9]

Synthesis of $[(triphos)IrH_3D]BF_4$ (4BF_4-d_1) and $[(triphos)IrH_2D_2]BF_4$ (4BF_4-d_2). The trihydride complex **2** (0.030 g, 3.66×10^{-2} mmol) was suspended in 0.7 mL of CD_2Cl_2 saturated with N_2. After the suspension was transferred into a 5-mm screw cap NMR tube cooled at −78 °C, 2.0 equiv (6.5 μL, 7.32×10^{-2} mmol) of $DBF_4 \cdot OMe_2$ was added via syringe. The tube was cautiously shaken until complete dissolution of **2** occurred to give a colorless solution. ^1H NMR analysis of this solution showed the quantitative disappearance of **2** and the formation of a mixture of different isotopomers of **4**BF_4 $[(triphos)IrH_{4-n}D_n]BF_4$. A careful integration of the $^1H\{^{31}P\}$ hydride resonances gave the following isotopomeric composition: **4**BF_4 (41%); **4**BF_4-d_1 (43%); **4**BF_4-d_2 (16%). ^1H NMR (CD_2Cl_2, 500.13 MHz, −30 °C): δ −8.220 (q, J(H,P) = 22.1 Hz, **4**BF_4), δ −8.147 (q of 1:1:1 triplets, J(H,P) = 22.1 Hz, J(H,D) = 4.6 Hz, **4**BF_4-d_1), δ −8.115 (m, transforms in the $^1H\{^{31}P\}$ NMR spectrum into a 1:2:3:2:1 quintet, J(H,D) = 4.8 Hz, **4**BF_4-d_2).

Synthesis of the Isotopomers $[(triphos)IrH_{4-n}D_n]BPh_4$. A 10-mm sapphire HPNMR tube was charged with a CD_2Cl_2 (2.2 mL) solution of **1** (0.050 g, 4.29×10^{-2} mmol) pressurized with a 1:1 H_2/D_2 mixture to *ca.* 30 atm at room temperature. ^1H NMR spectroscopy of the solution showed the formation of various isotopomers $[(triphos)IrH_{4-n}D_n]^+$. ^1H NMR (CD_2Cl_2, 200.13 MHz, 20 °C): δ(**4**$^+$-d_0−**4**$^+$-d_4): complex multiplet between −8.3 and −8.0 ppm.

Results and Discussion

Preparation and Properties of $[(triphos)Ir(H_2)(H)_2]BPh_4$. As illustrated in Scheme 1, the hydrogenation of a THF solution of the ethene dihydride complex **1** in an autoclave pressurized with H_2 (>5 atm) at room temperature transforms the starting ethene complex into the trihydride **2** and produces stoichiometric amounts of ethane, BPh_3, and benzene.[2] Between 3 and 5 atm of H_2 the reaction is less selective as variable amounts of the tetrahydrido dimer *cis*-$[(triphos)IrH(\mu\text{-}H)_2HIr(triphos)](BPh_4)_2$ (*cis*-**3**) are also formed. Decreasing the H_2 pressure favors the formation of the dimer, which becomes the only product when the hydrogenation of **1** is carried out with 2 atm of H_2 at 60 °C.

Monitoring the reaction between **1** and H_2 at room temperature by high-pressure NMR spectroscopy in THF-d_8 shows no intermediate species along the transformation of **1** into **2** in the pressure range from 3 to 30 atm.

The substitution of CH_2Cl_2 for THF in the hydrogenation of **1** affects significantly the nature of both the organic and metal products. Ethane is still formed, while neither **2**, nor BPh_3, nor benzene is produced. After the autoclave is depressurized and the solvent is removed, all iridium is recovered as a mixture of *cis*-**3**[2] and its geometric isomer *trans*-$[(triphos)IrH(\mu\text{-}H)_2HIr(triphos)](BPh_4)_2$ (*trans*-**3**) (Scheme 2). However, monitoring the reaction between **1** and H_2 (1−30 atm) at room temperature by HPNMR spectroscopy in CD_2Cl_2 shows that **1** converts quantitatively to the dihydrogen dihydride complex $[(triphos)Ir(H_2)(H)_2]BPh_4$ (**4**BPh_4) already at 3 atm of H_2. Only below this pressure, the latter complex starts decomposing irreversibly to the tetrahydrido dimers, which are the only isolable metal products.

The dihydrogen dihydride complex **4**BPh_4 can be isolated in the solid state exclusively by the solid−gas reaction of **1** with H_2 at 60 °C (Scheme 3). In a typical reaction, microcrystals of **1** are introduced into an autoclave pressurized with 5 atm of H_2. Heating at 60 °C for ≥3 h usually converts 200 mg of **1** to **4**BPh_4, which is collected as a creamy-white powder. Higher H_2 pressures shorten the reaction time, while higher temperatures result in the irreversible formation of the tetrahydrido dimer *cis*-**3**.[2] Alternatively, a constant flow of H_2 at ambient pressure is passed through a layer of solid **1** over a fibrous glass frit positioned into a tubular glass reactor heated at 60 °C.[2,14] As compared to the autoclave reaction, this procedure requires much longer times for the complete transformation of comparable amounts of the starting dihydride.

Like the homogeneous reaction, the heterogenous hydrogenation of **1** produces ethane.[2] As previously proposed, the formation of ethane in both the solid state and solution proceeds by insertion of the ethene ligand into one Ir−H bond of **1** to give the unsaturated Ir(III) ethyl hydride species $[(triphos)Ir(H)(C_2H_5)]^+$. σ-Donor molecules, even with weak coordinating capability, shift the equilibrium between ethene dihydride and ethyl hydride to the right through either the formation of stable octahedral ethyl hydride adducts (MeCN, DMF)[8] or the

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reductive elimination of ethane (CO).[8,15] The fact that the reaction of **1** in CD_2Cl_2 with 30 atm of D_2 does not produce deuterated ethane (HPNMR experiment) suggests that the reductive coupling of the ethyl and terminal hydride ligands is faster than the oxidative addition of H_2.

Compound **4**BPh_4 can be manipulated for a short time in the air and is indefinitely stable in the solid state under inert atmospheres (N_2 or Ar) below 5 °C. No appreciable decomposition is observed at room temperature within 5 days, whereas above 60 °C solid **4**BPh_4 starts converting to the tetrahydrido dimer *cis*-**3** (a 100-mg sample of **4**BPh_4 completely transforms into *cis*-**3** within 3 h at 90 °C).

The IR spectrum of **4**BPh_4 (Nujol mull) shows a medium-intensity ν(Ir−H) band at 2068 cm^{-1} and a less intense absorption at 2013 cm^{-1}. The latter band is most likely due to solid-state effects as it disappears in the spectrum recorded in CH_2Cl_2 solution under 20 atm of H_2. Similar solid-state IR absorptions in the ν(Ir−H) region have been observed for several cationic dihydride complexes of the formula [(triphos)IrH_2(L)]Y,[1b,8,12] *i.e.*, the parent complex **1** exhibits two Ir−H stretching absorptions at 2124 and 2062 cm^{-1}.[8] No vibration ascribable to the H−H stretch of the H_2 ligand is observed in the spectrum; these bands are generally very weak and may also be obscured by ν(C−H) absorptions.[16]

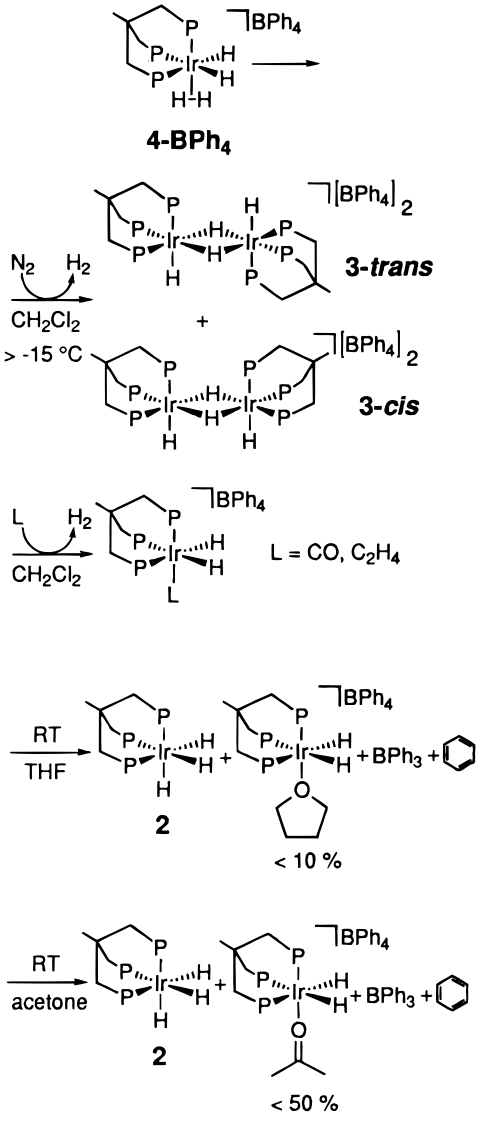
Compound **4**BPh_4 starts losing H_2 in CH_2Cl_2 already at −15 °C to give *cis*- and *trans*-**3**. In contrast, a solution of **4**BPh_4 prepared under nitrogen at low temperature (−78 °C) and stored at ≤−20 °C does not decompose within 1 week. In keeping with the presence of a weakly bound H_2 ligand, **4**BPh_4 quickly and selectively transforms into either **1** or the carbonyl complex [(triphos)IrH_2(CO)]$^+$ when it is dissolved in CH_2Cl_2 saturated with C_2H_4 or CO, respectively (Scheme 4).[9]

Replacing CH_2Cl_2 with THF has a dramatic effect on the stability of **4**BPh_4 in solution. At room temperature under nitrogen, **4**BPh_4 decomposes in THF within a few minutes to give the trihydride **2** as the largely predominant product (90−95%). The major side product is the THF adduct [(triphos)-Ir(H)$_2$(THF)]BPh_4 (**6**),[12] but some *cis*-**3** may occasionally form (^{31}P NMR experiment in THF-d_8) (Scheme 4). The trihydride **2** is exclusively formed when **4**BPh_4 is dissolved in THF saturated with H_2.

NMR spectroscopy shows that the dissolution of **4**BPh_4 in THF-d_8 does not evolve H_2, whereas benzene is formed (confirmed by GC−MS). The formation of benzene at the expense of the BPh_4^- counteranion has been proved by various experiments: (i) The production of benzene-d_1 occurs when the perdeuterated isotopomer **4**BPh_4-d_4 is dissolved in THF-d_8. (ii) Analytically pure BPh_3 was obtained from a preparative-scale reaction after the solvent was removed and the residue sublimed (70 °C, 0.5 Torr).[13] (iii) The dissolution of the BF_4^- derivative [(triphos)Ir(H_2)(H)$_2$]BF_4 (**4**BF_4) (see below) in THF-d_8 produces neither the trihydride **5** nor benzene (thus excluding that benzene may come from the triphos ligand). In contrast, the THF adduct [(triphos)Ir(H)$_2$(THF)]BF_4 is obtained together with some *cis*-**3** (<10%).

Another solvent in which **4**BPh_4, though partially, decomposes to **2**, BPh_3, and benzene is acetone. Indeed, dissolving **4**BPh_4 in acetone-d_6 results in the formation of a *ca.* 1:1 mixture of the trihydride **2** and the known solvento adduct [(triphos)-Ir(H)$_2$(OCMe$_2$)]BPh_4 (Scheme 4).

Scheme 4. Reactions of **4**BPh_4



The only way to convert **4**BPh_4 in CH_2Cl_2 to the trihydride **2** is the deprotonation of the H_2 ligand with bases.[5] For example, the addition of a slight excess of NEt_3 to a CH_2Cl_2 solution of **4**BPh_4 results in the clean and selective formation of **2** and [NEt_3H]BPh_4. Consistently, the protonation of **2** with HBF_4·OMe_2 in CD_2Cl_2 at low temperature gives **4**$^+$. The tetrafluoroborate salt **4**BF_4 can be isolated only through a solid−gas reaction, however. Although a detailed account of the chemistry, interconversion, and structure of the *cis* and *trans* stereoisomers of [(triphos)IrH(μ-H)$_2$HIr(triphos)]$^{2+}$ will be given elsewhere,[17] it may be useful to report here that the orange *trans* isomer is formed exclusively in CH_2Cl_2 solution by the dissolution of **4**BPh_4, the protonation of **2**, or the treatment of *cis*-**3** with a catalytic amount of a protic acid. The structure of the *trans* isomer has been determined by a single-crystal X-ray analysis (monoclinic, space group $P2_1$, a = 12.555(2) Å, b = 26.232(3) Å, c = 13.191(3) Å, β = 109.94(2)°, R = 0.057, d_{Ir-Ir} = 2.785 Å) while the structural assignment for the *cis* isomer is only suggested on the basis of its lower thermodynamic stability.[8,18] Both isomers are, in fact, highly fluxional on the NMR time scale, thus preventing reliable NOE experiments.

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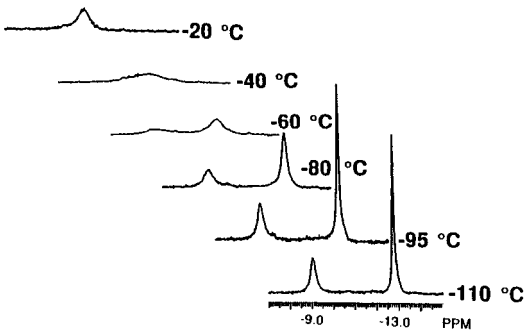

Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **4**BPh_4 in a 1:1 mixture of $CD_2Cl_2/CFCl_3$ (121.42 MHz, 85% H_3PO_4 reference).

NMR Spectroscopic Characterization of [(triphos)Ir(H_2)($H)_2$]$^+$ ($\mathbf{4}^+$). The complex cation $\mathbf{4}^+$ is stereochemically nonrigid in solution on the NMR time scale. A sequence of variable-temperature $^{31}P\{^1H\}$ NMR spectra of an isolated sample of **4**BPh_4 dissolved in a 1:1 $CD_2Cl_2/CFCl_3$ mixture saturated with H_2 is shown in Figure 1.

Above +10 °C, the loss of H_2 from the complex is quite fast and results in its extensive conversion to the tetrahydrido complexes *trans*- and *cis*-**3**. For this reason, the variable-temperature NMR study has been carried out on solutions of **4**BPh_4 prepared at low temperature.

In the fast-exchange regime (≥ -20 °C), a single resonance at −11.2 ppm ($\omega_{1/2} = 71$ Hz at −10 °C) is observed, which is consistent with the magnetic equivalence of the three phosphorus atoms of triphos (A_3 pattern). As the temperature is decreased, the signal steadily broadens until it coalesces at *ca.* −40 °C. Complete decoalescence of the resonance occurs at −80 °C to give two distinct resonances at −9.3 and −12.6 ppm in a 1:2 ratio (AM_2 pattern), respectively. For a further decrease of the temperature, narrowing of both signals occurs but no *J*(P,P) coupling becomes observable even at the lowest accessible temperature (−120 °C). Assuming the occurrence of an $A_3 \leftrightarrow AM_2$ *spectroscopic* exchange and applying the simplified equation $k = \pi(\Delta\nu)/\sqrt{2}$,[19] a $\Delta G^{\ddagger}_{233K}$ value of 10.3 kcal mol^{-1} may roughly be estimated at the coalescence temperature, introducing the experimental value of 472 Hz for $\Delta\nu$.

Figure 2 shows the variable-temperature ^1H NMR spectra in the hydride region of **4**BPh_4 dissolved in a 1:1 mixture of $CD_2Cl_2/CFCl_3$ saturated with H_2. At −10 °C, the spectrum contains a broad signal centered at −9.0 ppm ($\omega_{1/2} \approx 176$ Hz) with no resolvable coupling to the P nuclei. As the temperature is decreased, the hydride resonance broadens and at *ca.* −40 °C merges with the base line. Complete decoalescence of the resonance occurs at −60 °C to give two well-separated signals, which at −95 °C fall at δ −8.40 and −10.70, respectively. The higher field signal appears as a broad doublet and is assigned to two nonexchanging terminal hydrides. The ^2J(H,P) value of 110 Hz is typical of hydride ligands *trans* to a phosphorus atom in octahedral Ir(III) complexes of the general formula [(triphos)Ir$(H)_2$(L)]$^+$ (L = CO, C_2H_4, THF)). As an example, the octahedral complex [(triphos)IrH(C_2H_5)(CO)]$^+$ shows an almost identical ^2J(H,P_{trans})of 110.2 Hz.[8] The signal at lower field, assigned to the H_2 ligand, sharpens on going from the coalescence temperature ($\omega_{1/2} = 135$ Hz at −50 °C) to −90 °C. For a further decrease of the temperature, the H_2 resonance seems to resolve into a broad quartet with an average *J*(H,P) value of *ca.* 20 Hz, and then it broadens until a $\omega_{1/2}$ value of *ca.* 130 Hz is observed at −120 °C. The *J*(H,P) value of *ca.* 20 Hz is the result of averaging of a large *trans* *J*(H,P) and small *cis* *J*(H,P). Below this temperature, freezing out of the solvent does not allow one to acquire spectra that might have provided information on the inherent fluxionality of the H_2 ligand. Magnetic coupling of H_2 ligands to *trans* phosphorus nuclei, although uncommon, has already been observed in some metal complexes;[5] the *J*(H,P) value measured for $\mathbf{4}^+$ lies at the upper limit of the range reported for the known molecular hydrogen complexes ($\leq$3−19 Hz).[5,20]

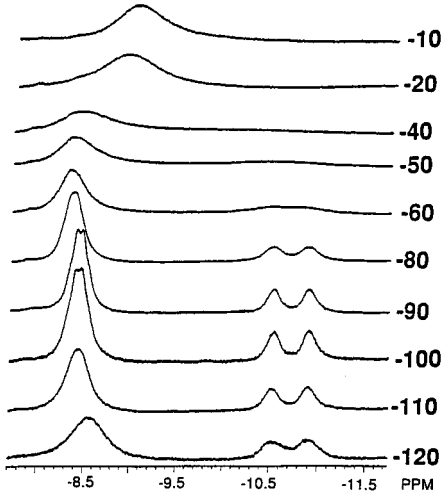

Figure 2. Hydride region of the variable-temperature ^1H NMR spectra of **4**BPh_4 recorded in a 1:1 mixture of $CD_2Cl_2/CFCl_3$ (300 MHz, TMS reference, temperatures are reported in °C).

Table 1. Variable-Temperature T_1 NMR Data for [(triphos)Ir$(H_2)(H)_2$]$^+$ [a]

	T_1, ms[b]		
temp, K	A	B	C
273	145		
253	115		
248	110		
228	74		
213		57	*c*
204		48	*c*
199		45	42
184		31	37
173		22	38
163		13	48

[a] All T_1 measurements were carried out at 300 MHz in a 1:1 $CD_2Cl_2/CFCl_3$ mixture. [b] The letter A denotes the T_1 values of the four hydride atoms in the fast-exchange motion. The letters B and C refer to the nonclassical and classical hydrides in the slow exchange motion, respectively. [c] Not measured due to incomplete decoalescence of the hydride resonance.

The free energy of activation for the exchange process can be estimated with some accuracy using the NMR coalescence technique.[19] Introducing a $\Delta\nu$ value of 651 Hz, a $\Delta G^{\ddagger}_{223K}$ value of 10.2 kcal mol^{-1} may be calculated at the coalescence temperature. This value is in excellent agreement with the free activation energy determined from the NMR coalescence analysis of the ^{31}P NMR spectra.

The longitudinal relaxation times for the hydride ligands in $\mathbf{4}^+$ have been measured with the standard inversion−recovery sequence at 300 MHz in $CD_2Cl_2/CFCl_3$ in the temperature range from 273 to 163 K (Table 1). A plot of T_1 (ms) *vs* inverse temperature (1000/*T*, K^{-1}) is presented in Figure 3.

At 273 K, in the fast-motion regime, the single resonance due to the four H ligands in the complex exhibits a relatively

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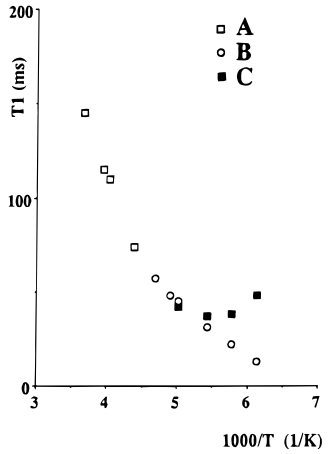

Figure 3. Plot of T_1 vs 1000/T for [(triphos)Ir(H$_2$)(H)$_2$]BPh$_4$ in a 1:1 mixture of CD_2Cl_2/$CFCl_3$ (300 MHz, TMS reference). A denotes the T_1 values of the four hydride atoms in the fast-exchange motion. B and C refer to the nonclassical and classical hydrides in the slow-exchange motion, respectively.

long T_1 value of 145 ms that decreases steadily on lowering the temperature to the coalescence. Below the coalescence temperature, different T_1 values characterize the two signals emerging from the base line. The T_1 value of the doublet resonance at higher field decreases with the temperature and goes through a broad minimum of 36 ms at 181 K; then it rises up smoothly (trace A). In the meanwhile, the T_1 of the other resonance decreases significantly without showing a minimum value even at the lowest temperature investigated (−110 °C) (trace B). Despite the possibility that the T_1 criterion to assess the nature of polyhydride complexes may lead to erroneous conclusions,[16a−c,21,22] one can safely conclude that the very short T_1 value at −110 °C (13 ms) points to the presence of an intact H_2 ligand in which an efficient dipole−dipole relaxation mechanism is at work.[23,24]

Overall, the temperature dependence of T_1 exhibited by **4**$^+$ is quite similar to that of [ReH$_2$(H$_2$)(CO)(PMe$_2$Ph)$_3$]BF$_4$ for which the slowed exchange process between the H and H_2 ligands reduces the contribution of the nonclassical protons and allows T_1 of the terminal hydride to lengthen quickly.[25]

Unambiguous evidence for the presence of a molecular hydrogen ligand in **4**$^+$ has been obtained by NMR studies of partially deuterated products. Deuterated isotopomers of **4**$^+$ can be prepared by different methods, which include the reactions of **1** with high pressures of H_2/D_2 mixtures in either the solid state or CD_2Cl_2 solution. Interestingly, the HPNMR reaction of **1** with a 1:1 mixture of H_2/D_2 (total gas pressure 30 atm) produces free HD (1:1:1 triplet at δ 4.57, ^1J(H,D) = 42.6 Hz) together with various deuterated isotopomers of **4**$^+$.[26] The simplest method to generate partially deuterated **4**$^+$, however, is the treatment of the trihydride **2** in CD_2Cl_2 with a slight excess of a deuterated protic acid or, *vice versa*, the protonation of **2**-d_3. The reactions *in situ* have also the advantage that **4**$^+$ generated like this is much more fluxional than **4**$^+$ from isolated **4**BPh$_4$ (*vide infra*); accordingly the T_1 analysis of the various deuterated isotopomers is not complicated by the slowing down

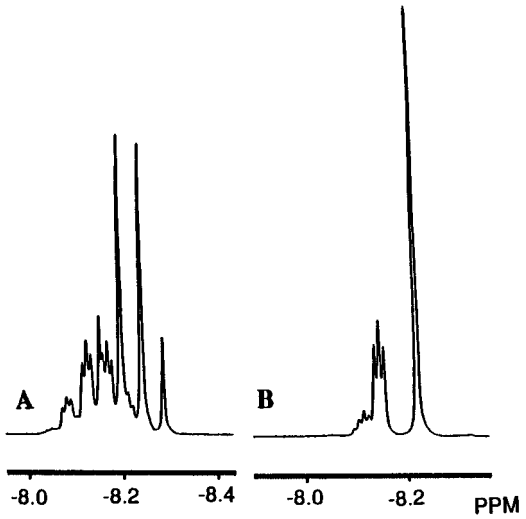

Figure 4. High-field region of the ^{1}H (A) and ^{1}H{^{31}P} (B) NMR spectra (CD_2Cl_2, 500 MHz, −30 °C) of a partially deuterated sample of [(triphos)Ir(H$_2$)(H)$_2$]BPh$_4$ (**4**BPh$_4$).

of the dynamic process that occurs at the low temperature required to avoid the decomposition of the complex. Indeed, when **4**$^+$ is generated in solution by protonation of **2** at low temperature, the ^{31}P{^{1}H} NMR spectra consist of a sharp singlet over the whole range of temperatures investigated (+10/−100 °C), while the ^{1}H NMR spectra show a narrow binomial quartet (J(H,P) = 22.1 Hz) for the four exchanging hydrides that does not coalesce within the temperature window of CD_2Cl_2.

The addition of 2.0 equiv of DBF$_4$·OMe$_2$ to a CD_2Cl_2 solution of **2** generates a mixture of isotopomers whose ^{1}H NMR spectrum in CD_2Cl_2 at −30 °C shows a complex multiplet in the hydride region (trace A in Figure 4). This signal is greatly simplified by broad-band phosphorus decoupling experiments that remove the relatively large coupling to the phosphorus nuclei. As a result, the complicated multiplet in the ^{1}H{^{31}P} NMR spectrum in the fast-exchange regime is transformed into three well-separated signals (trace B in Figure 4): a singlet due to **4**$^+$ (δ −8.220, 41%), a nonbinomial (1:1:1) triplet due to **4**$^+$-d_1 (δ −8.147, 43%), and a nonbinomial (1:2:3:2:1) quintet due to **4**$^+$-d_2 (δ −8.115, 16%). Surprisingly, no signal ascribable to the proton of the possible isotopomer **4**$^+$-d_3 is visible in the spectrum. The isotopomeric distribution does not change over 1 week of storage of the NMR tube at −20 °C.

The partially deuterated isotopomers show J(H,D) values of 4.6 Hz (**4**$^+$-d_1) and 4.8 Hz (**4**$^+$-d_2), respectively. From these average values, one can estimate the ^1J(H,D) value corresponding to the intact H_2 ligand with the assumption that the H/D exchange is faster than the NMR time scale and thus a statistical distribution of deuterium in a given isotopomer may be anticipated. Assuming the presence of one dihydrogen ligand and introducing a ^2J(H,D) value <2−3 Hz for classical hydride−deuteride species, a ^1J(H,D) ranging from 29 to 26 Hz (^2J(H,D) ≈ 0 Hz) may be calculated for **4**$^+$.[5,27] Such a value is consistent with the formulation of **4**$^+$ as a (dihydride)(η^2-dihydrogen) metal complex and also points to a rather short H−H distance.[16a−c,28]

An interesting feature of the ^{1}H NMR spectra of **4**, **4**$^+$-d_1, and **4**$^+$-d_2 in the fast-exchange regime is the large, downfield isotopic shift of the hydride resonances: $\Delta\delta_1 = \delta_{\mathbf{4}^+\text{-}d_1} - \delta_{\mathbf{4}^+\text{-}d_0}$ = 73 ppb and $\Delta\delta_2 = \delta_{\mathbf{4}^+\text{-}d_2} - \delta_{\mathbf{4}^+\text{-}d_1}$ = 32 ppb. These values

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are in good agreement with those reported by Poveda *et al.* for Tp*IrH$_4$ [Tp* = HB(3,5-Me$_2$Pz$_3$)][29] and by Albinati *et al.* for IrH(H$_2$)X$_2$(PR$_3$)$_2$ (X = Cl, Br, I; PR$_3$ = PPr$^i_3$, PBu$^t_2$Ph).[30]

Transition metal polyhydrido complexes generally exhibit upfield isotopic shifts in the range 0−50 ppb.[5,16a−c,31] The less common downfield shifts have been explained by taking into account either a nonstatistical intramolecular distribution of deuterium in the classical and nonclassical hydride sites or an isotopic perturbation of the resonance (IPR). As an example, through a quantitative analysis of the isotopic perturbation of the chemical shifts in the d_0−d_2 isotopomers of [TpIr(PMe$_3$)H$_3$]BF$_4$ (Tp = tris(pyrazolyl)borate), Heinekey and Oldham have rationalized the downfield isotopic shift in terms of a statistically preferred incorporation of deuterium in the terminal site.[32] In our opinion, the low-field shift exhibited by **4**$^+$ upon deuteration is better accounted for by the preferred incorporation of deuterium in either site than by an IPR effect that would involve a very fast chemical equilibrium between classical [Ir(H)$_4$] and nonclassical [Ir(H)$_2$(η^2-H$_2$)] tautomers of **4**.[5,16a−c,25,33] The occurrence of the latter mechanism in solution can safely be ruled out on the basis of the variable-temperature NMR studies.

The higher fluxionality on the NMR time scale of **4**$^+$ prepared *in situ* as compared to **4**$^+$ from **4**BPh$_4$ is ascribed to the presence of free acid that apparently lowers the energy barrier to the H/H$_2$ exchange.[34] In keeping with this hypothesis, the addition of a catalytic amount of tetrafluoroboric acid dimethyl ether adduct to a CD$_2$Cl$_2$ solution of **4**BPh$_4$ causes an instantaneous sharpening of the ^{31}P NMR resonance. Also, the immediate decoalescence of both the ^{31}P and ^{1}H$_{hydride}$ signals occurs when a catalytic amount of a protic acid is syringed into an NMR tube containing a solution of **4**BPh$_4$ maintained at the coalescence temperature.

Besides protic acids, the energy barrier to the H/H$_2$ exchange process in **4**$^+$ in CH$_2$Cl$_2$ is remarkably lowered by water and alcohols such as MeOH or EtOH that, in catalytic amounts, allow this complex cation to maintain the fast-exchange regime down to −100 °C.

The exchange of protons between a dihydrogen ligand and water or alcohols is a common process for dihydrogen metal complexes and is largely used for the synthesis of HD complexes.[5] It is analogously well-known that protons can be exchanged between hydride ligands and protic acids.[5,35] No report has appeared so far on the interaction of nonclassical polyhydride complexes with acids, however.

Since the H$_2$ ligand in **4**$^+$ (like in the vast majority of η^2-H$_2$ metal complexes) exhibits acidic character,[5] the added acid should preferentially interact with one of the terminal hydrides that generally possess residual nucleophilic properties.[36] In principle, an acid−base interaction of this type would lead to the generation of a dihydrogen molecule and thus to the conversion of **4**$^+$ to transient [triphos)IrH(H$_2$)$_2$]$^{2+}$ that may regenerate **4**$^+$ by the deprotonation of either H$_2$ molecule. A process of this type would involve the stronger acidity of HBF$_4$ than **4**$^+$. The hypothesis that a fast intermolecular proton exchange may be responsible for accelerating the intramolecular scrambling of the four hydrogen ligands in **4**$^+$ raises the question about the nature and mechanism of the fluxionality of this complex cation. In other words, one may argue that, even in the absence of added acid, the high fluxionality of the Brønsted acid **4**$^+$ might have a substantial intermolecular contribution in CH$_2$Cl$_2$. This seems highly improbable in light of variable-temperature NMR experiments on solutions of **4**BPh$_4$ with increasing concentrations (from 20 to 60 mg in 0.8 mL of CD$_2$Cl$_2$) that showed no significant variation of $\Delta G^{\ddagger}$ at the coalescence temperature. Accordingly, the stereochemical nonrigidity of **4**$^+$ seems to be intrinsically intramolecular, though an intermolecular contribution cannot definitely be ruled out in light of the dependence of the dynamic process on traces of water.

The intramolecular hydrogen atom exchange for nonclassical polyhydride complexes of the type L$_n$M(H$_2$)H$_x$ ($x \geq 2$) has recently been reviewed by Berke and Gusev[37] and by Morris and Jessop.[5] In the particular case of the tetrahydride complexes L$_n$M(H$_2$)H$_2$, a common feature is the observation of a fast exchange between the four hydrogen ligands which may not be slowed significantly within the range of temperatures that are usually investigated in variable-temperature NMR experiments. Typical examples of such polyhydrides exhibiting a fast dihydrogen/hydride fluxionality that cannot be frozen out at low temperature are, *inter alia*, the Rh(III) complex [{HB(3,5-Me$_2$Pz)$_3$}Rh(H$_2$)H$_2$][38] [3,5-Me$_2$Pz = tris(3,5-dimethylpyrazolyl)borate], the Fe(II) complex *mer*-(PEtPh$_2$)$_3$Fe(H$_2$)H$_2$,[39] and the Ir(III) complexes [IrCl(H$_2$)H$_2$(PR$_3$)$_2$] (PR$_3$ = PCy$_3$, P-*i*-Pr$_3$).[40] A factor that contributes to determining the high mobility of the hydrogen atoms in these complexes is suggested to be the *cis* arrangement of the dihydrogen and hydride ligands (incipient H···H$_2$ bonding interaction).[41] In the case at hand, the triphos

(28) An empirical linear relationship between d_{H-H} and J(H,D) has recently been proposed: 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. Using the equation d_{H-H} = (−0.0167J(H,D) + 1.42) Å, an approximate distance d_{H-H} in the range 0.94−0.99 Å can be calculated for **4**BPh$_4$ from the J(H,D) coupling constant.

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ligand, which invariably adopts a facial coordination mode,[42] seems to be properly tailored for enhancing the hydride fluxionality in complexes like $\mathbf{4}^+$.

As for the mechanism of exchange between the H_2 and H ligands in $\mathbf{4}^+$, the situation is extremely complicated. A perusal of the relevant literature shows that the H atom exchange may proceed through several pathways, including associative, dissociative, and even concerted mechanisms.[5] In the particular case of [$IrCl_2(H_2)H_2$(P-*i*-$Pr_3)_2$], Zilm and co-workers showed by proton solid-state NMR spectroscopy that the mechanism of interconversion of H_2 and H ligands cannot involve an interaction between the dihydrogen and a *cis* hydride.[43] Even small changes in the electronic and steric properties of the ancillary ligands may result in totally different exchange mechanisms. Illustrative examples are provided by the cationic complexes [$(PMe_2Ph)_3$(CO)$Re(H_2)H_2$]$^+$ and [$(PMe_3)_3$(CO)-$Re(H_2)H_2$]$^+$ reported by Luo and Crabtree[25] and Berke and co-workers,[37,44] respectively. These two complexes display almost identical low-temperature ^{1}H NMR spectra and should adopt the same pentagonal-bipyramidal structure in the ground state. Nonetheless, the stereochemical nonrigidity exhibited by the two complexes in solution has been interpreted in terms of two different mechanisms: an intramolecular process involving H−H bond cleavage, followed by formation of a symmetric transition state with four terminal hydrides, for the PMe_3 derivative,[44] and an associative pathway of a terminal hydride ligand with the H_2 molecule to give a transient trihydrogen intermediate for the PMe_2Ph derivative.[25]

The possibility that either mechanism may account for the fast hydride exchange in $\mathbf{4}^+$ cannot be discarded. On the other hand, any unambiguous mechanistic conclusion for the fluxionality of $\mathbf{4}^+$ cannot be provided at this stage, particularly in the absence of detectable intermediates along the scrambling process, the lack of a rigorous line-shape analysis of the NMR spectra over the complete dynamic range of the fast- and slow-motion regimes, and the dependence of the energy barrier to exchange on the presence of either traces of water or protic acids.

Conclusions

We have shown here that a dihydrogen metal complex may be sufficiently acidic to bring about the protonolysis of its counteranion when this is BPh_4^-. The process involves the formal heterolytic splitting of H_2 with formation of a metal−hydride bond. In a sense, our discovery warns the chemist against the use of metal complexes with tetraphenylborate counteranions in homogeneous hydrogenation reactions, particularly when these are carried out in polar solvents. Indeed, the formation *in situ* of a new M−H bond, changing the structure of the catalyst precursor, may dramatically affect the mechanism of activation of both H_2 and the substrate to hydrogenate.

The isolation and characterization of the Ir(III) nonclassical polyhydride [(triphos)Ir(H_2)(H)$_2$]Y (Y = BPh_4^-, BF_4^-) has also allowed us to provide a correct interpretation of the solid−gas hydrogenation of [(triphos)Ir(C_2H_4)(H)$_2$]BPh_4 at 60 °C.[2] Indeed, the metal product of this reaction is just the η^2-H_2 complex and not the unsaturated species [(triphos)Ir(H)$_2$]BPh_4 as erroneously reported. On the other hand, the authentication of this peculiar dihydrogen complex has been made much easier by the recent availability of the HPNMR techniques.

Finally, it is worth stressing that the results presented here provide further experimental evidence of the close connection between lability and acidity of η^2-H_2 ligands.

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