An acidity scale of phosphonium tetraphenylborate salts and ruthenium dihydrogen complexes in dichloromethane[1]

Tianshu Li, Alan J. Lough, Cristiano Zuccaccia, Alceo Macchioni, and Robert H. Morris

Abstract: Equilibrium constants (K^{DM}) for reactions between acids and bases of the title compounds in CD_2Cl_2 (DM) have been determined by ^{31}P and ^{1}H NMR spectroscopy at room temperature. $[HPCy_3]BPh_4$ and $[HPCy_3]BF_4$, with pK^{DM} assigned by literature convention to 9.7, have been used as the anchor compounds for the pK^{DM} determinations. A continuous scale of pK^{DM} values covering the range 9.7 to 5.7 is created with the acidic compounds $[HPR_3]BPh_4$. Those acids with pK^{DM} greater than 6 are stable, while those with more acidic cations HPR_3^+ protonate BPh_4^- to produce R_3PBPh_3 and benzene. The literature pK^{THF} values reported for $[HPBu_2Ph]BPh_4$, $[HPMePh_2]BPh_4$, and $[HPEtPh_2]BPh_4$ are questionable because of this protonation reaction. NOE and PGSE ^{1}H NMR techniques are used to show that $[HPCy_2Ph]BPh_4$ in DM exists as ion pairs and higher aggregates up to quadrupoles at the concentrations used in the acid–base studies. The new dihydrogen complexes $[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$ (dach = (1*R*,2*R*)-(–)-diaminocyclohexane) and $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BF_4$ ($tmeP_2(NH)_2$ = $PPh_2C_6H_4CH_2NHCMe_2CMe_2NHCH_2C_6H_4PPh_2$) were prepared by reaction of $RuHCl(PPh_3)_2(dach)$ and $RuHCl\{tmeP_2(NH)_2\}$ with HBF_4. Their crystal structures are reported, and the pK^{DM} values of their BPh_4^- salts were determined to be 8.6 and 6.9, respectively.

Key words: acidity, dihydrogen complex, hydride, phosphonium, dichloromethane.

Résumé : Opérant à la température et dans le CD_2Cl_2 (DM) comme solvant et faisant appel à la spectroscopie RMN du ^{1}H et du ^{31}P, on a déterminé les constantes d'équilibre, K^{DM}, des réactions entres les acides et les bases des composés mentionnés dans le titre. La valeur de 9,7 attribuée par convention dans la littérature pour les composés $[HPCy_3]BPh_4$ et $[HPCy_3]BF_4$ a été utilisé comme composés de référence pour les déterminations des pK^{DM}. On a créé une échelle continue de valeurs de pK^{DM} s'étalant de 9,7, à 5,7 en faisant appel aux composés acides $[HPR_3]BPh_4$. Ces acides dont les valeurs de pK^{DM} sont supérieures à 6 sont stables alors que ceux des cations plus acides HPR_3^+ se protonent au BPh_4^- pour conduire à la formation de R_3PBPh_3 et de benzène. Les valeurs de pK^{THF} rapportées dans la littérature pour les $[HPBu_2Ph]BPh_4$, $[HPMePh_2]BPh_4$ et $[HPEtPh_2]BPh_4$ ne sont pas fiables en raison de cette réaction de protonation. On a utilisé les techniques d'effet Overhauser nucléaire et d'écho de spin a champ pulsé PGSE en RMN du ^{1}H pour montrer que dans le DM, aux concentrations utilisées pour les études acide–base, le $[HPCy_2Ph]BPh_4$ existe sous la forme de paire d'ions et d'agrégats plus importants allant jusqu'à des quadrupoles. La réaction du $RuHCl(PPh_3)_2(dach)$ et $RuHCl\{tmeP_2(NH)_2\}$ avec du HBF_4 a permid de préparer les deux nouveaux complexes de dihydrogène suivants $[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$ (dach = (1*R*,2*R*)-(–)-diaminocyclohexane) et $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BF_4$ ($tmeP_2(NH)_2$ = $PPh_2C_6H_4CH_2NHCMe_2CMe_2NHCH_2C_6H_4PPh_2$) dont on a déterminé les structures cristallines et les valeurs de pK^{DM} de leurs sels BPh_4^- qui s'établissent respectivement à 8,6 et 6,9.

Mots clés : acidité, complexe de dihydrogène, hydrure, phosphonium, dichlorométhane.

[Traduit par la Rédaction]

Introduction

The quantitative study of the acidity of transition metal hydride and dihydrogen complexes serves to better the understanding of the reactions of these species in catalytic reactions, including those of hydrogenases. Our previous work focused mainly on the use of tetrahydrofuran (THF) as a useful solvent in the study of metal hydride and dihydrogen

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complexes with a wide range of pK_α^{THF} values (1). The use of α in this acidity symbol indicates that the effects of ion pairing on the acid–base equilibria are approximately accounted for by use of the Fuoss equation. This approach has since been used by Leito and co-workers (2). Tetrahydrofuran cannot be used as a solvent for very acidic compounds because it can be protonated and undergo ring-opening reactions. Dichloromethane is a good solvent for this purpose because it is relatively noncoordinating and it dissolves many neutral and cationic metal complexes without reaction, as long as they are not too reducing or nucleophilic. Several pK^{DM} values of metal hydride and dihydrogen complexes in CH_2Cl_2 have been reported by the groups of Jia, Morris, and co-workers (3–7). Only a short continuous ladder of acids in the range of 9.7 to 7.0 was built on the basis of equilibria referenced to $[HPCy_3]BPh_4/PCy_3$ as a standard with pK = 9.7 (Fig. 1) (4). This is the same reference value used for the pK_α^{THF} scale (and pseudo pK_a^{aq} scale) (4, 8), but it will have to be redefined when an absolute value is determined relative to the solvated proton in CH_2Cl_2. There is no continuous ladder based on cationic acids with exclusively one type of anion (e.g., BPh_4^-) in CD_2Cl_2. In this study, we make a limited scale of acidic compounds with BPh_4^- anions. In a second paper we will describe a more extensive ladder involving BF_4^- salts. Although phosphonium salts are of utility as air-stable sources of air-sensitive trialkylphosphines (9), we show here that the tetraphenylborate salts of the more acidic aryl phosphonium compounds are unstable.

We also report the pK^{DM} of two new ruthenium dihydrogen trans-to-chloride complexes. These were prepared while exploring the application of such ruthenium hydrides for the catalytic hydrogenation of compounds with polar bonds (10, 11). Cationic ruthenium dihydrogen complexes have attracted interest with the recent report of Noyori and co-workers (12) that *trans*-[Ru(H_2)(H)((*R*)-binap)((*R,R*)-dpen)]$^+$ is an intermediate in the asymmetric catalytic H_2-hydrogenation of prochiral ketones catalyzed by RuH(BH_4)((*R*)-binap)((*R,R*)-dpen) in isopropanol. Bergens and co-workers (13) spectroscopically identified this unstable dihydrogen complex in deuterated isopropanol and reported that at least 1 equiv. of base is necessary to convert this complex to a catalytically active species.

Results and discussions

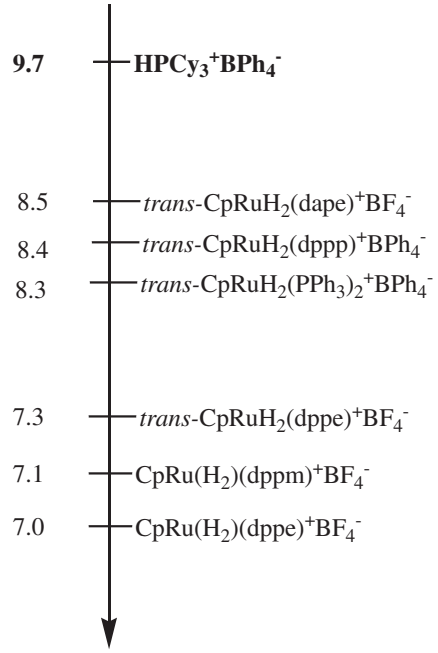
The preparation of $[HPR_3]BPh_4$

The tetrafluoroborate salts $[HPR_3]BF_4$ can be readily prepared by protonation of PR_3 (PR_3 = PCy_3, P-*n*-Bu_3, PCy_2Ph, P-*t*-Bu_2Ph) with $H(Et_2O)BF_4$ in diethyl ether (eq. [1]). As reported previously (1), these salts react with $NaBPh_4$ in ethanol to form the corresponding salts $[HPR_3]BPh_4$ (eq. [2]). However, we found that there is a limitation to this preparation. When the phosphonium salts HPR_3^+ (PR_3 = PBu_2Ph, PMe_2Ph, $PEtPh_2$, P(*p*-toly)$_3$, PPh_3) are more acidic than $HPCy_2Ph^+$, the borane adducts $PR_3{\cdot}BPh_3$ are isolated instead of the tetraphenylborate salts $[HPR_3]BPh_4$. A phenyl group of the BPh_4^- is protonated to form benzene (eq. [3]). The $PR_3{\cdot}BPh_3$ compounds were identified by ^{31}P and ^1H NMR.

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

[2] $[HPR_3]BF_4 + NaBPh_4 \rightarrow [HPR_3]BPh_4 + NaBF_4$

Fig. 1. The acidity ladder of pK^{DM} values of the cationic ruthenium complexes with $[HPCy_3]BPh_4$ as a standard.



[3] $[HPR_3]BPh_4 \rightarrow C_6H_6 + PR_3{\cdot}BPh_3$

There have been scattered reports of the protonation of the tetraphenylborate anion. Our group encountered it in the preparations of cationic hydrogen isocyanide complexes that were sometimes produced instead of the complexes Fe(TIM)$(CNBPh_3)_2$ (14) and RuH$(CNBPh_3)(dppe)_2$ (15), for example. This has also been reported by Pombeiro and co-workers (16) in the preparation of *trans*-[FeH$(CNBPh_3)(dppe)_2$]. The acidic dihydrogen complex [Ir(H_2)H(triphos)]BPh_4 decomposes to IrH_3(triphos), BPh_3, and benzene (17). However, several cationic dihydrogen and hydride complexes with tetraphenylborate counterions have been reported (for example, refs. 18–28), and so these are likely to be less acidic than $HPCy_2Ph^+$.

NOE and PGSE NMR measurements of $[HPCy_2Ph]BPh_4$

Ion pairing in low dielectric constant solvents like CH_2Cl_2 can lead to changes in reactivity and catalytic activity and selectivity (29). Table 1 shows the results of the study of NOE between ions (31) of the compound $[HPCy_2Ph]BPh_4$. Only the *meta*-aryl hydrogens of the anion (mH_a) can be used as a "reporter", since the resonances of oH_c and oH_a are superimposed. These meta protons are at about the same distance from both the hydrogen on the phosphorus and the hydrogen (H1) on each of the two ipso carbons of the cyclohexyl groups (Fig. 2, Table 1), thus demonstrating the interpenetration of the cation and anion. It is not surprising that more acidic salts can readily undergo transfer of the phosphorus proton to a phenyl ring carbon of the BPh_4^- anion, resulting in B—C bond cleavage.

The pulsed field gradient spin-echo (PGSE) NMR diffusion method (32, 33) is a powerful technique in determining the solution properties of ion pairs (34–36). From the mea-

Fig. 2. ^{1}H NOESY spectrum of $[HPCy_2Ph]BPh_4$ (27 mmol L^{-1}, CD_2Cl_2, 400 MHz, 299 K).

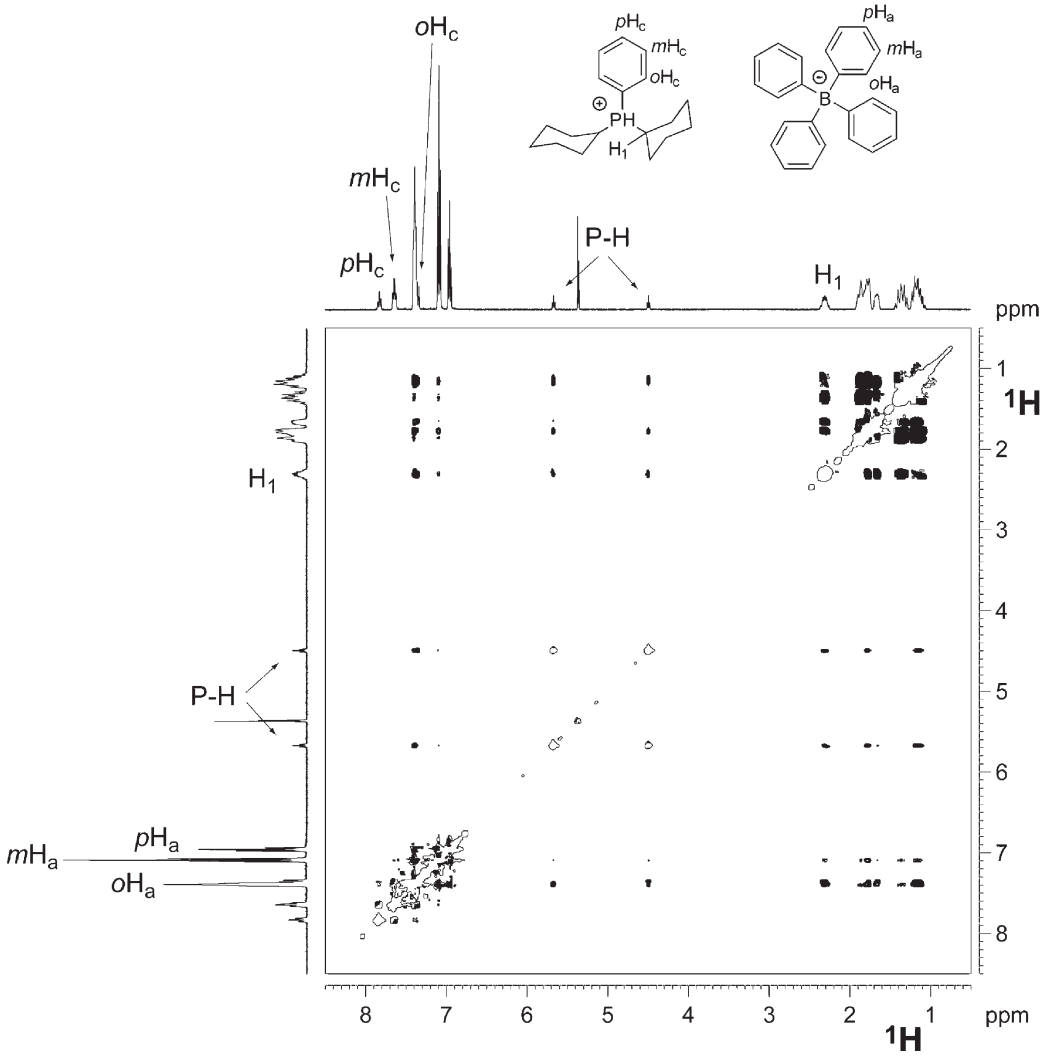


Table 1. Experimental NOE (au) and average interionic distances ($<r>_{exp}$ (Å)) determined using a 27 mmol L^{-1} solution of $[HPCy_2Ph]BPh_4$ in CD_2Cl_2 (the distance between pH$_a$ and oH$_a$ has been used as reference distance).

Pairs	NOE_{exp}	NOE_{corr}[a]	$<r>_{exp}$
pH_a/oH_a	2.66	1	4.04[b]
oH_c/P-H	4.02	6.03	2.99
mH_a/P-H	0.63	0.71	4.27
oH_a/P-H	1.76	1.98	3.60
P-H/H1	3.48	5.2	3.06
mH_a/mH_c	0.45	0.17	5.43
mH_a/H1	0.98	0.54	4.47

[a]Reference 30.
[b]Reference distance.

sured self-diffusion coefficients (D_t), the average hydrodynamic radius (r_H) and volume (V_H) of the diffusing particles were derived, taking advantage of the Stokes–Einstein equation that relates D_t with $1/r_H$. TMSS [tetrakis(trimethylsilyl)silane], whose r_H and V_H are known from the literature (37), was used as internal standard. The methodology to obtain accurate r_H and V_H values has been described elsewhere (38). The average hydrodynamic volumes for cation (V_H^+) and anion (V_H^-) determined from ^{1}H PGSE experiments were contrasted with the van der Waals volume of the ion pair (V_{IP}). The cationic and anionic aggregation numbers (N^+ and N^-) were calculated as the ratios V_H^+/V_{IP} and V_H^-/V_{IP} (Table 2).

The salt $[HPCy_2Ph]BPh_4$ in CH_2Cl_2 forms aggregates higher than ion pairs even at the lowest concentration investigated (entry 1, Table 2). The aggregation number for the cations, N^+, is 1.2 and that of the anions, N^-, is 1.6, indicating a dynamic equilibration of ion pairs, triples (e.g., $(HPCy_2Ph^+)(BPh_4^-)_2$), and quadrupoles. The tendency to aggregate increases as the concentration increases, resulting in N^+ and N^- values of 1.8 and 2.0, respectively, at 0.03 mol L^{-1} (entries 1–3 in Table 2). This is the range of concentrations used in our acid equilibrium studies, and so, such aggregation is a potential complication in interpreting our results.

pK^{DM} determination

The acid (BH^+) and base (B) reaction equilibria are built based on eq. [4]. The equilibrium constants K_{eq} for reactions

Fig. 3. An acidity scale ladder of phosphonium tetraphenylborate salts in CD_2Cl_2 showing pK^{DM} values.

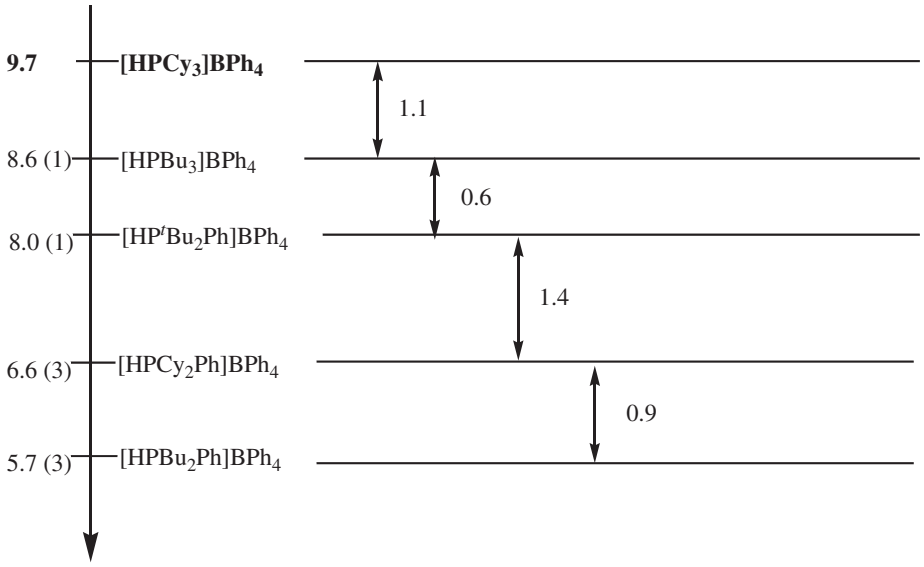


Table 2. Diffusion coefficients (D (10^{-10} m^2 s^{-1})), hydrodynamic radii (r_H (Å)), hydrodynamic volumes (V_H (Å^3)), and aggregation number values (N) for $[HPCy_2Ph]BPh_4$ in CD_2Cl_2.

Entry	Concn. (mmol L^{-1})	D^+	D^-	r_H^+	r_H^-	V_H^+	V_H^-	N^+	N^-
1	1.5	11.1	9.90	5.37	5.88	648	850	1.19	1.56
2	9	10.3	9.72	5.68	5.97	767	892	1.40	1.63
3	27	9.42	9.04	6.13	6.35	967	1072	1.77	1.97

Note: N is the ratio between the experimentally determined hydrodynamic volume and the van der Waals volume of the ion pair; + and – refer to the cation and anion of $[HPCy_2Ph]BPh_4$, respectively.

in CD_2Cl_2 were measured by use of quantitative $^{31}P\{^1H\}$ and ^1H NMR at room temperature. In view of the PGSE experiments, eq. [4] is a simplification of the actual ion-pairing equilibria that are present. However the ^{31}P NMR experiment measures the total phosphorus concentration, and these species are all in rapid equilibrium. If the extent and nature of ion pairing is the same for $B_1H^+X^-$ and $B_2H^+X^-$, then eq. [4] represents a practical, first-order description of the chemistry. K_{eq} in the range 10^3 to 10^{-3} can be measured with a 10%–30% error. The difference in pK^{DM} between the two acids $B_1H^+BPh_4^-$ and $B_2H^+BPh_4^-$ is calculated from the equilibrium constants (K_{eq}) by use of eq. [5].

$$[4] \quad B_1 + B_2H^+X^- \overset{K_{eq}}{\rightleftharpoons} B_1H^+X^- + B_2$$

$$[5] \quad \Delta pK^{DM} = \Delta pK_{eq} = pK^{DM}(B_1H^+X^-) - pK^{DM}(B_2H^+X^-)$$

$$[6] \quad \Delta pK^{DM} = \Delta pK_{fi}^{DM} = pK_{fi}^{DM}(B_1H^+) - pK_{fi}^{DM}(B_2H^+)$$

Ideally, we want the pK_{fi}^{DM} values for the free ions BH^+, independent of the counterion X^-, and not the ion-paired species BH^+X^- and its aggregates. If the extent of ion pairing is the same for $B_1H^+X^-$ and $B_2H^+X^-$, then pK^{DM} and pK_{fi}^{DM} values will be approximately the same (eq. [6]). $[HPCy_3]BPh_4$, with a free ion $pK_{fi}^{DM}(HPCy_3^+) = 9.7$, was chosen as the anchor for the scale in CD_2Cl_2, as in the THF scale (1). Overlapping equilibria were examined with more acidic compounds to create a continuous ladder of values (e.g., eqs. [7] and [8]).

$$[7] \quad PCy_3 + [HBu_3]BPh_4 \underset{pK_{eq} = -1.1}{\rightleftharpoons} \underset{9.7}{[HPCy_3]BPh_4} + PBu_3$$

$$[8] \quad pK_{fi}^{DM}(HPBu_3^+) = 9.7 + pK_{eq} = 8.6$$

A short acidity scale ladder of phosphonium tetraphenylborate salts in CD_2Cl_2 was built by this method (shown in Fig. 3). The estimated errors for the equilibrium constants are listed in Tables 3 and 4. The cumulative error in pK^{DM} value is calculated by eq. [9]. The errors in the last digit are shown in parentheses in Fig. 3. They represent the combination of the cumulative errors relative to the reference value of 9.7 and the estimated errors for K_{eq}.

$$[9] \quad \text{Cumulative error in } pK^{DM} = \pm 0.08\ |pK^{DM} - 9.7|$$

The equilibrium constant K_{eq} in the reaction between $HPCy_2Ph^+$ and PBu_2Ph has to be obtained by the immediate measurement of the NMR spectrum after mixing. Right after mixing, a signal due to $HPBu_2Ph^+$ can be observed. Longer standing (1 h) of the mixture causes a decay of $HPBu_2Ph^+$ to produce the $PBu_2Ph{\cdot}BPh_3$ species (Scheme 1). This suggests that $HPCy_2Ph^+$ with the pK^{DM} value of 6.6 is the most acidic BPh_4^- salt that can be obtained.

Table 3. Equilibrium constants for acid–base reaction of phosphonium salts in CD_2Cl_2.

Acid	Concn. (mmol L^{-1})	Base	Concn. (mmol L^{-1})	Time to reach equilibrium (h)	Error[a] (%)	K_{eq}	pK_{eq}
$[HPBu_3]BPh_4$	35	PCy_3	33	<4	5	11.8	–1.1
[HP-*t*-Bu_2Ph]BPh_4	38	PBu_3	35	<4	5	4.0	–0.6
[HP-*t*-Bu_2Ph]BPh_4	43	PCy_2Ph	46	<1	10	0.037	1.4
$[HPCy_2Ph]BPh_4$	43	PBu_2Ph	43	<1	5	0.12	0.9

[a]The error in the equilibrium constant determination is estimated from the magnitude of the constant and the *S/N* of each species in the spectrum of the equilibrium mixture.

Table 4. Equilibrium constants for reactions of ruthenium hydride complexes in CD_2Cl_2.

Entry	Acid (pK^{DM})	Concn. (mmol L^{-1})	Base	Concn. (mmol L^{-1})	Time to reach equilibrium (h)	K_{eq}	pK_{eq}	pK^{DM}
1	[HP-*t*-Bu_2Ph]BPh_4 (8.0)	21	$RuHCl(PPh_3)_2$(dach)	19	<1	6	–0.8	8.8
2	$[HPBu_3]BPh_4$ (8.6)	18	$RuHCl(PPh_3)_2$(dach)	16	<1	0.65	0.19	8.4
3	$[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$	14	PBu_3([$HPBu_3$]BF_4 8.2)	18	<1	0.50	–0.3	8.5
4	$[HPCy_2Ph]BPh_4$ (6.6)	20	$RuHCl(PPh_3)_2$(dach)	18	<1	153	–2.2	8.8
5	$[HPCy_2Ph]BPh_4$ (6.6)	16	$RuHCl\{tmeP_2(NH)_2\}$	20	<1	2.6	–0.4	7.0
6	$[HPBu_3]BPh_4$ (8.6)	21	$RuHCl\{tmeP_2(NH)_2\}$	20	<1	0.019	1.7	6.8
7	[HP-*t*-Bu_2Ph]BPh_4 (8.0)	17	$RuHCl\{tmeP_2(NH)_2\}$	20	<1	0.08	1.1	6.9
8	$[HPBu_2Ph]BF_4$ (5.8)	21	$RuHCl\{tmeP_2(NH)_2\}$	20	<1	5.9	–0.8	6.6
9	$[HPCy_2Ph]BF_4$ (6.7)	22	$RuHCl\{tmeP_2(NH)_2\}$	20	<1	1.0	0	6.7

Scheme 1.

$$PBu_2Ph + [HPCy_2Ph]BPh_4 \underset{K = 0.12}{\rightleftharpoons} [HPBu_2Ph]BPh_4 + PCy_2Ph \quad (10\ min)$$

$$\downarrow -C_6H_6$$

$$Bu_2PhP \cdot BPh_3 \quad (1\ h)$$

The pK^{DM} values of Fig. 3 show the expected substituent effect of an increase in acidity of the phosphonium with a change from alkyl to phenyl group. Replacing Cy or Bu by Ph causes a decrease of approx 3 units of pK^{DM}. The pK^{DM} values for phosphonium salts with pK^{DM} value greater than 6.5 are in reasonable agreement with the corresponding pK_α^{THF} values (Fig. 4). However, the reported values (1) of pK_α^{THF} for $[HPBu_2Ph]BPh_4$ (6.7), $[HPMePh_2]BPh_4$ (6.3), and $[HPEtPh_2]BPh_4$ (5.3) are questionable, and these equilibria may in fact involve the protonation of tetraphenylborate.

Synthesis and structure of ruthenium dihydrogen complexes

The complex $RuHCl(dach)(PPh_3)_2$ is a precursor to an active ketone hydrogen catalyst, $RuH_2(dach)(PPh_3)_2$ (11). The protonation of $RuHCl(dach)(PPh_3)_2$ by $HBF_4{\cdot}Et_2O$ in THF gives the new dihydrogen complex $[Ru(\eta^2\text{-}H_2)Cl(dach)(PPh_3)_2]BF_4$ (Scheme 2). The molecular structure of this dihydrogen complex is shown in Fig. 5.

The overall geometry is octahedral. The η^2-dihydrogen ligand is situated trans to the chloride. The Ru—H distances to the dihydrogen ligand are both 1.63(5) Å. The H—H distance is 0.78 (6) Å. Hydrogen-bonding interactions of $F_3BF\cdots HN$ (F···H 2.0 and 2.2 Å) and $C_4H_8O\cdots HN$ (O···H 2.1 Å) are observed in the X-ray crystal structure.[3] The trans geometry of the complex appears to be maintained in solution on the basis of the observation of a singlet in the $^{31}P\{^1H\}$ NMR spectrum. The dihydrogen resonance for this complex is a singlet at –10.8 ppm, and it is broad because of the rapid dipolar relaxation of the nuclei in the η^2-dihydrogen ligand.

The dihydrogen complex $[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$ in C_6D_6 reacts with D_2 gas to give isotopomers, including $[Ru(HD)Cl(PPh_3)_2(dach)]BF_4$. This probably proceeds via H–D exchange with the dach N—H bonds. The observation of $^1J_{HD}$ = 28.5 Hz in the Ru(HD) isotopomer provides more evidence of the side-on-bonded H_2-coordination. This corresponds to an H—H distance of 0.94 Å on the basis of eq. [10] (39). The X-ray derived value of 0.78(6) Å is probably underestimated because of the problem of locating hydrogen atoms by this method and the rotation of the H_2 ligand.

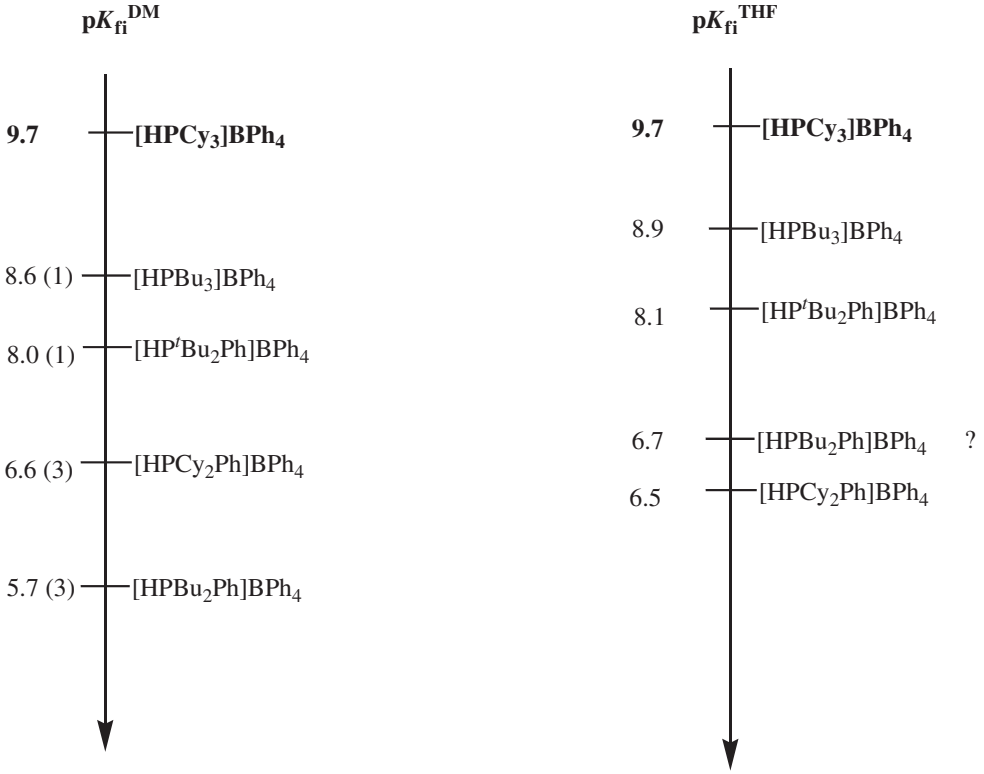
$$[10] \quad d(H\text{—}H) = -0.0167\ (^1J_{HD}) + 1.42$$

Synthesis and structure of $[Ru(\eta^2\text{-}H_2)Cl\{tmeP_2(NH)_2\}]BF_4$

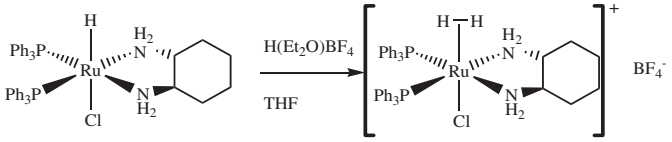
$[Ru(\eta^2\text{-}H_2)Cl\{tmeP_2(NH)_2\}]BF_4$ is observed in the reaction of $RuHCl\{tmeP_2(NH)_2\}$ with HBF_4 in CD_2Cl_2 by NMR

[3]Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4082. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 274511 and 274512 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 4. A comparison of the acidity ladders for $[HPR_3]BPh_4$ salts in CD_2Cl_2 and THF.



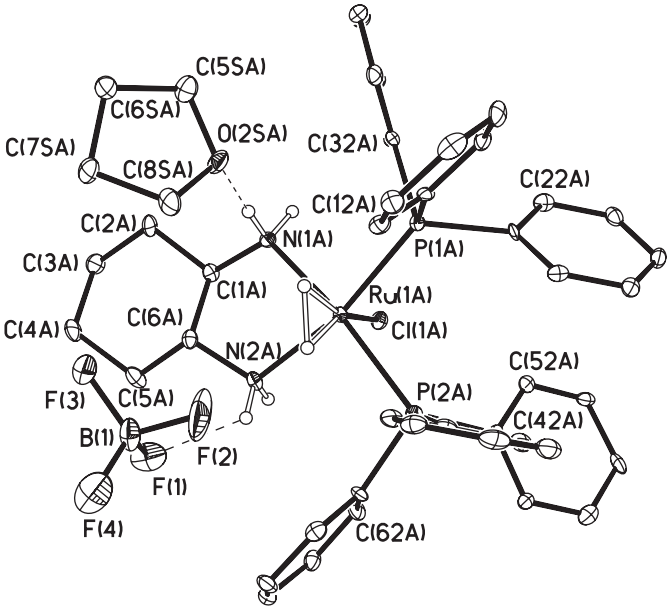
Scheme 2.



spectroscopy. There are two isomers, A and B, of the RuHCl complex in the ratio of 3:2 (40). Isomer A is believed to have two NH hydrogen atoms that are syn to the hydride. Isomer B has one NH hydrogen atom syn to the hydride and the other NH hydrogen atom syn to the chloride. Therefore, two isomers of the Ru dihydrogen complex are formed by protonation of isomers A and B (shown in Scheme 3).

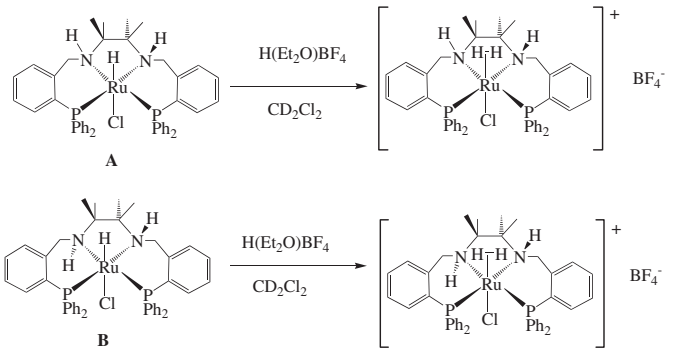
A crystal of one isomer of the dihydrogen complexes was obtained from the reaction. The molecular structure of the dihydrogen complex (Fig. 6) is derived from isomer B with one NH hydrogen atom syn to the chloride. The distances Ru—H1 and Ru—H2 are 1.79(2) and 1.79(3) Å, respectively. These long Ru—H distances might signal a weak Ru—H_2 interaction, and this interaction might explain why the dihydrogen ligand is usually lost during isolation. There is an intramolecular electrostatic NH···Cl interaction observed in the structure with an H···Cl distance of 2.5 Å. $[Ru(\eta^2\text{-}H_2)Cl(dach)(PPh_3)_2]BF_4$ has an NH···Cl distance of 2.8 Å. The other NH hydrogen atom is syn to the dihydrogen ligand and hydrogen bonds with the BF_4 anion (NH···F distance of 2.0 Å). The ^{31}P NMR spectrum suggests that two isomers are formed in the ratio of 1:2 (A:B). Isomer A exhibits a singlet at 36.4 ppm. Isomer B exhibits two doublets at 40.6 and 30.5 ppm. The dihydrogen resonance for this complex is similar to that of $[Ru(\eta^2\text{-}H_2)Cl(dach)(PPh_3)_2]^+$ and

Fig. 5. Structure of $[Ru(\eta^2\text{-}H_2)Cl(dach)(PPh_3)_2]BF_4 \cdot THF$ as determined by single crystal X-ray diffraction.



exhibits a broad singlet at –10.9 ppm. $[Ru(HD)Cl\{tmeP_2(NH)_2\}]BF_4$ was prepared by the reaction of $RuHCl\{tmeP_2(NH)_2\}$ and HBF_4–D_2O in CD_2Cl_2. The observation of $^1J_{HD}$ = 28 Hz in the Ru(HD) isotopomer suggests an H—H distance of 0.95 Å on the basis of eq. [10]. When

Scheme 3.



$[Ru(\eta^2\text{-}H_2)Cl\{tmeP_2(NH)_2\}]BF_4$ reacts with D_2, there is no hydride signal in the ^1H NMR spectrum, consistent with the formation of $[Ru(\eta^2\text{-}D_2)Cl\{tmeP_2(NH)_2\}]BF_4$. Apparently there is no D–H exchange between D_2 and the NH groups.

The pK^{DM} measurements for the dihydrogen complexes

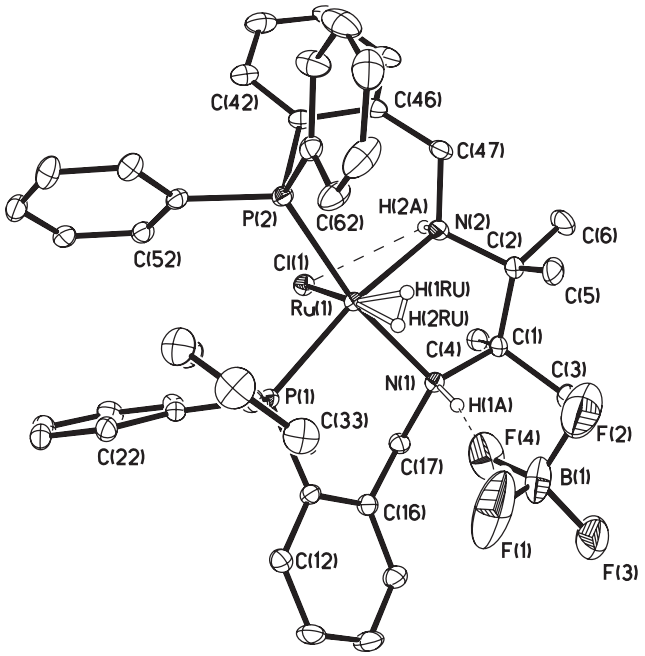
The equilibria between the hydrido complexes $RuHCl(dach)(PPh_3)_2$ or $RuHCl\{tmeP_2(NH)_2\}$ and the phosphonium salts were established within 1 h at 20 °C (Figs. 7 and 8). The equilibria involving the BPh_4^- salts $[HPBu_3]BPh_4$, $[HP\text{-}t\text{-}Bu_2Ph]BPh_4$, and $[HPCy_2Ph]BPh_4$ produced an average pK^{DM} value of 8.6 ± 0.2 for the dihydrogen complex $[Ru(\eta^2\text{-}H_2)Cl(dach)(PPh_3)_2]BPh_4$. A corresponding reaction with $[HPBu_3]BF_4$ gave a pK^{DM} value of 8.5 ± 0.2 for the corresponding BF_4^- salt of the dihydrogen complex. The variation in the values obtained could be a result of ion-pairing effects and NH···FBF_3^- hydrogen bonding in the case of equilibria involving the BF_4^- anion.

Three equilibria were established between $RuHCl\{tmeP_2(NH)_2\}$ and phosphonium tetraphenylborate salts $[HPBu_3]BPh_4$, $[HP\text{-}t\text{-}Bu_2Ph]BPh_4$, and $[HPCy_2Ph]BPh_4$, to give a consistent pK^{DM} value of 6.9 for $[Ru(\eta^2\text{-}H_2)Cl\{tmeP_2(NH)_2\}]BPh_4$. Two equilibria between $RuHCl\{tmeP_2(NH)_2\}$ and $[HPBu_2Ph]BF_4$ and $[HPCy_2Ph]BF_4$ suggest an average pK^{DM} value of 6.7 for $[Ru(\eta^2\text{-}H_2)Cl\{tmeP_2(NH)_2\}]BF_4$.

Comparison of the acidity of ruthenium dihydrogen complexes

The pK^{DM} values of some related dihydrogen complexes are listed in Table 5. The complexes $[Ru(H_2)Cl(dppe)_2]PF_6$ and $[Ru(H_2)Cl(dppp)_2]PF_6$ are dihydrogen complexes with four phosphorus (phosphine) donors and have pK^{DM} values of approximately 4.7 and 3.3, respectively (entries 1 and 2, Table 5) (41, 42).[4] $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BPh_4$ and $[Ru(H_2)Cl(dach)(PPh_3)_2]BPh_4$ are a different class of dihydrogen complex with two phosphorus (phosphine) and two nitrogen (amine) ligands, and they have pK^{DM} 6.9 and 8.6, respectively (entries 4 and 5, Table 5). The replacement of phosphine ligands with more electron-donating amine ligands decreases the acidity of the complexes. However, $[Ru(H_2)Cl(PPh_3)(PMP)]BF_4$ with three phosphorus (phosphine) ligands and one nitrogen (pyridyl) ligand (6) does not follow this trend (entry 3, Table 5), suggesting that the pyridine donor is more like a phosphine than an amine on ruthenium.

Fig. 6. Structure of $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]$ BF_4 as determined by single crystal X-ray diffraction.



Conclusions

A continuous acidity ladder of five phosphonium tetraphenylborate salts in CD_2Cl_2 at room temperature has now been established by use of ^{31}P NMR spectroscopy. The pK^{DM} values are generally consistent with values previously measured in THF. NOE and PGSE measurements show that ion pairs and higher aggregates are present in solution, complicating the interpretation of the results. When the pK^{DM} is lower than 6.6, the BPh_4^- salts tend to decompose. The acidities of the new dihydrogen complexes, $[Ru(H_2)Cl(PPh_3)_2(dach)]BPh_4$ and $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BPh_4$, are determined to be p$K^{DM}$ 8.6 and 6.9, respectively, through the use of several consistent equilibria with phosphonium salts. The pK^{DM} values for the BF_4^- salts are similar. The crystal structures of $[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$ and $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BF_4$ are determined. We will describe elsewhere the use of tetrafluoroborate salts to extend the ladder to lower pK^{DM} values, below the limit set by the decomposition of BPh_4^- salts.

Experimental

General methods

All preparations and manipulations were carried out under hydrogen, nitrogen, or argon atmospheres with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. Tetrahydrofuran (THF), diethyl ether (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

[4] T. Li, A.J. Lough, and R.H. Morris. In preparation.

Fig. 7. The equilibria established between $RuHCl(dach)(PPh_3)_2$ and phosphonium salts in 1 h at 20 °C.

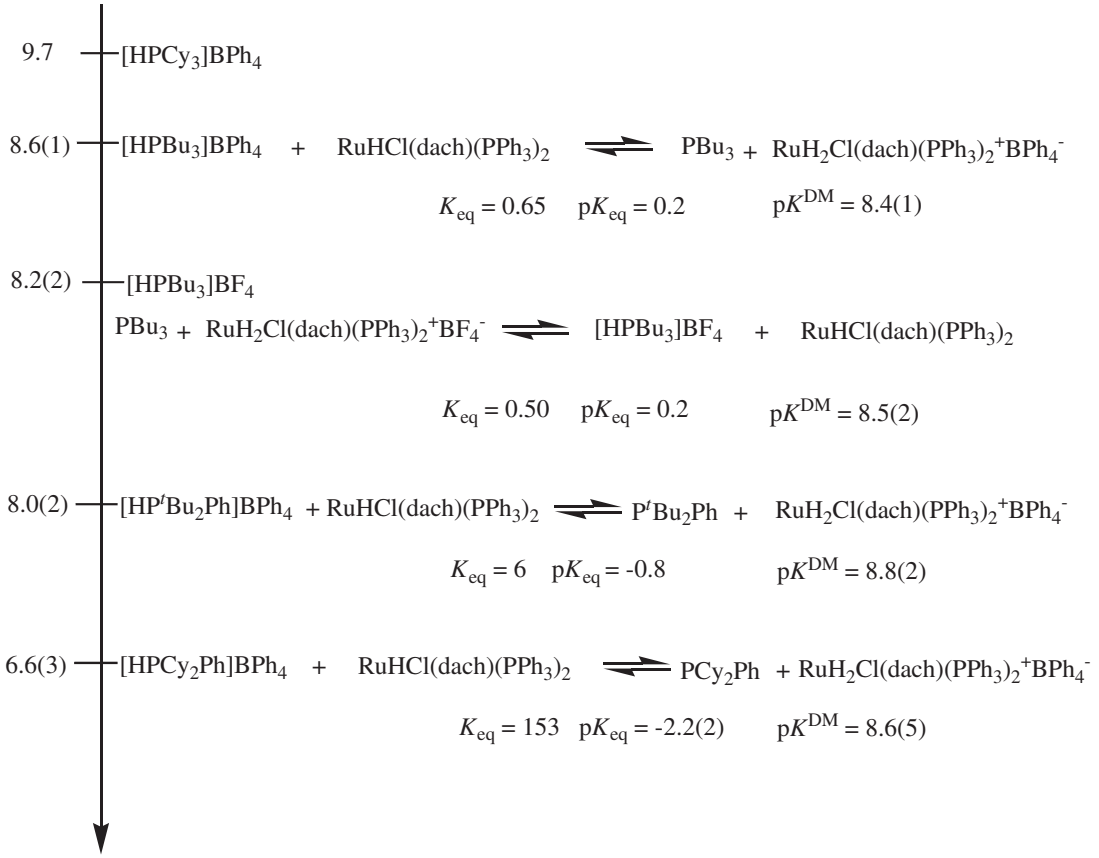


Table 5. Comparison of the acidity of ruthenium dihydrogen complexes.

Entry	Type	Complex	pK^{DM}	Ref.
1	$[RuP_4(H_2)Cl]X$	$[Ru(H_2)Cl(dppe)_2]PF_6$[a]	4.7	42
2		$[Ru(H_2)Cl(dppp)_2]PF_6$[b]	3.3	41
3	$[RuP_3N(H_2)Cl]X$	$[Ru(H_2)Cl(PPh_3)(PMP)]BF_4$[c]	4.0[d]	6
4	$[RuP_2N_2(H_2)Cl]X$	$[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BPh_4$	6.9	This work
5		$[Ru(H_2)Cl(dach)(PPh_3)_2]BPh_4^-$	8.6	This work

[a]dppe = 1,2-bis(diphenylphosphine)ethane.
[b]dppp = 1,3-bis(diphenylphosphine)propane.
[c]PMP = 2,6-$(Ph_2PCH_2)_2C_5H_3N$.
[d]The literature value of 5.1 has been adjusted (42).

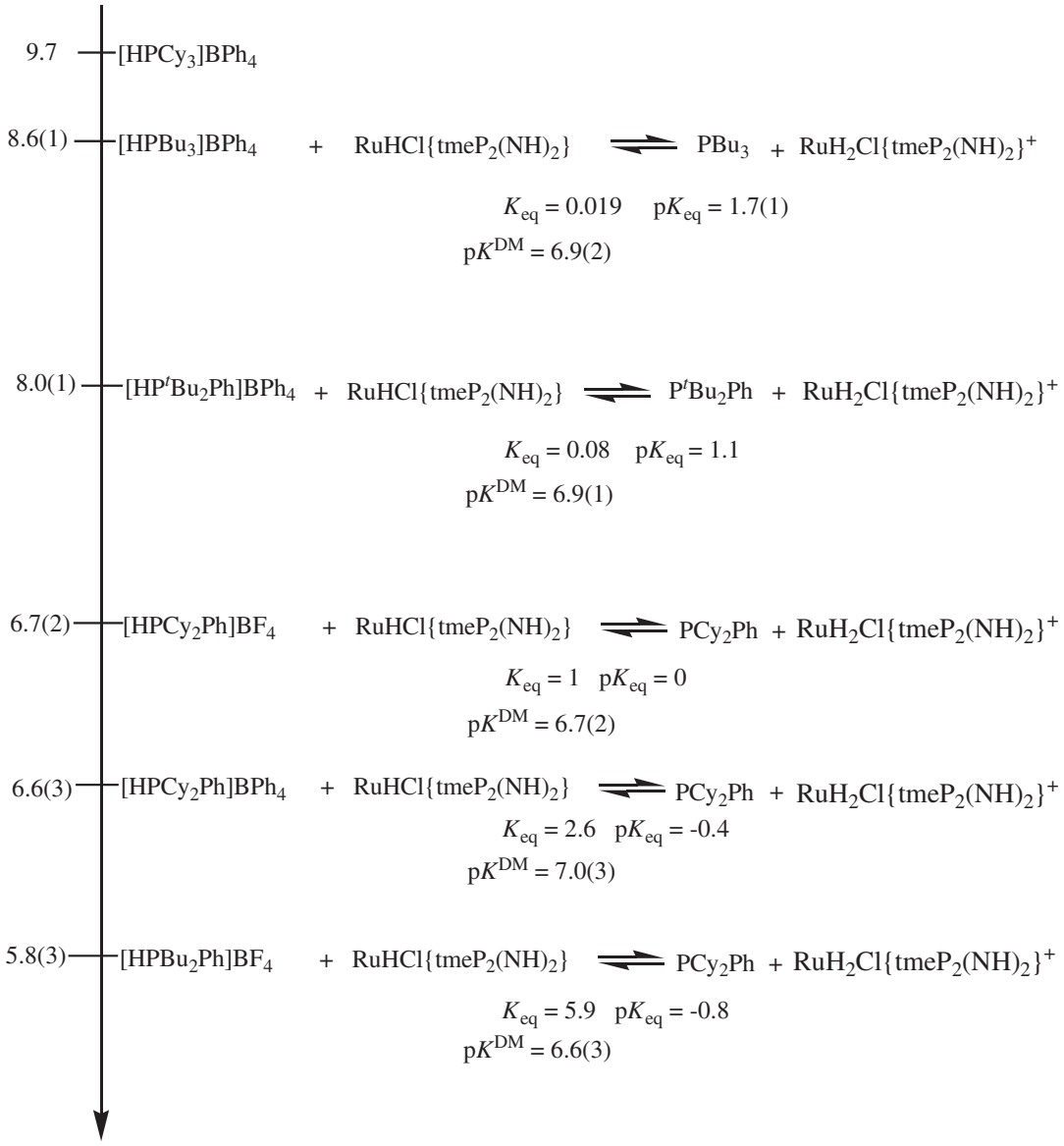
spectra were recorded on a Varian Unity-500 (500 MHz for ^1H), a Varian Unity-400 (400 MHz for ^1H), or on a Varian Gemini 300 MHz spectrometer (300 MHz for ^1H and 121.5 MHz for ^{31}P). All ^{31}P chemical shifts were measured relative to 10% $P(OMe)_3$ in C_6D_6. This reference solution was placed in a 2 mm capillary tube inside the 5 mm sample NMR tube. ^1H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. The phosphine compounds were received from commercial suppliers (Aldrich Chemical Co., Stem Co.) and used without further purification. $NaBPh_4$ was supplied by Aldrich Chemical Co. $RuCl_3$ hydrate was obtained from Johnson Matthey. The compounds $RuHCl(PPh_3)_2$-(dach) (10) and *trans*-$RuHCl\{tmeP_2(NH)_2\}$ (40) were prepared according to literature procedures. Protonated salts that have not already been reported in the literature have been found to have the correct elemental analyses by the Analyst Laboratory of the University of Toronto.

$[HPR_3]BPh_4$

All phosphonium salts $[HPR_3]BPh_4$ (PR_3 = PCy_3, P-*n*-Bu_3, P-*t*-Bu_2Ph, PCy_2Ph) were isolated by use of the reported preparation (4), with typical yields of 80%–90%. The attempted preparations of $[HPR_3]BPh_4$ (PR_3 = PBu_2Ph, PMe_2Ph, $PEtPh_2$, PPh_3) were unsuccessful as these decompose. $PR_3 \cdot BPh_3$ (PR_3 = PBu_2Ph, PMe_2Ph, $PEtPh_2$, PPh_3) compounds were obtained instead. The ^{31}P NMR chemical shifts are reported in Table 6. NMR data for $[HPCy_2Ph]BPh_4$ (CD_2Cl_2, 299 K, *J* values in Hz, refer to Fig. 2 for the labelling) follow.

^1H NMR δ: 7.83 (t, $^3J_{HH}$ = 7.7, pH_c), 7.64 (td, $^3J_{HH}$ = 7.8, $^4J_{HP}$ = 3.3, mH_c), 7.39 (m, oH_a), 7.36 (dd, $^3J_{PH}$ = 19.4,

Fig. 8. The equilibria established between $RuHCl\{tmeP_2(NH)_2\}$ and the phosphonium salt in 1 h at 20 °C.



$^3J_{HH}$ = 7.8, *o*H_c), 7.09 (t, $^3J_{HH}$ = 7.5, *m*H_a), 6.95 (tt, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.3 *p*H_a), 5.08 (dt, $^1J_{PH}$ = 471.0, $^3J_{HH}$ = 6.3, P-H), 2.30 (m, H_1), 1.81, 1.66, 1.35, 1.15 (m, cyclohexyl resonances).

$[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$

$RuHCl(PPh_3)_2$(dach) (203 mg, 0.26 mmol) was dissolved in THF (2 mL). HBF_4 (54 wt% in Et_2O, 90 mg, 0.30 mmol) was added to the solution under Ar and stirred for 0.5 h. Et_2O (6 mL) was added to give a yellow-green precipitate. The solid was filtered and washed with diethyl ether (2 × 3 mL). The solid product was obtained by filtration and dried under vacuum. Crystals of $[Ru(H_2)Cl(PPh_3)_2(dach)]BF_4$ were prepared by slow diffusion of diethyl ether into a saturated solution of the complex in THF. Yield: 190 mg, 87%. ^{1}H NMR (C_6D_6) δ: 7.4–7.0 (m, 30H, Ph), 3.3 (br, 2H, NH_2), 2.8–2.6 (m, 8H, CH_2), 2.2 (br, 2H, NH_2), 1.2 (m, 2H, C*H*), –10.75 (br, 2H, RuH_2). ^{31}P NMR δ: 46.1 (s). Anal.

Table 6. ^{31}P NMR chemical shifts of phosphines and phosphonium salts in CD_2Cl_2.

Bases	δ ^{31}P	Acids	δ ^{31}P
PCy_3	9.8	$[HPCy_3]BPh_4$	29.5
		$[HPCy_3]BF_4$	29.5
PBu_3	–31.1	$[HPBu_3]BPh_4$	10.7
P-*t*-Bu_2Ph	39.4	[HP-*t*-Bu_2Ph]BPh_4	52.3
PCy_2Ph	2.9	$[HPCy_2Ph]BPh_4$	27.1
		$[HPCy_2Ph]BF_4$	27.0
PBu_2Ph	–24.6	$[HPBu_2Ph]BF_4$	14.9
		$PBu_2Ph{\cdot}BPh_3$	–4.4
$PMePh_2$	–27.1	$[HPMePh_2]BF_4$	2.0
		$PMePh_2{\cdot}BPh_3$	–9.5
$PEtPh_2$	–11.8	$[HPEtPh_2]BF_4$	12.5
		$PEtPh_2{\cdot}BPh_3$	–4.0

calcd. for $C_{42}H_{46}N_2P_2BClF_4Ru$: C 58.08, H 5.46, N 3.33; found: C 58.40, H 5.33, N 3.24.

The reaction of RuHCl{tmeP_2(NH)$_2$} with HBF_4

A mixture of two isomers (see Discussion) of RuHCl{tmeP_2(NH)$_2$} (10 mg, 0.012 mmol) was dissolved in CD_2Cl_2 (1 mL) in an NMR tube under Ar. HBF_4 (54 wt% in Et_2O, 10 mg, 0.06 mmol) was added to the solution. ^{1}H NMR δ: 7.6–6.8 (m, 28H, Ph), 4.8 (m, C*H*$_2$), 4.6 (m, C*H*$_2$), 4.4 (m, N*H*), 3.9 (m, N*H*), 1.8–1.2 (m, 12H, C*H*$_3$), –10.9 (brs, 2H, Ru*H*$_2$); T_1 = 19 ms at 400 MHz NMR spectrometer at 293 K. ^{31}P NMR δ: 41.0 (d, $^2J_{PP}$ = 25 Hz, 40%, isomer B), 30.5 (d, 37%, isomer B), 37.0 (s, 23%, isomer A). Crystals of [Ru(H$_2$)Cl{tmeP_2(NH)$_2$}]BF_4 were prepared by slow diffusion of diethyl ether into the NMR solution of the complex in CD_2Cl_2 under Ar.

The reaction of [Ru(H$_2$)Cl(PPh$_3$)$_2$(dach)]BF_4 with D_2

[Ru(H$_2$)Cl(PPh$_3$)$_2$(dach)]BF_4 (10 mg, 0.011 mmol) was dissolved in C_6D_6 (1 mL) in a 5 mm NMR tube under Ar. The solution was frozen in liquid N_2 and degassed – refilled with D_2 gas for three cycles. The NMR tube was sealed with a flame under D_2 and warmed up to room temperature. An ^{1}H NMR spectrum was collected immediately and after 15 h. A 1:1:1 triplet of 1:2:1 triplets at –10.74 ppm ($^1J_{HD}$ = 28.5 Hz, $^2J_{HP}$ = 8.7 Hz) was observed over time due to Ru(HD).

The reaction of [Ru(H$_2$)Cl{tmeP_2(NH)$_2$}]BF_4 with D_2

The procedure used for the dach complex was followed. No H–D coupling was observed. The hydride signal at –10.9 ppm disappeared after 15 h.

The reaction of RuHCl{tmeP_2(NH)$_2$} with HBF_4(Et_2O)–D_2

RuHCl{tmeP_2(NH)$_2$} (isomer A, 10 mg, 0.012 mmol) was dissolved in CD_2Cl_2 (1 mL) in an NMR tube. DBF_4 (1 drop, prepared by mixing HBF_4, 54 wt% in Et_2O, 0.40 g, 0.025 mol and degassed D_2O, 1.1 g, in a Schlenk flask) was added to the solution. A 1:1:1 triplet of triplets was observed over time due to Ru(HD). ^{1}H NMR δ: –10.9 (tt, RuHD, $^1J_{HD}$ = 28.5 Hz, $^2J_{HP}$ = 8.4 Hz). ^{31}P NMR δ: 40.6 (d, $^2J_{PP}$ = 25 Hz, isomer B), 30.5 (d, isomer B).

Determination of equilibrium constants in CD_2Cl_2

Solutions of samples were mixed under N_2 as described in Tables 3 and 4. In general, equilibrium constants were determined by ^{1}H and ^{31}P{^{1}H} NMR. Usually, signals for all of the species in equilibrium could be located and integrated in the ^{31}P{^{1}H} NMR and, in the case of hydride complexes, in the ^{1}H NMR spectra as well. The chemical shifts for the pure phosphines and phosphonium salts (Table 6) were determined and referenced to the P(OMe)$_3$ standard at 141.5 ppm. In some cases, when the chemical shifts of two species are very similar, mass-balance arguments can be used to estimate the equilibrium concentration of the species from their starting concentrations. Thermodynamic data for the equilibria in CD_2Cl_2 are shown in Tables 3 and 4.

NOE measurements

The ^{1}H NOESY NMR experiment was acquired by the standard three-pulse sequence (43). Each transient (direct dimension) was acquired using 2K points; the number of transients (indirect dimension) was 1K, and the number of scans was set at 16. A relaxation delay of 2 s and a mixing time of 0.5 s were used. The average interionic distances were obtained taking into account that the volumes of the NOE cross peaks are proportional to ($n_I n_S/n_I+n_S$), where n_I and n_S are the number of equivalent I and S nuclei, respectively (30).

PGSE measurements

^{1}H PGSE NMR measurements were performed using the standard stimulated echo pulse sequence (32) on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil, at 299 K without spinning. The shape of the gradients was rectangular, their duration was 5 ms, and their strength (G) was varied during the experiments. All the spectra were acquired using 32K points, a spectral width of 5000 Hz, and processed with a line broadening of 1.0 Hz. The semilogarithmic plots of $\ln(I/I_0)$ vs. G^2 (where I and I_0 are the intensities of the observed spin echo in the presence or in the absence of the field gradient, respectively) (34, 35) were fitted using a standard linear regression algorithm; the R factor was always higher than 0.99. r_H, V_H, and N values were derived from experimentally determined D_t data as described in ref. 31.

X-ray diffraction structure determination of [Ru(H$_2$)Cl(PPh$_3$)$_2$(dach)]BF_4 and [Ru(H$_2$)Cl{tmeP_2(NH)$_2$}]BF_4

Crystals suitable for X-ray diffraction were obtained by vapor diffusion. Data were collected on a Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package (44). For the second structure (the tmeP_2(NH)$_2$ complex), absorption corrections were carried out using SORTAV (45). The structures were solved and refined using SHELXTL V6.1 (46) for full-matrix least-squares refinements that are based on F^2. The H atoms of the dihydrogen were refined independently with isotropic displacement parameters, but in the first structure these parameters were tied to the U_{eq} values of the Ru atoms. All other H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom. Crystallographic data for the compounds are given in Tables 7 and 8, and selected bond distances and angles in Tables 9 and 10.

Acknowledgment

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Table 7. Crystallographic data for $[Ru(\eta^2H_2)Cl(dach)(PPh_3)_2]BF_4 \cdot THF$.

a (Å)	12.0771(5)	Formula	$C_{46}H_{54}N_2P_2BClF_4ORu$
b (Å)	12.2479(4)	Formula weight	936.18
c (Å)	16.5468(5)	Space group	$P\bar{1}$
α (°)	70.917(2)	T (K)	100(1)
β (°)	89.536(2)	λ (Å)	0.710 73
γ (°)	69.588(2)	ρ_{calc} (mg/m^3)	1.445
V (Å^3)	2152.28(13)	R_1 (all data)	0.071
Z	2	wR_2	0.123

Table 8. Crystallographic data for $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BF_4$.

a (Å)	14.7990(3)	Formula	$C_{44}H_{48}BClF_4N_2P_2Ru$
b (Å)	12.6530(3)	Formula weight	890.11
c (Å)	21.7310(4)	Space group	$P2_1/c$
α (°)	90	T (K)	150(1)
β (°)	92.670(1)	λ (Å)	0.710 73
γ (°)	90	ρ_{calc} (mg/m^3)	1.455
V (Å^3)	4064.8(2)	R_1 (all data)	0.074
Z	4	wR_2	0.109

Table 9. Selected bond distances and angles for $[Ru(\eta^2\text{-}H_2)Cl(dach)(PPh_3)_2]BF_4$.

Distances (Å)			
Ru(1)—H(1Ru)	1.63(5)	Ru(1)—H(2Ru)	1.63(5)
H(1Ru)—H(2Ru)	0.78(6)	Ru(1)—P(1A)	2.3242(8)
Ru(1)—P(2A)	2.3537(8)	Ru(1)—N(1A)	2.17(1)
Ru(1)—N(2A)	2.19(1)	Ru(1)—Cl(1)	2.4143(8)
Angles (°)			
H(1Ru)-Ru(1)-H(2Ru)	27(2)	H(1Ru)-Ru(1)-N(1)	81(2)
H(2Ru)-Ru(1)-N(1)	103(2)	H(1Ru)-Ru(1)-N(2)	90(2)
H(2Ru)-Ru(1)-N(2)	70(2)	N(1)-Ru(1)-N(2)	78.1(3)
P(1)-Ru(1)-P(2)	98.14(3)	N(1)-Ru(1)-P(1)	90.4(2)
N(2)-Ru(1)-P(1)	167.1(2)	N(1)-Ru(1)-P(2)	169.7(4)
N(2)-Ru(1)-P(2)	93.9(2)	H(1Ru)-Ru(1)-Cl(1)	163(2)
H(2Ru)-Ru(1)-Cl(1)	164(2)	P(1)-Ru(1)-Cl(1)	96.94(3)
P(2)-Ru(1)-Cl(1)	91.43(3)	N(1)-Ru(1)-Cl(1)	81.9(5)
N(2)-Ru(1)-Cl(1)	87.2(4)		

Table 10. Selected bond distances and angles for $[Ru(H_2)Cl\{tmeP_2(NH)_2\}]BF_4$.

Distances (Å)			
Ru(1)—H(1Ru)	1.79(2)	Ru(1)—P(2)	2.3205(8)
Ru(1)—H(2Ru)	1.79(3)	Ru(1)—P(1)	2.3412(7)
Ru(1)—N(2)	2.150(2)	Ru(1)—Cl(1)	2.4210(8)
Ru(1)—N(1)	2.175(2)		
Angles (°)			
H(1Ru)-Ru(1)-H(2Ru)	19(2)	H(2Ru)-Ru(1)-P(1)	81(2)
H(1Ru)-Ru(1)-N(2)	85(2)	N(2)-Ru(1)-P(1)	170.38(7)
H(2Ru)-Ru(1)-N(2)	100(2)	N(1)-Ru(1)-P(1)	92.48(6)
H(1Ru)-Ru(1)-N(1)	90(2)	P(2)-Ru(1)-P(1)	97.81(3)
H(2Ru)-Ru(1)-N(1)	82(2)	H(1Ru)-Ru(1)-Cl(1)	165(2)
N(2)-Ru(1)-N(1)	78.05(9)	H(2Ru)-Ru(1)-Cl(1)	174(2)
H(1Ru)-Ru(1)-P(2)	86(2)	N(2)-Ru(1)-Cl(1)	81.39(7)
H(2Ru)-Ru(1)-P(2)	97(2)	N(1)-Ru(1)-Cl(1)	91.86(7)
N(2)-Ru(1)-P(2)	91.73(7)	P(2)-Ru(1)-Cl(1)	89.52(3)
N(1)-Ru(1)-P(2)	169.35(6)	P(1)-Ru(1)-Cl(1)	97.41(3)
H(1Ru)-Ru(1)-P(1)	97(2)		

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