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An Acidity Scale of Tetrafluoroborate Salts of Phosphonium and Iron Hydride Compounds in [D_2]Dichloromethane

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Abstract: Equilibrium constants (K) for reactions between acids and the conjugate base forms of a number of phosphonium salts, [HPR_3][BF_4], and iron hydrides, [$Fe(CO)_3H(PR_3)_2$][BF_4], in CD_2Cl_2 have been determined by means of ^{31}P and ^1H NMR spectroscopy at 20 °C. The anchor compound chosen for p$K^{CD_2Cl_2}$ determinations was [$HPCy_3$][BF_4] with a p$K^{CD_2Cl_2}$ value of 9.7, as assigned by literature convention (Cy: cyclohexyl). A continuous scale of p$K^{CD_2Cl_2}$ values covering the range from 9.7 to −3 was created and correlated with the ΔH values reported by Angelici and co-workers and literature pK_a values. The p$K^{CD_2Cl_2}$ values for 15 other hydride or dihydrogen complexes of the iron group elements and of diethyl ether were also placed on this scale. The crystal structures of [$Fe(CO)_3H(PCy_2Ph)_2$][BF_4] and [$Fe(CO)_3(PCy_2Ph)_2$] revealed that the *trans*-oriented, bulky, unsymmetrical phosphane ligands distort the equatorial plane of the complexes. The acidity of iron carbonyl hydrides is an important feature of the reactions of iron hydrogenase enzymes.

Keywords: acidity · carbonyl ligands · hydride ligands · iron · phosphanes

Introduction

We are studying the acid–base chemistry of transition metal hydride ([M–H]) and dihydrogen complexes ([M–H_2])[1] to better understand the mechanism of catalytic hydrogenation reactions[2] and the action of hydrogenases.[3–9] Tetrahydrofuran (THF) is an excellent solvent to use when studying weakly acidic hydrides, their strong conjugate base forms, and weakly coordinated complexes, such as those containing the dihydrogen ligand.[1,10–13] However, THF cannot be used as a solvent for very acidic compounds because it becomes protonated and undergoes ring-opening reactions. Dichloromethane is an excellent solvent for acidic hydride and dihydrogen complexes because it is weakly coordinating and it dissolves many neutral and cationic metal complexes without undergoing reaction. However, it is not suitable for dissolving hydrides that are too reducing or nucleophilic. Several pK_a values for cationic metal hydride and dihydrogen complexes in CD_2Cl_2 have been previously reported by us and the group of Jia.[14–19] The initial approach used was to find equilibria between these complexes and protonated phosphanes in which pK_a^{aq} values were reported to give a pseudoaqueous value by using ^1H and ^{31}P NMR spectroscopy.[15,16,18] A second approach was to construct a continuous set of overlapping equilibria to provide a more accurate ordering of acid strengths. For example, a ladder of acids with p$K^{CD_2Cl_2}$ values ranging from 9.7 to 7.0 was built and referenced arbitrarily to [$HPCy_3$][BPh_4] (Cy: cyclohexyl, pK_a = 9.7) (Table 1).[15] More recently, this ladder was extended by using phosphonium tetraphenylborate salts, of which [$HPBu_2Ph$][BPh_4] has a p$K^{CD_2Cl_2}$ value of 5.7, for example.[19] The p$K^{CD_2Cl_2}$ values are generally consistent with those values previously measured in THF.[1]

One limitation when using [BPh_4]$^-$ salts is that acids with p$K^{CD_2Cl_2}$ values of less than 6 react with this anion to produce benzene and BPh_3.[19] The aim of the current work is to make a continuous ladder based on cationic acids with the [BF_4]$^-$ anion in CD_2Cl_2. Iron hydride complexes [$Fe(CO)_3H(PR_3)_2$]$^+$ were chosen, based upon previous work by Angelici and co-workers,[20] to extend the ladder in the direction of stronger acids. We have strengthened the p$K^{CD_2Cl_2}$ scale by adding new rungs to the ladder, which correspond to the phosphonium salts and iron carbonyl hydride complexes reported herein.

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Table 1. The $\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ values for cationic acids $[\mathrm{HB}]^+$ arbitrarily referenced to $[\mathrm{HPCy_3}]^+$ salts at 9.7 in $\mathrm{CD_2Cl_2}$.[15,16,19]

Acid[a]	$\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ of $[\mathrm{BPh_4}]^-$ salt	$\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ of $[\mathrm{BF_4}]^-$ salt
$[\mathrm{HPCy_3}]^+$	9.7	9.7
$[\mathrm{HPBu_3}]^+$	8.6(1)	–
$[\mathrm{RuCl(dach)(H_2)(PPh_3)_2}]^+$	8.6(1)	–
trans-$[\mathrm{Ru(Cp)(dape)(H)_2}]^+$	–	8.5
trans-$[\mathrm{Ru(Cp)(dppp)(H)_2}]^+$	8.4	–
trans-$[\mathrm{Ru(Cp)(H)_2(PPh_3)_2}]^+$	8.3	–
$[\mathrm{HP}t\mathrm{Bu_2Ph}]^+$	8.0(1)	–
trans-$[\mathrm{Ru(Cp)(dppe)(H)_2}]^+$	–	7.3
$[\mathrm{Ru(Cp)(dppm)(H_2)}]^+$	–	7.1
$[\mathrm{Ru(Cp)(dppe)(H_2)}]^+$	–	7.0
$[\mathrm{RuCl(H_2)\{tmeP_2(NH)_2\}}]^+$	6.9(3)	–
$[\mathrm{HPCy_2Ph}]^+$	6.6(3)	–
$[\mathrm{HPBu_2Ph}]^+$	5.7(3)	–

[a] Abbreviations: dach: (1*R*,2*R*)-(−)-diaminocyclohexane; Cp: η^5-$\mathrm{C_5H_5}$; dape: $\mathrm{(tol)_2PCH_2CH_2P(tol)_2}$, (tol: *p*-tolyl); dppp: $\mathrm{Ph_2PCH_2CH_2CH_2PPh_2}$; dppm: $\mathrm{PPh_2CH_2PPh_2}$; dppe: 1,2-bis(diphenylphosphino)ethane; $\{\mathrm{tmeP_2(NH)_2}\}$: $\mathrm{PPh_2C_6H_4CH_2NHCMe_2CMe_2NHCH_2C_6H_4PPh_2}$.

Table 2. ^{31}P NMR spectroscopic chemical shifts of phosphanes and phosphonium salts in $\mathrm{CD_2Cl_2}$.

Base	δ [ppm]	Acid	δ [ppm]
$\mathrm{PCy_3}$	9.8	$[\mathrm{HPCy_3}][\mathrm{BF_4}]$	29.5
$\mathrm{PBu_3}$	−31.1	$[\mathrm{HPBu_3}][\mathrm{BF_4}]$	13.3
$\mathrm{PEt_3}$	−18.8	$[\mathrm{HPEt_3}][\mathrm{BF_4}]$	22.6
$\mathrm{PCy_2Ph}$	−2,9	$[\mathrm{HPCy_2Ph}][\mathrm{BF_4}]$	27.1
$\mathrm{PMe_2Ph}$	−45.0	$[\mathrm{HPMe_2Ph}][\mathrm{BF_4}]$	0.6
$\mathrm{PBu_2Ph}$	−24.6	$[\mathrm{HPBu_2Ph}][\mathrm{BF_4}]$	14.9
$\mathrm{PCyPh_2}$	−4.1	$[\mathrm{HPCyPh_2}][\mathrm{BF_4}]$	15.6
$\mathrm{PMePh_2}$	−27.1	$[\mathrm{HPMePh_2}][\mathrm{BF_4}]$	2.0
$\mathrm{PEtPh_2}$	−11.8	$[\mathrm{HPEtPh_2}][\mathrm{BF_4}]$	12.5
$\mathrm{P(tol)_3}$	−8.1	$[\mathrm{HP(tol)_3}][\mathrm{BF_4}]$	3.85
$\mathrm{PPh_3}$	−5.5	$[\mathrm{HPPh_3}][\mathrm{BF_4}]$	12.0

Table 3. ^{31}P and ^{1}H NMR spectroscopic chemical shifts of $[\mathrm{Fe(CO)_3(PR_3)_2}]$ and $[\mathrm{Fe(CO)_3H(PR_3)_2}][\mathrm{BF_4}]$ in $\mathrm{CD_2Cl_2}$.

Base	$\delta(^{31}\mathrm{P})$ [ppm]	Acid	$\delta(^{31}\mathrm{P})$ [ppm]	$\delta(^{1}\mathrm{H})$ [ppm]
$[\mathrm{Fe(CO)_3(PCy_3)_2}]$	84.7	$[\mathrm{Fe(CO)_3H(PCy_3)_2}][\mathrm{BF_4}]$	67.5	−9.1
$[\mathrm{Fe(CO)_3(PCy_2Ph)_2}]$	84.1	$[\mathrm{Fe(CO)_3H(PCy_2Ph)_2}][\mathrm{BF_4}]$	65.1	−8.4
$[\mathrm{Fe(CO)_3(PCyPh_2)_2}]$	82.2	$[\mathrm{Fe(CO)_3H(PCyPh_2)_2}][\mathrm{BF_4}]$	56.4	−8.5
$[\mathrm{Fe(CO)_3\{PPh_2(tol)\}_2}]$	80.1	$[\mathrm{Fe(CO)_3H\{PPh_2(tol)\}_2}][\mathrm{BF_4}]$	54.0	−7.8
$[\mathrm{Fe(CO)_3\{P(tol)_3\}_2}]$	78.3	$[\mathrm{Fe(CO)_3H\{P(tol)_3\}_2}][\mathrm{BF_4}]$	52.5	−7.8
$[\mathrm{Fe(CO)_3(PPh_3)_2}]$	81.1	$[\mathrm{Fe(CO)_3H(PPh_3)_2}][\mathrm{BF_4}]$	54.8	−7.8
$[\mathrm{Fe(CO)_3\{P(}p\text{-}\mathrm{FC_6H_4)_3\}_2}]$	79.2	$[\mathrm{Fe(CO)_3H\{P(}p\text{-}\mathrm{FC_6H_4)_3\}_2}][\mathrm{BF_4}]$	53.2	−8.0

Experimental Section

General: All preparations and manipulations were carried out under a nitrogen or an argon atmosphere by using standard Schlenk, vacuum line, and glove-box techniques in dry, oxygen-free solvents. THF, diethyl ether ($\mathrm{Et_2O}$), and hexanes were dried and distilled from sodium benzophenone ketyl. Dichloromethane was dried and distilled from calcium hydride. Deuterated solvents were degassed and dried over activated molecular sieves. NMR spectra were recorded by using a Varian Unity-500 (500 MHz for ^{1}H), a Varian Unity-400 (400 MHz for ^{1}H), or a Varian Gemini 300 MHz spectrometer (300 MHz for ^{1}H and 121.5 MHz for ^{31}P). All ^{31}P NMR spectroscopic chemical shifts were measured relative to 10 % $\mathrm{P(OMe)_3}$ in $\mathrm{C_6D_6}$. This reference solution was placed in a 2 mm capillary tube inside the 5 mm NMR tube containing the sample. ^{1}H NMR spectroscopic chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. The phosphane compounds were received from commercial suppliers (Aldrich and Strem) and were used without further purification. $[\mathrm{Fe(bda)(CO)_3}]$[21] (bda: benzylideneacetone) was prepared according to literature procedures. Phosphonium salts that have not already been reported in the literature were found to have the correct elemental analyses by the Analyst Laboratory of the University of Toronto. CCDC-624440 and -624441 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_/cif.

$[\mathrm{HPR_3}][\mathrm{BF_4}]$: All phosphonium salts $[\mathrm{HPR_3}][\mathrm{BF_4}]$ ($\mathrm{PR_3}$: $\mathrm{PCy_3}$, $\mathrm{PBu_3}$, $\mathrm{PCy_2Ph}$, $\mathrm{PBu_2Ph}$, $\mathrm{PMe_2Ph}$, $\mathrm{PCyPh_2}$, $\mathrm{PEtPh_2}$, $\mathrm{P(tol)_3}$, (tol: *p*-tolyl), $\mathrm{PPh_3}$) were isolated according to the reported preparation,[15] with typical yields of 80–90 %. The ^{31}P NMR spectroscopic chemical shifts are reported in Table 2.

$[\mathrm{Fe(CO)_3(PR_3)_2}]$:[22] $[\mathrm{Fe(bda)(CO)_3}]$ (≈300 mg, 1 mmol) and $\mathrm{PR_3}$ (2.2 equiv; $\mathrm{PR_3}$: $\mathrm{PCy_3}$, $\mathrm{PCy_2Ph}$, $\mathrm{PCyPh_2}$, $\mathrm{PPh_2(tol)}$, $\mathrm{P(tol)_3}$, $\mathrm{PPh_3}$, $\mathrm{P(}p\text{-}\mathrm{FC_6H_4)_3}$) in THF (10 mL) were stirred for 24 h under Ar at room temperature to give a light yellow solution or yellow precipitate. Half of the solvent was removed under vacuum. Hexanes (20 mL) were added to the mixture to give a yellow precipitate. The product was isolated by means of filtration, washed with hexanes, and then dried under vacuum. The product was recrystallized by using $\mathrm{CH_2Cl_2}$/hexanes (40–70 %). ^{31}P NMR spectroscopy chemical shifts are reported in Table 3.

$[\mathrm{Fe(CO)_3H(PR_3)_2}][\mathrm{BF_4}]$: $[\mathrm{H(Et_2O)}][\mathrm{BF_4}]$ (1 equiv) in $\mathrm{CH_2Cl_2}$ (2 mL) was added to $[\mathrm{Fe(CO)_3(PR_3)_2}]$ (≈100 mg) in $\mathrm{CH_2Cl_2}$ (10 mL) to give a colorless or light yellow solution. The mixture was stirred for 1 h before the solvent was removed under vacuum. Hexanes (10 mL) were added to give a white or light yellow precipitate. The product was obtained by means of filtration, washed with hexanes, and dried under vacuum. The product was recrystallized by using $\mathrm{CH_2Cl_2}$/hexanes (≈80 %). The ^{1}H (hydride) and ^{31}P NMR spectroscopic hydride chemical shifts are reported in Table 3.

Determination of equilibrium constants in $\mathrm{CD_2Cl_2}$: Samples were mixed under $\mathrm{N_2}$ as described in Tables 4 and 5. In general, equilibrium constants were determined by means of ^{1}H and ^{31}P NMR spectroscopy. Usually, signals for all of the species in equilibrium could be located and integrated in the ^{31}P NMR spectra (with inverse gated decoupling for quantitative integration), and also in the ^{1}H NMR spectra for the hydride complexes. The chemical shifts for the pure phosphanes and phosphonium salts (Table 2) were determined and referenced to $\mathrm{P(OMe)_3}$ at $\delta = 141.5$ ppm. In some cases, in which the chemical shifts of two species are very similar, mass-balance arguments could be used to estimate the equilibrium concentration of the species from their starting concentrations. The resulting equilibrium constants in $\mathrm{CD_2Cl_2}$ are shown in Tables 4 and 5.

X-ray diffraction structure determination of $[\mathrm{Fe(CO)_3(PCy_2Ph)_2}]$ and $[\mathrm{Fe(CO)_3H(PCy_2Ph)_2}][\mathrm{BF_4}]$: Crystals suitable for X-ray diffraction were obtained by means of vapor diffusion between a solution of the crystals in $\mathrm{CH_2Cl_2}$ and hexanes. Data were collected by using a Nonius Kappa-CCD diffractometer with $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å). CCDC data were integrated and scaled by using the DENZO-SMN software package,[40] and the structures were solved and refined by using SHELXTL V6.0.[41] The crystallographic data are listed in Table 6. The hydride was located and refined with isotropic thermal parameters.

Table 4. Equilibrium constants for acid–base reaction of phosphonium salts in CD_2Cl_2.

Acid	c [mmol L^{-1}]	Base	c [mmol L^{-1}]	t[a] [h]	K_{eq}	Error [%][b]	pK_{eq}
$[HPCy_3][BF_4]$	49	PBu_3	50	<2	0.03	10	1.5
$[HPBu_3][BF_4]$	34	PCy_2Ph	38	<1	0.03	10	1.5
$[HPBu_3][BF_4]$	83	PEt_3	85	<1	0.81	5	0.1
$[HPCy_2Ph][BF_4]$	44	PBu_2Ph	45	<2	0.14	5	0.9
$[HPMe_2Ph][BF_4]$	44	PBu_2Ph	45	<1	1.3	5	−0.1
$[HPMe_2Ph][BF_4]$	62	$PCyPh_2$	60	<1	0.045	10	1.4
$[HPEtPh_2][BF_4]$	50	$PMePh_2$	50	<1	0.50	5	0.3
$[HPEtPh_2][BF_4]$	50	$PCyPh_2$	40	<2	4.7	5	−0.7
$[HPCyPh_2][BF_4]$	56	$PMePh_2$	50	<1	0.13	5	0.9
$[HPCyPh_2][BF_4]$	54	PBu_2Ph	54	<4	27.5	10	−1.4
$[HPCyPh_2][BF_4]$	34	$P(tol)_3$	33	<1	0.044	10	1.4
$[HP(tol)_3][BF_4]$	51	$PEtPh_2$	47	<1	7.4	5	−0.9
$[HP(tol)_3][BF_4]$	50	$PMePh_2$	50	<1	3.8	5	−0.6

[a] Time taken to reach equilibrium. [b] The error in the equilibrium constant determination is estimated from the magnitude of the constant and the signal/noise ratio of each species in the spectrum of the equilibrium mixture.

Results and Discussion

Preparation of $[HPR_3][BF_4]$: $[HPR_3][BF_4]$ can be readily prepared through protonation of PR_3 (PR_3: PCy_3, PBu_3, PCy_2Ph, PBu_2Ph, PMe_2Ph, $PCyPh_2$, $PEtPh_2$, PPh_3) with $[H(Et_2O)][BF_4]$ in diethyl ether as shown in Equation (1):

$$PR_3+[H(Et_2O)][BF_4] \rightarrow [HPR_3][BF_4] \qquad (1)$$

p$K^{CD_2Cl_2}$ determination: The acid dissociation equilibrium constant (K_a) of an acid ($[BH]^+$) in CD_2Cl_2 is defined by using Equation (2):

$$[BH]^+ \rightleftharpoons [H(CD_2Cl_2)]^+ + B \qquad (2)$$

However, the concentration of the acid form in the solvent, ($[H(CD_2Cl_2)]^+$), is not readily determined. Therefore, the relative acidity (p$K^{CD_2Cl_2}$) of phosphonium salts and metal hydrides was studied. The acid ($[BH]^+$) and base (B) reaction equilibria are based on Equation (3):

$$B^1+[B^2H]^+[BF_4]^- \xrightleftharpoons{K_{eq}} [B^1H]^+[BF_4]^-+B^2 \qquad (3)$$

The equilibrium constants (K_{eq}) for reactions in CD_2Cl_2 were measured by means of quantitative ^{31}P and ^{1}H NMR spectroscopy at room temperature. K_{eq} values in the range 10^3 to 10^{-3} can be measured with 10 to 30 % error. The difference in p$K^{CD_2Cl_2}$ between the two acids $[B^1H]^+[BF_4]^-$ and $[B^2H]^+[BF_4]^-$ was calculated from the K_{eq} value by using Equation (4):

$$\Delta pK^{CD_2Cl_2} = pK_{eq} = pK^{CD_2Cl_2}([B^1H]^+[BF_4]^-) - pK^{CD_2Cl_2}([B^2H]^+[BF_4]^-) \qquad (4)$$

Table 6. Crystallographic data for $[Fe(CO)_3(PCy_2Ph)_2]$ and $[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$.

	$[Fe(CO)_3(PCy_2Ph)_2]$	$[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$
formula	$C_{39}H_{54}FeO_3P_2$	$C_{39}H_{55}BF_4FeO_3P_2$
M_r	688.61	776.43
space group	$P2(1)/c$	$Pmn2(1)$
a [Å]	16.7920(5)	14.5561(4)
b [Å]	10.3300(3)	10.1860(3)
c [Å]	21.8130(6)	16.6463(4)
T [K]	150(1)	150(1)
α [°]	90	90
β [°]	106.205(2)	90
γ [°]	90	90
ρ_{calcd} [mg m^{-3}]	1.259	1.045
V [Å^3]	3633.38(18)	2468.1(1)
Z	4	2
R_1 (all data)	0.1027	0.0819
wR_2	0.1809	0.2121

Table 5. Equilibrium constants for the reactions of iron hydride complexes in CD_2Cl_2.

Acid	c [mmol L^{-1}]	Base	c [mmol L^{-1}]	t[a] [h]	K_{eq}	Error [%]	pK_{eq}
$[Fe(CO)_3H(PCy_3)_2][BF_4]$	13	PPh_3	18	<1	0.0017	20	2.8 ± 0.2
$[Fe(CO)_3H(PCy_3)_2][BF_4]$	15	$PEtPh_2$	22	<1	0.14	5	0.85
$[HPEtPh_2][BF_4]$	20	$[Fe(CO)_3(PCy_3)_2]$	15	<1	5.55	5	−0.74
$[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$	13	$[Fe(CO)_3(PCy_3)_2]$	15	<4	0.069	10	1.2 ± 0.1
$[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$	18	PPh_3	15	<1	0.032	10	1.5 ± 0.1
$[HPEtPh_2][BF_4]$	22	$[Fe(CO)_3(PCy_2Ph)_2]$	18	<1	0.25	5	0.6[b]
$[HPPh_3][BF_4]$	14	$[Fe(CO)_3(PCyPh_2)_2]$	13	<1	0.50	5	0.30
$[HPPh_3][BF_4]$	17	$[Fe(CO)_3(PCy_3)_2]$	17	<1	609	20	−2.8 ± 0.2
$[Fe(CO)_3H\{P(tol)_3\}_2][BF_4]$	10	$[Fe(CO)_3(PCyPh_2)_2]$	12	<4	15.8	10	−1.2 ± 0.1
$[Fe(CO)_3H\{P(tol)_3\}_2][BF_4]$	18	$[Fe(CO)_3\{PPh_2(tol)_2\}]$	15	<4	0.18	5	0.74
$[Fe(CO)_3H\{P(tol)_3\}_2][BF_4]$	16	$[Fe(CO)_3(PPh_3)_2]$	14	<1	0.063	10	1.2 ± 0.1
$[Fe(CO)_3H(PPh_3)_2][BF_4]$	8	$[Fe(CO)_3\{PPh_2(tol)_2\}]$	7	<4	0.37	5	0.43
$[Fe(CO)_3H(PPh_3)_2][BF_4]$	15	$[Fe(CO)_3\{P(p\text{-}FC_6H_5)_3\}_2]$	11	<1	0.0054	20	2.3 ± 0.2
$[Fe(CO)_3H\{P(p\text{-}FC_6H_5)_3\}_2][BF_4]$	15	Et_2O	50	<1	0.024	20	1.6 ± 0.2
$[HOEt_2][BF_4]$	30	$[Fe(CO)_3\{P(p\text{-}FC_6H_5)_3\}_2]$	15	<1	93	20	−1.8 ± 0.2

[a] Time taken to reach equilibrium. [b] A side reaction occurs. The PCy_2Ph ligand is substituted by $PEtPh_2$.

Ideally, we wanted to obtain the $\mathrm{p}K_{\mathrm{fi}}^{\mathrm{CD_2Cl_2}}$ values for the free ions $[\mathrm{BH}]^+$, independent of the counter ion ($[\mathrm{BF_4}]^-$), and not values for the ion-paired species $[\mathrm{BH}]^+[\mathrm{BF_4}]^-$. If the thermodynamics of ion pairing, solvation, and hydrogen bonding is the same for $[\mathrm{B^1H}]^+[\mathrm{BF_4}]^-$and $[\mathrm{B^2H}]^+[\mathrm{BF_4}]^-$, then we expect that the $\Delta\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ and $\Delta\mathrm{p}K_{\mathrm{fi}}^{\mathrm{CD_2Cl_2}}$ values will also be the same, as shown in Equation (5):

$$\Delta\mathrm{p}K^{\mathrm{CD_2Cl_2}} = \Delta\mathrm{p}K_{\mathrm{fi}}^{\mathrm{CD_2Cl_2}} = \mathrm{p}K_{\mathrm{fi}}^{\mathrm{CD_2Cl_2}}([\mathrm{B^1H}]^+)-\mathrm{p}K_{\mathrm{fi}}^{\mathrm{CD_2Cl_2}}([\mathrm{B^2H}]^+) \tag{5}$$

$[\mathrm{HPCy_3}][\mathrm{BF_4}]$ with a free ion ($\mathrm{p}K_{\mathrm{fi}}^{\mathrm{CD_2Cl_2}}(\mathrm{HPCy_3}^+)=9.7$) was chosen as the arbitrary anchor for the scale in $\mathrm{CD_2Cl_2}$ in a similar manner to the THF scale.[1] Overlapping equilibria were examined with more acidic compounds to create a continuous ladder of values. For examples, see Equations (6) and (7):

$$[\mathrm{HPCy_3}][\mathrm{BF_4}]+\mathrm{PBu_3} \xrightleftharpoons{\mathrm{p}K_{\mathrm{eq}}=1.5} \mathrm{PCy_3}+[\mathrm{HPBu_3}][\mathrm{BF_4}] \tag{6}$$

$$\mathrm{p}K^{\mathrm{CD_2Cl_2}}[\mathrm{HPBu_3}]^+ = 9.7-\mathrm{p}K_{\mathrm{eq}} = 8.2 \tag{7}$$

An acidity scale ladder of phosphonium tetrafluoroborate salts in $\mathrm{CD_2Cl_2}$ (Figure 1) was built by means of the overlapping equilibria method. The estimated errors for the equilibrium constants are listed in Tables 4 and 5. The cumulative error in the $\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ value is calculated by using Equation (8):[1]

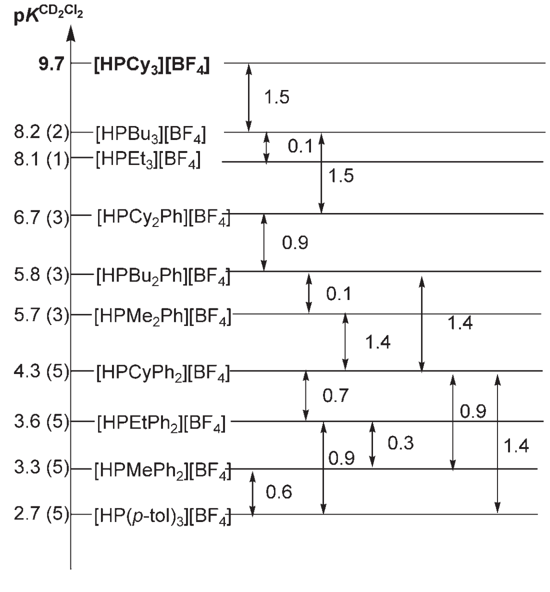


Figure 1. An acidity scale ladder for phosphonium tetrafluoroborate salts in $\mathrm{CD_2Cl_2}$ showing $\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ values.

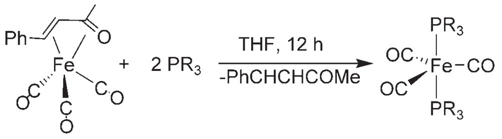
$$\text{Cumulative error in } \mathrm{p}K^{\mathrm{CD_2Cl_2}} = \pm 0.08|\mathrm{p}K^{\mathrm{CD_2Cl_2}}-9.7| \tag{8}$$

The errors in the last digit are shown in parentheses in Figure 1. They represent a combination of the cumulative errors relative to the reference value of 9.7 and the estimated errors for K.

We have not attempted to estimate corrections for ion pairing. We assume that the phosphonium salts have similar interion distances and similar ion-pair energetics so that these factors cancel out in the equilibrium shown in Equation (6).

The presence of a more electron-donating substituent on the phosphonium salt results in a decrease in acidity as expected (i.e., the $\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ values increase as $\mathrm{Me}<\mathrm{Et}<\mathrm{Bu}<\mathrm{Cy}$). By using $[\mathrm{BF_4}]^-$ salts, the acidity ladder reaches a $\mathrm{p}K^{\mathrm{CD_2Cl_2}}$ value of 2.7 for $[\mathrm{HP(tol)_3}][\mathrm{BF_4}]$.

Synthesis and structures of iron complexes: $[\mathrm{Fe(CO)_3(PR_3)_2}]$ and $[\mathrm{Fe(CO)_3H(PR_3)_2}][\mathrm{BF_4}]$ complexes were chosen to extend the acidity ladder measured in $\mathrm{CD_2Cl_2}$ in the more acidic direction. Yellow complexes $[\mathrm{Fe(CO)_3(PR_3)_2}]$ were reported by Angelici and Wang,[20] and Nolan and co-workers.[22–25] These complexes are conveniently synthesized from $[\mathrm{Fe(bda)(CO)_3}]$ and $\mathrm{PR_3}$ in which $\mathrm{PR_3}$ is $\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$, and $\mathrm{PMe_3}$ (Scheme 1). We adapted the same method and prepared $[\mathrm{Fe(CO)_3(PR_3)_2}]$ complexes in which $\mathrm{PR_3}$ is $\mathrm{PCy_3}$, $\mathrm{PCy_2Ph}$, $\mathrm{PCyPh_2}$, $\mathrm{PPh_2(tol)}$, $\mathrm{P(tol)_3}$, $\mathrm{PPh_3}$, and $\mathrm{P(}p\text{-}\mathrm{FC_6H_4)_3)}$.



Scheme 1. Preparation of $[\mathrm{Fe(CO)_3(PR_3)_2}]$ complexes.

The X-ray crystal structure of $[\mathrm{Fe(CO)_3(PCy_2Ph)_2}]$ is shown in Figure 2 and the bond lengths and angles are listed in Table 7. $[\mathrm{Fe(CO)_3(PCy_2Ph)_2}]$ has a distorted trigonal bipyramidal geometry. The two phosphane ligands are located in axial positions with a P-Fe-P angle of 158.66(4)°. They adopt a conformation in which the cyclohexyl rings, one from each ligand, are face to face in the equatorial plane of the complex. The C(2)-Fe(1)-C(3) angle is widened to

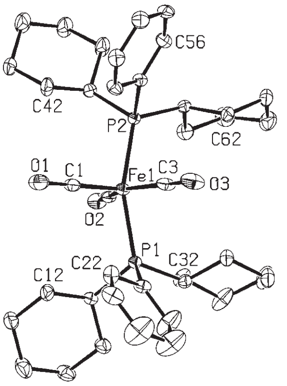


Figure 2. X-ray crystal structure of $[\mathrm{Fe(CO)_3(PCy_2Ph)_2}]$.

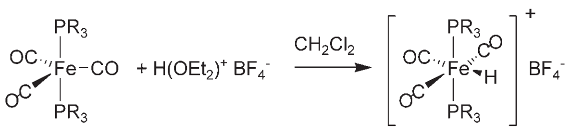
Table 7. Selected bond lengths [Å] and angles [°] for $[Fe(CO)_3(PCy_2Ph)_2]$.

Fe(1)–C(1)	1.774(4)	Fe(1)–C(2)	1.770(3)
Fe(1)–C(3)	1.764(4)	Fe(1)–P(1)	2.2378(9)
Fe(1)–P(2)	2.2337(9)		
C(3)-Fe(1)-C(2)	146.1(2)	C(3)-Fe(1)-C(1)	107.2(2)
C(2)-Fe(1)-C(1)	106.6(2)	C(3)-Fe(1)-P(2)	87.2(1)
C(2)-Fe(1)-P(2)	87.1(1)	C(1)-Fe(1)-P(2)	100.3(1)
C(3)-Fe(1)-P(1)	86.0(1)	C(2)-Fe(1)-P(1)	87.4(1)
C(1)-Fe(1)-P(1)	101.0(1)	P(2)-Fe(1)-P(1)	158.66(4)

146.1(2)° by this intrusion of the cyclohexyl groups. The other C-Fe-C angles diminish, but the FeC_3 grouping remains planar so that the sum of the three C-Fe-C angles adds up to 360°. There is approximate C_s symmetry in which a mirror plane cuts though the carbonyl ligands and iron. The complex exhibits a singlet at $\delta = 84$ ppm in the ^{31}P NMR spectrum.

There is a report of such distortions in *trans*-(tricarbonyl)-bis(*trans*-2,2,3,4,4-pentamethyl-1-phenylphosphetane)iron, which contains a P-Fe-P angle of 162.4° and one C-Fe-C angle of 133.3°.[26] Surprisingly, $[Fe(CO)_3(PPh_2Cy)_2]$ does not have steric hindrance in the equatorial plane, and therefore, has a P-Fe-P angle of 178.45(6)° and C-Fe-C angles of 118–122°.[22]

The pale yellow or white hydride $[Fe(CO)_3H(PR_3)_2][BF_4]$ complexes were prepared through protonation of $[Fe(CO)_3(PR_3)_2]$ in CH_2Cl_2 (Scheme 2), which is formally an oxidative addition reaction (Fe^0/Fe^{II}). THF cannot be used as a solvent when PR_3 is PPh_3 and $P(p\text{-}FC_6H_4)_3$ because these iron hydride complexes are deprotonated by THF. Attempts to exchange $[BF_4]^-$ for $[BPh_4]^-$ in the hydride complex through treatment with $NaBPh_4$ resulted in the formation of $[Fe(CO)_3(PR_3)_2]$, BPh_3, and benzene.



Scheme 2. Preparation of the hydride complexes.

The structure of the cation of $[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$ is shown in Figure 3 and selected bond lengths and angles are listed in Table 8. $[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$ has octahedral geometry, as expected for low-spin Fe^{II}, but there are distortions owing to the face-to-face cyclohexyl groups forming a sandwich with the hydride ligand. In essence, the conformations of the ligands have changed very little from the unprotonated structure shown in Figure 2.

The hydride complex exhibits a triplet at $\delta = -8.4$ ppm in the ^1H NMR spectrum for the hydride ligand and a singlet at $\delta = 65$ ppm in the ^{31}P NMR spectrum for the two equivalent phosphane ligands.

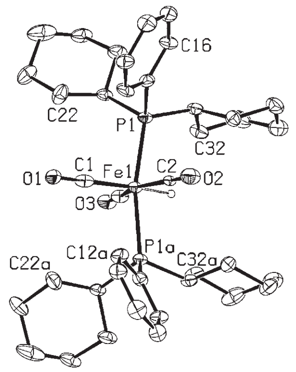


Figure 3. Structure of the cation of $[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$ as determined by means of X-ray diffraction.

Table 8. Selected bond lengths [Å] and angles [°] for $[Fe(CO)_3H(PCy_2Ph)_2][BF_4]$.

Fe(1)–C(1)	1.815(8)	Fe(1)–C(2)	1.790(6)
Fe(1)–C(3)	1.791(9)	Fe(1)–P(1)	2.2920(9)
Fe(1)–P(1a)	2.2920(9)	Fe(1)–H(1)	1.48(7)
C(3)-Fe(1)-C(2)	157.8(3)	C(3)-Fe(1)-C(1)	102.1(4)
C(2)-Fe(1)-C(1)	100.1(3)	C(3)-Fe(1)-P(1a)	88.17(6)
C(2)-Fe(1)-P(1a)	89.12(5)	C(1)-Fe(1)-P(1a)	97.05(3)
C(3)-Fe(1)-P(1)	88.17(6)	C(2)-Fe(1)-P(1)	89.12(5)
C(1)-Fe(1)-P(1)	97.05(3)	P(1a)-Fe(1)-P(1)	165.88(6)
H(1)-Fe(1)-C(2)	91(4)	H(1)-Fe(1)-C(3)	66(4)
H(1)-Fe(1)-C(1)	169(4)	H(1)-Fe(1)-P(1a)	83.02(8)
H(1)-Fe(1)-P(1)	83.02(8)		

An acidity scale for iron hydride complexes in CD_2Cl_2: Overlapping equilibria between $[Fe(CO)_3(PR_3)_2]$ and $[Fe(CO)_3H(PR_3)_2][BF_4]$ were established to create a continuous acidity scale for iron hydride complexes in CD_2Cl_2 (Figure 4).

To anchor our $[Fe(CO)_3H(PR_3)_2][BF_4]$ scale, equilibria were established between $[HPEtPh_2][BF_4]$ ($pK^{CD_2Cl_2} = 3.6$) and $[Fe(CO)_3(PCy_3)_2]$ (Figure 4). We have not corrected the equilibrium constant for the differences between the ion-pair energetics of the phosphonium and iron hydride salts. Previously, this correction was done for a pK_α^{THF} scale of metal hydrides and phosphonium salts[1] and protonated nitrogen bases[10,12] by using the Fuoss equation, but this approach is inaccurate.[27] The continuous acidity ladder of all of the $[BF_4]^-$ salts from this work is shown in Table 9.

Angelici and co-workers reported the heats of protonation of phosphane compounds and iron carbonyl complexes in dichloroethane (DCE) by using trifluoromethylsulfonic acid (HOTf).[29,30] Some of the $-\Delta H_{MH}$ and $-\Delta H_{PH}$ values available are also included in Table 9. A plot of $-\Delta H_{MH}$ and $-\Delta H_{PH}$ values versus $pK^{CD_2Cl_2}$ is shown in Figure 5, and Equation (9) shows the conversion equation ($R^2 = 0.98$). By using this equation, we can predict the $pK^{CD_2Cl_2}$ values of compounds with known $-\Delta H_{MH}$ or $-\Delta H_{PH}$ values.

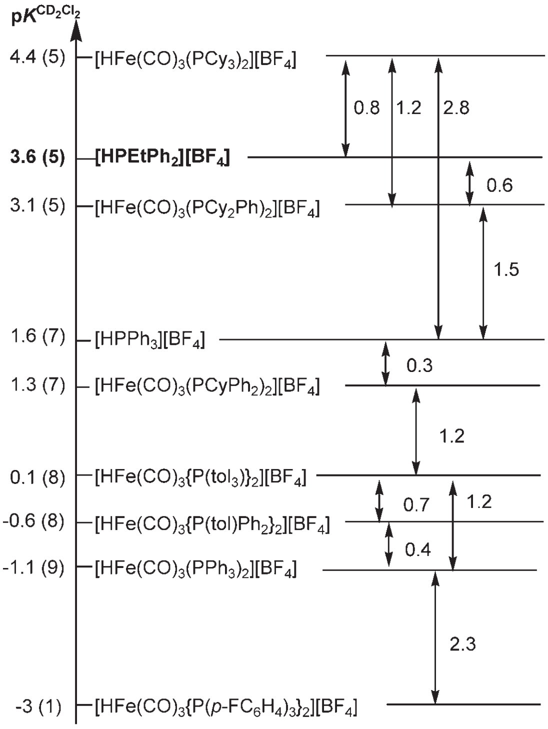


Figure 4. An acidity scale ladder of the iron hydride complexes and phosphonium tetraphenylborate salts in CD$_2$Cl$_2$ showing $\Delta pK^{CD_2Cl_2}$ values.

Table 9. The complete acidity ladder of [Fe(CO)$_3$H(PR$_3$)$_2$][BF$_4$] and [HPR$_3$][BF$_4$] in CD$_2$Cl$_2$, the available heats of protonation, and pK_a values.

Acid	p$K^{CD_2Cl_2}$	pK_a	$-\Delta H_{HP}$ or $-\Delta H_{HM}$ [kcal mol^{-1}][a]
[HPCy$_3$]$^+$	9.7	9.7	34.2
[HPBu$_3$]$^+$	8.2	8.4	–
[HPEt$_3$]$^+$	8.1	8.7	–
[HPCy$_2$Ph]$^+$	6.7	7.4	–
[HPBu$_2$Ph]$^+$	5.8	–	–
[HPMe$_2$Ph]$^+$	5.7	6.8	–
[Fe(CO)$_3$H(PCy$_3$)$_2$]$^+$	4.4	–	–
[HPCyPh$_2$]$^+$	4.3	5.1	–
[HPEtPh$_2$]$^+$	3.6	4.9	–
[Fe(CO)$_3$H(PCy$_2$Ph)$_2$]$^+$	3.4	–	–
[HPMePh$_2$]$^+$	3.3	4.6	24.7
[HP(tol)$_3$]$^+$	2.7	3.8[b]	–
[HPPh$_3$]$^+$	1.6	2.7[b]	21.2
[Fe(CO)$_3$H{P(tol)$_3$}$_2$]$^+$	0.1	–	–
[Fe(CO)$_3$H{P(tol)Ph$_2$}$_2$]$^+$	−0.6	–	–
[Fe(CO)$_3$H(PPh$_3$)$_2$]$^+$	−1.1	–	14.1
[Fe(CO)$_3$H(P{p-FC$_6$H$_4$)$_3$}$_2$]$^+$	−3.4	–	–

[a] Determined in dichloroethane. [b] These values are now known to be at least 1.6 units too high.[28]

$$-\Delta H^{DCE}_{FeH\,or\,PH}(HB^+OTf^-) = 1.8pK^{CD_2Cl_2}([HB]^+[BF_4]^- \text{ or } [HFe]^+[BF_4]^-)+17.48 \quad (9)$$

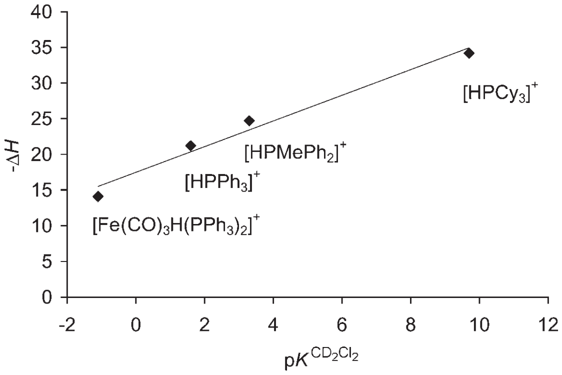


Figure 5. A plot of $-\Delta H_{FeH}$ and $-\Delta H_{PH}$ values in kcal mol^{-1} (the anion is [OTf]$^-$) versus p$K^{CD_2Cl_2}$ (the anion is [BF$_4$]$^-$).

The plot suggests that the solvation effects are similar in CD$_2$Cl$_2$ and DCE. The $-\Delta H_{FeH}$ and $-\Delta H_{HP}$ values were measured for cations by using [OTf]$^-$, whereas the p$K^{CD_2Cl_2}$ values were determined by using [BF$_4$]$^-$. The slope of the plot of Figure 5 is 1.8. pK values are related to free energies, whereas ΔH values are enthalpies, which means that differences in entropy are not accounted for in such a plot. A plot of free energy versus $-\log K$ should have a slope of $2.303RT = 1.35$. The difference between these two slopes must represent continuous changes in entropy and differences in solvation, ion pairing, and hydrogen bonding between the more basic and more acidic compounds.

A set of pK_a values are used by convention in the literature to describe the general acidic properties of protonated phosphanes. Most of these values have been obtained by means of extrapolation from nonaqueous or mixed solvents to aqueous conditions. These pK_a values are shown in Table 9 and a plot of the pK_a values versus the p$K^{CD_2Cl_2}$ values is shown in Figure 6 as diamond-shaped points. A best-fit line through ten points gives Equation (10) ($R^2 = 0.99$):

$$pK_a = 0.85\,pK^{CD_2Cl_2}([HPR_3]^+[BF_4]^-)+1.60 \quad (10)$$

The pK_a values used for PCy$_3$, PBu$_3$, PEt$_3$, PPh$_3$, and PMe$_2$Ph were measured in nitromethane by Streuli and ex-

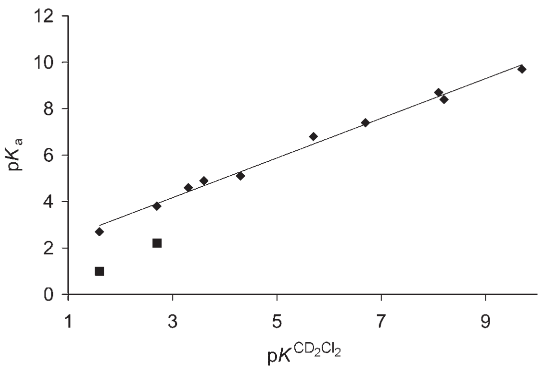


Figure 6. Correlation between pK_a and p$K^{CD_2Cl_2}$ scale. The points marked with diamonds are from Table 9, whereas those marked with squares refer to pK_a values determined in CH$_3$CN/H$_2$O (v/v = 85:15) and are from ref. [28].

trapolated to water.[31] The pK_a value used for P(tol)$_3$ was obtained experimentally by Allman and Goel.[32] Giering and co-workers estimated pK_a values for PCyPh$_2$ and PCy$_2$Ph by means of interpolation between the values for PPh$_3$ and PCy$_3$.[33] Kochi and coworker estimated pK_a values for PMePh$_2$ and PEtPh$_2$ by using Hammett correlation analyses.[34]

However, there is recent evidence that, at least for the triarylphosphanes, these literature pK_a values are too high. For example, $[HPPh_3]^+$ and $[HP(tol)_3]^+$ have pK_a values in CH$_3$CN/H$_2$O (v/v = 85:15) of 1.05 and 2.18, respectively.[28] The hypothetical aqueous values would be even lower.

Table 10. Converted selected p$K^{CD_2Cl_2}$ values of metal hydride and dihydrogen complexes measured in CD$_2$Cl$_2$ on the basis of the aqueous reference to p$K^{CD_2Cl_2}$ values (sorted by the acidity in CD$_2$Cl$_2$ from strong to weak).[a]

Dihydrogen or dihydride	Anion	Base	p$K^{CD_2Cl_2}$ literature	p$K^{CD_2Cl_2}$ converted
trans-$[Os(CH_3CN)(dppe)_2(H_2)]^{2+}$	$2[BF_4]^-$	Et$_2$O	-2 ± 1[36]	-4 ± 1
$[Ru(CO)(^{H}Cn)(H_2)(PPh_3)]^{2+}$	$2[BF_4]^-$	Et$_2$O	-1.3[17]	-3 ± 1
$[Ru(CO)(H_2)(PPh_3)(Tp)]^+$	$[BF_4]^-$	$[Ru(CO)(^{H}Cn)H(PPh_3)]^+$	-0.6[17]	-2 ± 1
$[Ru(^{Me}Cn)(dppe)(H_2)]^{2+}$	$2[CF_3SO_3]^-$	*trans*-[RuCl(dppe)$_2$H]	3.8[17]	2.5
$[Ru(^{H}Cn)(PPh_3)_2(H_2)]^{2+}$	$2[BF_4]^-$	*trans*-[RuCl(dppe)$_2$H]	4.5[17]	3.2
$[RuCl(H_2)(pmp)(PPh_3)]^+$	$[BF_4]^-$	P(tol)$_3$	5.1[14]	4.0
trans-$[RuCl(dppe)_2(H_2)]^+$	PF_6^-	PEtPh$_2$	6.0[15,16]	4.7
$[Ru(Cp)(dppe)(H_2)]^+$	$[BF_4]^-$	[Ru(Cp)H(PPh$_3$)$_2$]	7.0[15,16]	7.0
$[Ru(Cp)(dppm)(H_2)]^+$	$[BF_4]^-$	[Ru(Cp)H(PPh$_3$)$_2$]	7.1[15,16]	7.1
$[OsCl(H_2)(pmp)(PPh_3)]^+$	$[BF_4]^-$	[Ru(Cp)H(PPh$_3$)$_2$] [Ru(Cp)H(dppm)]	7.2[14]	7.2[14]
$[Ru(H_2)(PPh_3)_2(Tp)]^+$	$[BF_4]^-$	[Ru(Cp)(dppm)H]	7.6[16]	7.6
$[Ru(dppe)(H_2)Tp]^+$	$[BF_4]^-$	[Ru(Cp)(dppm)H]	7.9[16]	7.9
$[Ru(Cp)(dape)(H_2)]^+$	$[BF_4]^-$	[Ru(Cp)H(PPh$_3$)$_2$]	8.1[15]	8.1
$[Ru(Cp)(H)_2(PPh_3)_2]^+$	$[BPh_4]^-$, $[BF_4]^-$	PCy$_3$	8.3[15,16]	8.3
$[Ru(Cp)(dppp)(H)_2]^+$	$[BPh_4]^-$	[Ru(Cp)H(PPh$_3$)$_2$]	8.4[15,16]	8.4
$[Ru(CH_3CN)(H_2)(PPh_3)(Tp)]^+$	$[BF_4]^-$	[Ru(Cp)H(PPh$_3$)$_2$]	8.9[17]	8.9

[a] Abbreviations: ^{H}Cn: 1,4,7-triazacyclononane, ^{Me}Cn: 1,4,7-trimethyl-1,4,7-triazacyclononane, Tp: hydrotris(-pyrazolyl), pmp: 2,6-(Ph$_2$PCH$_2$)$_2$C$_5$H$_3$N.

Acidity of diethyl ether: The protonation equilibrium of diethyl ether was measured in aqueous sulfuric acid by Perdoncin and Scorrano and the pK_a of $[HOEt_2]^+$ was reported as –2.4.[35] This value has been used to estimate the p$K^{CD_2Cl_2}$ values of some very acidic complexes in CD$_2$Cl$_2$, such as *trans*-[Os(CH$_3$CN)(dppe)$_2$(H$_2$)][(BF$_4$)$_2$][36] and [Ru(CO)(^{H}Cn)(H$_2$)(PPh$_3$)][(BF$_4$)$_2$] (dppe: 1,2-bis(diphenylphosphino)ethane, ^{H}Cn: 1,4,7-triazacyclononane).[17] Therefore, the p$K^{CD_2Cl_2}$ value of [HOEt$_2$][BF$_4$] is important to allow a better estimate of the p$K^{CD_2Cl_2}$ values of these complexes. [Fe(CO)$_3$H{P(p-FC$_6$H$_4$)$_3$}$_2$][BF$_4$], the most acidic complex on the acidity ladder (Table 9), reacts with diethyl ether and at equilibrium, a K_{eq} value of 0.024 was obtained, as shown in Equation (11):

$$[Fe(CO)_3H\{P(p\text{-}FC_6H_4)_3\}_2][BF_4] + Et_2O \xrightleftharpoons{K_{eq}=0.018} [Fe(CO)_3\{P(p\text{-}FC_6H_4)_3\}_2] + [HOEt_2][BF_4] \tag{11}$$

The reverse equilibrium reaction between [HOEt$_2$][BF$_4$] and [Fe(CO)$_3${P(p-FC$_6$H$_4$)$_3$}$_2$] was also studied and a K_{eq} value of 0.011 was obtained. Therefore, the p$K^{CD_2Cl_2}$ value of [HOEt$_2$][BF$_4$] was found to be -4.7 ± 1 when the p$K^{CD_2Cl_2}$ value of [Fe(CO)$_3$H{P(p-FC$_6$H$_4$)$_3$}$_2$][BF$_4$] is -3 ± 1.

Correcting the existing p$K^{CD_2Cl_2}$ values: As mentioned in the Introduction, p$K^{CD_2Cl_2}$ values of metal hydride and dihydrogen complexes in CD$_2$Cl$_2$ have been reported and anchored to the pK_a value of phosphonium salts, Et$_2$O, or metal hydride complexes. In this study, we established a new acidity scale in [D$_2$]dichloromethane. The existing p$K^{CD_2Cl_2}$ values of the selected metal hydride and dihydrogen complexes in CD$_2$Cl$_2$ were converted to the new dichloromethane scale (shown in Table 10). To locate the very acidic complexes, more equilibria with [Fe(CO)$_3$(PPh$_3$)$_2$] or [Fe(CO)$_3${P(p-FC$_6$H$_4$)$_3$}$_2$] need to be established.

Iron hydride acidity and hydrogenase: The mechanism of action of iron hydrogenases involves reversible protonation/deprotonation of iron centers coordinated by carbonyl, thiolate, and in all known cases except one,[37] cyanide ligands.[38,39] These acid–base reactions occur at around pH 7 in the interior of the protein, which has a low dielectric constant. The present work emphasizes the acidifying effect that carbonyl ligands have on iron hydrides.

Conclusion

A continuous scale of very acidic compounds, [HPR$_3$][BF$_4$] and [Fe(CO)$_3$H(PR$_3$)$_2$][BF$_4$], in CD$_2$Cl$_2$ was constructed with a p$K^{CD_2Cl_2}$ range of 9.7 to –3. The p$K^{CD_2Cl_2}$ value of diethyl ether was found to be –5. Existing p$K^{CD_2Cl_2}$ values of selected metal hydride and dihydrogen complexes in CD$_2$Cl$_2$ were converted to the new scale. When an absolute acid standard in CD$_2$Cl$_2$ becomes available, these values will all have to be shifted to more positive values. Thus for this reason, and owing to the difficulties in determining the ion-pairing contribution, the p$K^{CD_2Cl_2}$ values reported here are not thermodynamically accurate pK_a values, but are useful nevertheless for estimating the relative acidity of compounds in CD$_2$Cl$_2$. The crystal structures of [Fe(CO)$_3$(PCy$_2$Ph)$_2$] and [Fe(CO)$_3$H(PCy$_2$Ph)$_2$][BF$_4$] are reported and found to be distorted by the conformation adopted by the bulky, unsymmetrical phosphane ligands. $[BPh_4]^-$ and $[BF_4]^-$ anions do not have a large effect on p$K^{CD_2Cl_2}$ values, but the $[BF_4]^-$ salts allow a much wider range of acid strengths to be measured.

Acknowledgement

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