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Promoting effect of ionic liquids on ligand substitution reactions

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Abstract

Ionic liquid solvents *N*-hexylpyridinium bistrifylimide ([C_6pyr][Tf_2N]] and 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) promoted the displacement of anionic ligands by pyridine derivatives in *trans*-$(Ph_3P)_2Rh(CO)NO_3$ to a much greater extent than did dichloromethane. Thus, addition of a slight excess of 2-fluoropyridine to *trans*-$(Ph_3P)_2Rh(CO)NO_3$ in [C_4mim][PF_6] gave a 29:71 product mixture of *trans*-$(Ph_3P)_2Rh(CO)NO_3$:[*trans*-$(Ph_3P)_2Rh(CO)$(2-fluoropyridine)][NO_3], while the ratio was 91:9 in dichloromethane.

Keywords: Ionic liquids; Ligand substitution; Rhodium; Solvent properties

1. Introduction

In recent years, the development of air and moisture stable ionic liquids (ILs) has resulted in a significant resurgence of interest in their application to a wide range of fields [1,2]. Ionic liquids have a number of interesting properties, such as low volatility, low flammability, large liquid range, variable miscibility with water and organic solvents, high polarity, and potentially low coordinating ability, that make them attractive solvents for a range of applications. Based on these properties, ILs have been suggested as alternatives to organic solvents in a wide variety of homogeneous metal-catalyzed processes [3–7].

There have been a number of attempts to quantify the solvent properties of ILs using solvatochromic dyes [8–18], linear free energy relationships (LFER) [19,20], partitioning studies [21], and other approaches [22,23]. Although a range of solvent properties has been reported, there is a general consensus that ILs have polarities comparable to polar aprotic solvents, such as DMF and acetonitrile, or protic solvents, such as short-chain alcohols. Despite this apparent high polarity, 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) has a coordinating ability comparable to that of dichloromethane [10,11]. This combination of properties is unique among potential solvent media. A polar, weakly coordinating solvent should promote catalytic processes with key steps involving charge-separated intermediates or transition states. Indirect evidence for this sort of acceleration has been noted in some catalytic processes [10,24–27].

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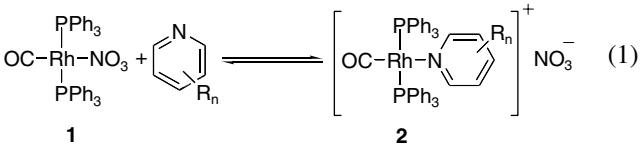
Although ILs have been applied to a wide range of catalytic reactions, there have been relatively few careful studies regarding the effects of these solvents on reaction rate, mechanism, or selectivity [28–32]. Studies of complex multi-step catalytic processes can provide some information about overall solvent effects, but a more thorough understanding of these properties requires looking at solvent effects on individual reaction steps. Welton [33–35] has studied S_N2 substitution reactions in ILs and found that halide nucleophilicity is dependent on the hydrogen-bonding properties of the anion and cation. Examples of similarly detailed studies of fundamental organometallic reactions in ILs are limited to a recent report of the bimolecular rate constant for solvent displacement in $(\eta^6\text{-}C_6H_6)Cr(CO)_2$(solvent) [36].

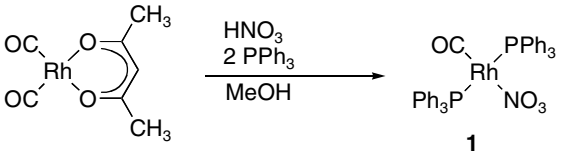
Ligand substitution is a key step in every homogeneous catalytic process. We and others have hypothesized that ILs would promote the displacement of anionic ligands by neutral molecules leading to charge-separated species [10,24–27]. This step plays key roles in important catalytic cycles such as hydrogenation, Ziegler–Natta-type polymerization, hydrocarboxylation, and Heck coupling. Herein we report our initial results on the effect of IL solvents on the displacement of anionic ligands at a d^8 Rh(I) center by pyridine derivatives [37], which serves as a model for this type of catalytic step (Eq. (1)). We find that ILs strongly promote the formation of the charge-separated ligand substitution products, and that the extent of this effect depends on the nature of the ionic liquid.



1 2 (1)

2. Results and discussion

$Rh(CO)(PPh_3)_2NO_3$ (**1**) was synthesized using previously reported procedures (Eq. (2)) [38]. Complex **1** was sparingly soluble in the ILs tested. Concentrations of **1** no larger than 0.01 M in 1-butyl-3-methylimidizolium hexafluorophosphate ($[C_4mim][PF_6]$) could be achieved after stirring for one day at room temperature. Moderate heating aided complex dissolution, but would often lead to the formation of an uncharacterized side-product possessing an IR-active stretch at 2432 cm^{-1}. The 0.01 M solutions of **1** provided carbonyl stretch intensities of up to 0.7 absorption units using a 0.5-mm FTIR solution cell with CaF_2 windows, which makes them suitable for Beer's Law applications. Complex **1** dissolved more readily in 1-hexylpyridinium bistrifylimide ($[C_6pyr][NTf_2]$) to give 0.01 M solutions after several hours of stirring at room temperature. Attempts to dissolve **1** in other IL solvents, such as 1-butyl-3-methylimidizolium bistrifylimide, 1-butyl-3-methylimidizolium triflate, and 1-hexylpyridinium *N*-(trifluoromethylsulfonyl)nonafluorobutylsulfonimide (MBI) were unsuccessful.



(2)

1

IL solutions of **1** were analyzed to determine the carbonyl stretching frequencies and molar absorption coefficient (ϵ) values (Table 1). In all cases, the observed bands were visibly more broadened in the ILs than those seen in CH_2Cl_2 solutions, suggesting a weak interaction of the IL solvent with the carbonyl ligands of the complexes. The broadening resulted in a 400–500-M^{-1} cm^{-1} drop in ϵ for both IL solvents and starting complexes.

To determine the spectral properties and ϵ values of the ligand substitution products, a small set of $[Rh(CO)(PPh_3)_2L]^+X^-$ complexes (**2**) was prepared. Addition of $AgSbF_6$ to a toluene or CH_2Cl_2 solution of $Rh(CO)(PPh_3)_2Cl$ in the presence of an excess amount of the corresponding pyridine gave good yields of the cationic pyridine complexes (Eq. (3)) [37]. Molar absorptivity values (ϵ) for the cationic complexes (**2**) were the same within experimental error ($\pm 0.1 \times 10^3$ M^{-1} cm^{-1}) independent of the identity of the pyridine ligand. These values also matched those measured for **1** within experimental error in both dichloromethane and the ionic liquids. Direct comparisons of absorbance values should thus be suitable to determine relative concentrations of **1** and **2** in ligand substitution reactions (see Table 2).

Table 1
FTIR spectroscopic data of $Rh(CO)(PPh_3)_2NO_3$

X	Solvent	λ_{max} (cm^{-1})	ϵ ($\times 10^{-3}$ M^{-1} cm^{-1})
NO_3	CH_2Cl_2	1983	1.5 ± 0.1
NO_3	$[C_4mim][PF_6]$	1987	1.0 ± 0.1
NO_3	$[C_6pyr][NTf_2]$	1986	1.1 ± 0.1

Table 2
FTIR spectroscopic data of $[Rh(CO)(PPh_3)_2L]^+$

L	Solvent	λ_{max} (cm^{-1})	ϵ ($\times 10^{-3}$ M^{-1} cm^{-1})
3-Picoline	CH_2Cl_2	2009	1.6
3-Picoline	$[C_6pyr][NTf_2]$	2001	1.1
2-Fluoropyridine	CH_2Cl_2	2011	1.6
2-Fluoropyridine	$[C_4mim][PF_6]$	2004	1.2
2-Fluoropyridine	$[C_6pyr][NTf_2]$	2005	1.2
2,6-Difluoropyridine[a]	CH_2Cl_2	2012	1.4
2,6-Difluoropyridine[a]	$[C_6pyr][NTf_2]$	2008	1.1

[a] Slightly impure.

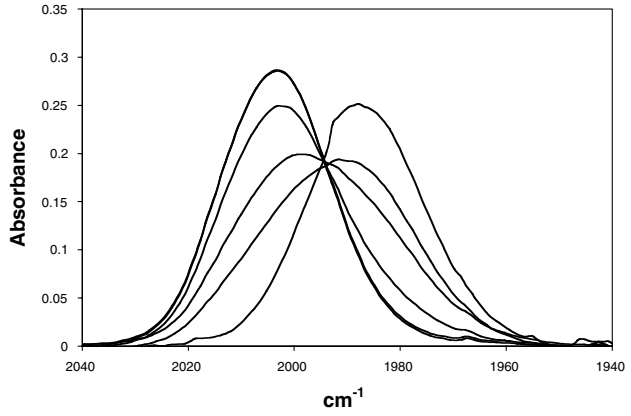
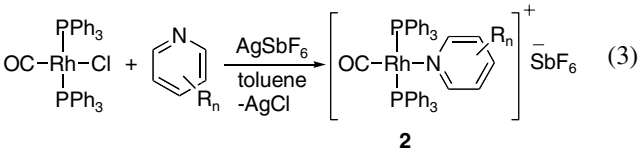


Fig. 1. Overlaid FTIR spectra of CO stretching region of 2-picoline/**1** with 2-picoline:Rh ratios of 0, 0.27, 0.47, 0.79, 0.94, 1.27, [Rh] = 0.01 M.



(3)

To determine if ligand substitution occurred cleanly in IL solvents, a 0.01-M solution of **1** in [C_6pyr][Tf_2N] was treated with varying amounts of 2-picoline (0–0.013 M). The reaction mixtures were stirred overnight to ensure full equilibration [39] and then were analyzed by FTIR spectroscopy. In each case, a only a single maximum was observed, although reactions with intermediate amounts of 2-picoline (0.3–0.8 2-picoline:Rh) gave broad unsymmetrical peaks. No change was seen on increasing the 2-picoline:Rh ratio from 0.94 to 1.27, so the reaction goes to completion with as little as one equivalent of 2-picoline. An overlay of the carbonyl stretching region of the FTIR spectra shows an isosbestic point at 1995 cm^{-1} consistent with clean conversion of **1**–**2** (Fig. 1).

A more extensive set of ligand substitution reactions were performed by adding pyridine derivatives with a range of coordinating abilities to 0.01 M solutions of **1** in CH_2Cl_2, [C_4mim][PF_6], and [C_6pyr][Tf_2N] (Eq. (1)). Reaction mixtures were stirred at room temperature overnight. FTIR spectra were then obtained to determine the relative concentrations of **1** and **2** (Table 3). In cases where both the reactant and product were present, overlap of the two carbonyl stretches was observed. This complication was more significant for reactions in ionic liquids due to broadening of bands and consequent reduction in the peak separation between the two signals. Statistical deconvolution techniques based upon a Gaussian line-shape routine were applied to derive the actual absorption maxima and to determine absorbance values for **1** and **2** [40]. The data was corroborated by

Table 3
Degree of ligand substitution in the reaction of $Rh(CO)(PPh_3)_2NO_3$ with L

Entry	L (pK_a)[a]	Solvent	λ_{max} (**1**)	λ_{max} (**2**)	% of **2**[b]
1	4-Dimethylaminopyridine (9.7)[c]	CH_2Cl_2		2002	>95
2	2,4-Lutidine (6.99)[d]	CH_2Cl_2	1985	2009	81
3	2,6-Lutidine (6.60)[d]	CH_2Cl_2	1984	2006	80
4	2-Picoline (5.97)[d]	CH_2Cl_2	1985	2009	80
5	3-Picoline (5.66)[d]	CH_2Cl_2	1985	2010	73
6	Quinoline (4.90)[d]	CH_2Cl_2	1985	2010	63
7	2-Bromopyridine (0.90)[d]	CH_2Cl_2	1983	2010	20
8	2-Fluoropyridine (−0.44)[d]	CH_2Cl_2	1984	2012	9
9	2,6-Difluoropyridine (−5.32)[e]	CH_2Cl_2	1984		<5
10	4-Dimethylaminopyridine (9.7)[c]	[C_4mim][PF_6]		1998	>95
11	2,4,6-Collidine(7.43)[d]	[C_4mim][PF_6]		1999	>95
12	2-Picoline (5.97)[d]	[C_4mim][PF_6]		2002	>95
13	3-Picoline(5.66)[d]	[C_4mim][PF_6]		2003	>95
14	Pyridine (5.23)[d]	[C_4mim][PF_6]		2003	>95
15	2-Bromopyridine (0.90)[d]	[C_4mim][PF_6]		2002	>95
16	2-Fluoropyridine (−0.44)[d]	[C_4mim][PF_6]	1986	2004	71
17	2,6-Difluoropyridine (−5.32)[e]	[C_4mim][PF_6]	1986	2004	12
18	4-Dimethylaminopyridine (9.7)[c]	[C_6pyr][NTf_2]		1997	>95
19	2,6-Lutidine (6.60)[d]	[C_6pyr][NTf_2]		2001	>95
20	2-Picoline (5.97)[d]	[C_6pyr][NTf_2]		2003	>95
21	Quinoline (4.90)[d]	[C_6pyr][NTf_2]		2004	>95
22	2-Fluoropyridine (−0.44)[d]	[C_6pyr][NTf_2]	1988	2006	67
23	2,6-Difluoropyridine (−5.32)[e]	[C_6pyr][NTf_2]	1986		<5

[a] pK_a of the pyridinium conjugate acid.
[b] Percent conversion to **2** as determined by IR. Values >95% or <5% indicate that the minor component was not observed.
[c] pK_a value taken from [41a].
[d] pK_a value taken from [41b].
[e] pK_a value taken from [41c].

subtracting a height adjusted standard spectrum of **1** from the reaction solution spectrum. Comparisons of the **2** peak heights of the extrapolated spectra to those from the statistically generated data typically showed deviations of $\leqslant 2\%$ unless the relative concentration of either component fell to about 5%, the limit for detection by deconvolution due to the broad nature of these bands. In those cases, the overall equilibrium levels show variations of 5% or less. Examples of deconvoluted spectra for the reaction of 2-fluoropyridine and **1** in $[C_4mim][PF_6]$ and $[C_6pyr][Tf_2N]$ are shown in Figs. 2 and 3, respectively.

Alkylated pyridine derivatives gave 70–80% conversion of **1** to complex **2** in dichloromethane (Table 3, entries 2–5). Only a strongly basic pyridine, 4-dimethylaminopyridine, resulted in **2** being the only species detectable in dichloromethane solution. The amount of **2** generated in dichloromethane was significantly decreased with less basic halogenated pyridine derivatives, however. Thus, 2-bromopyridine addition led to only 20% conversion to **2** (entry 7), while 2-fluoropyridine gave only a small amount of **2** in dichloromethane (entry 8). No ligand substitution product (**2**) was observed when **1** was treated with 2,6-difluoropyridine in dichloromethane.

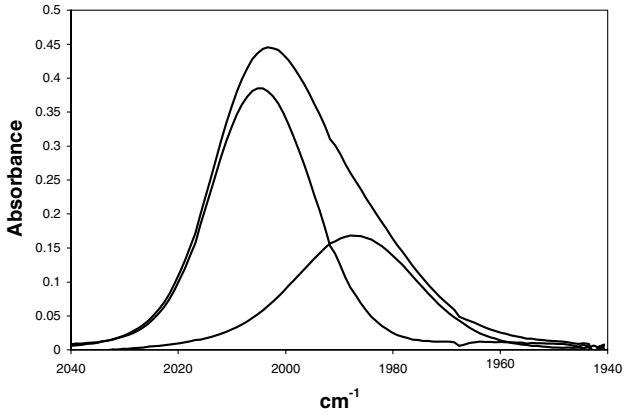


Fig. 2. Deconvoluted FTIR spectra for 2-fluoropyridine/**1** in $[C_4mim][PF_6]$. λ_{max} (**1**) = 1987 cm^{-1}, λ_{max} (**2**) = 2005 cm^{-1}, **1**:**2** = 29:71.

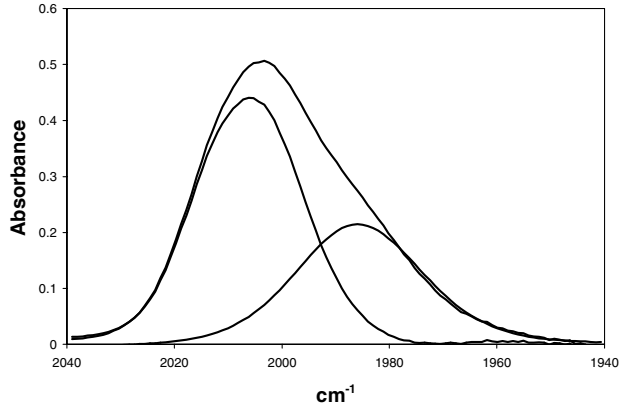


Fig. 3. Deconvoluted FTIR spectra for 2-fluoropyridine/**1** in $[C_6pyr][Tf_2N]$. **1**:**2** = 29:71. λ_{max} (**1**) = 1986 cm^{-1}, λ_{max} (**2**) = 2006 cm^{-1}, **1**:**2** = 33:67.

In contrast, interactions of alkylated pyridine derivatives and **1** in ionic liquid solvents led to complete conversion to **2** (<5% **1**, entries 11–14). Even weakly basic 2-bromopyridine gave >95% conversion when reacted with **1** in $[C_4mim][PF_6]$ (entry 15). Weakly coordinating fluorinated pyridines did not give complete nitrate displacement in the ILs, however. Addition of 2-fluoropyridine addition led to 71% and 67% conversion to **2** when reacted with **1** in $[C_4mim][PF_6]$ and $[C_6pyr][NTf_2]$, respectively (entries 16 and 22), significantly higher levels of substitution than occurred with 2-fluoropyridine in dichloromethane (Fig. 4). 2,6-Difluoropyridine, however, gave little or no ligand substitution product in the ionic liquid solvents (entries 17 and 23). For both fluorinated pyridine derivatives, $[C_4mim][PF_6]$ gave higher conversions to **2** than did $[C_6pyr][NTf_2]$.

The promoting effect of ILs on the ligand substitution reaction can be seen more clearly by comparing the basicity of the pyridine ligands, based on the pK_a of the conjugate pyridinium acid [41], versus the mole fraction of **2** in the ligand substitution reactions (Fig. 5). For dichloromethane, a linear dependence of the equilibrium mole fraction of **2** on the basicity of the pyridine ligand was found. Since most pyridines tested in the ILs gave complete conversion, there were not enough data points to fully evaluate the linearity in IL solvents. The *y*-intercept for the dichloromethane data was -1.19, while intercepts of -5.32 and -6.02 were found for $[C_6pyr][NTf_2]$ and $[C_4mim][PF_6]$, respectively. Thus, the basicity of the pyridine ligand required to give a particular degree of ligand substitution was significantly lower for the IL solvents than for dichloromethane. The lower *y*-intercept of $[C_4mim][PF_6]$ compared with $[C_6pyr][NTf_2]$ suggests that it is better able to promote the ligand dissociation reaction; however, the reason for this

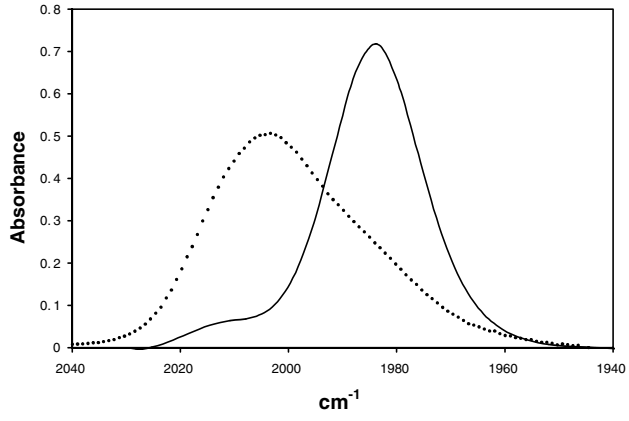


Fig. 4. FTIR spectra of the carbonyl stretching region of reaction mixtures of **1** with 2-fluoropyridine in CH_2Cl_2 (—) and $[C_6pyr][NTf_2]$ (···).

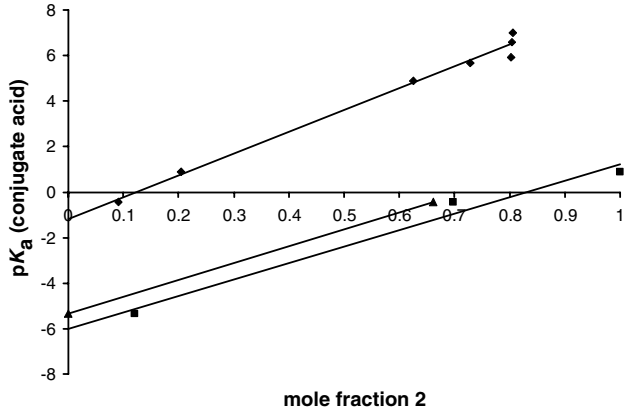


Fig. 5. Conjugate acid pK_a of substituted pyridines vs. mole fraction **2** for substitution reactions in CH_2Cl_2 (◆, $y = 9.59x - 1.19$, $R^2 = 0.9895$), $[C_6pyr][NTf_2]$ (▲, $y = 7.34x - 5.32$), and $[C_4mim][PF_6]$ (■, $y = 7.26x - 6.02$).

difference is not clear. The imidazolium cation in $[C_4mim][PF_6]$ would be expected to be a better H-bond donor than the pyridinium cation, so it may better stabilize the nitrate anion, thus promoting nitrate displacement. The poor solubility of **1** in ILs precluded a more systematic comparison of cation and anion effects on the equilibrium for this complex.

3. Conclusions

This work provides the first measurement of the promoting effect of ionic liquid solvents on the displacement of anionic ligands by neutral ligands. Equilibrium ratios have been measured for the displacement of nitrate from **1** by pyridine derivatives in dichloromethane and ILs. The IL solvents stabilize the charge-separated Rh-pyridine complex to a much greater extent than dichloromethane, resulting in higher equilibrium concentrations of complex **2**. As a result, even weakly basic pyridine ligands can displace the nitrate ligand. These results are relevant to catalytic processes in which displacement of an anionic ligand by a neutral reactant (i.e., an olefin or CO) converts a catalytically inactive species into an active species. Therefore, ionic liquids should be expected to promote catalytic processes in which anionic ligands compete for coordination to the active site. Unlike polar organic solvents, however, weakly coordinating ILs should not compete for coordination to the catalytically active species.

4. Experimental

Standard Schlenk and drybox techniques were used for all reactions unless noted. All solvents used were purified and dried before use following procedures found in Perrin and Armarego [42]. ^1H, ^{13}C and ^{31}P NMR spectra were obtained on either a Brüker AX360 or a Brüker AX500 spectrometer. ^1H and ^{13}C NMR spectra are reported as positive parts per million (ppm) downfield from a tetramethylsilane (TMS) standard. ^{31}P NMR spectra are referenced from an external H_3PO_4 standard. All FTIR spectra were obtained on a BIO-RAD FTS-40 spectrometer.

All ionic liquids were prepared by standard procedures [8,43]. Ionic liquids were dried in vacuo overnight at 70 °C prior to use. Water contents determined by Karl-Fischer titration were typically <200 ppm. Halide contents were measured using halide-selective electrodes and were determined to be <100 ppm. $Rh(CO)(PPh_3)_2NO_3$ (**1**) was synthesized using previously reported procedures [38]. $Rh(CO)_2(acac)$ and $Rh(CO)(PPh_3)_2Cl$ were acquired from Strem Chemicals. All other ligands, reagents and solvents were purchased from Aldrich Chemicals, Acros Organics, or Fisher Scientific.

4.1. *[Rh(CO)(PPh$_3$)$_2$L][SbF$_6$] (2)*

$Rh(CO)(PPh_3)_2Cl$ (91.3 mg, 0.13 mmol) was mixed with $AgSbF_6$ (62.7 mg, 0.18 mmol) in a Schlenk flask. Dry, deoxygenated toluene (15 mL) was added via syringe, yielding a yellow solution and a yellow paste. After stirring for 1.5 h, the supernatant was transferred by syringe to another flask. The paste was washed with another 8 mL of toluene. The supernatant samples were combined and treated with the appropriate substituted pyridine (0.6 mmol) to precipitate the desired product. Decantation of the supernatant was followed by vacuum drying at 40–45 °C for several hours to yield a yellow powder. $[Rh(CO)(PPh_3)_2(3\text{-picoline})][SbF_6]$ (**2a**): ^1H NMR (360 MHz, CD_2Cl_2): δ 7.52 (m, 18H, Ph), 7.41 (m, 12H, Ph), 7.13 (br, 2 H, pyr-H), 6.62 (m, 1H, pyr-H), 1.68 (s, 3H, pyr-Me). $[Rh(CO)(PPh_3)_2(2\text{-fluoropyridine})][SbF_6]$ (**2b**): ^1H NMR (360 MHz, CD_3OD): δ 7.82 (br, 2H, pyr), 7.59 (m, 12H, Ph), 7.43 (m, 18H, Ph), 6.82 (br, 1H, pyr), 6.62 (br, 1H, pyr). $[Rh(CO)(PPh_3)_2(2,6\text{-difluoropyridine})][SbF_6]$ (**2c**): ^1H NMR (360 MHz, CD_2Cl_2): δ 7.58 ppm (m, 18H, Ph), 7.42 (m, 12H, Ph), 6.33 (d, $J = 8.63$ Hz, pyr).

4.2. General procedure for equilibration studies

A stock solution was prepared by dissolving $Rh(CO)(PPh_3)_2NO_3$ (53.2 μmol) in 5 mL of solvent (dichloromethane, $[C_4mim][PF_6]$, or $[C_6pyr][NTf_2]$) in a volumetric flask in the drybox to give a 0.01-M solution. A standard amount (0.60 mL, 6.4 μmol Rh) of this solution was added to a septum sealed vial under nitrogen. The pyridine (8–10 μmol) was added to the Rh solution and stirred overnight. A portion of the solution was then transferred under nitrogen to an IR solution cell (0.5 mm) with CaF_2 windows and analyzed by IR spectroscopy. In cases where overlapping peaks were observed,

the spectra were transferred to an Excel spreadsheet and deconvoluted [40].

Acknowledgements

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References

[1] J.M. Davis Jr., P.A. Fox, Chem. Commun. (2003) 1209–1212.
[2] J.S. Wilkes, Green Chem. 4 (2002) 73–80.
[3] T. Welton, Chem. Rev. 99 (1999) 2071–2083.
[4] C.M. Gordon, Appl. Catal. A 222 (2001) 101–117.
[5] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667–3692.
[6] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem. 182–183 (2002) 419–437.
[7] C.E. Song, Chem. Commun. (2004) 1033–1043.
[8] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168–1178.
[9] A.J. Carmichael, K.R. Seddon, J. Phys. Org. Chem. 13 (2000) 591–595.
[10] P. Wasserscheid, C.M. Gordon, C. Hilgers, M.J. Muldoon, I.R. Dunkin, Chem. Commun. (2001) 1186–1187.
[11] M.J. Muldoon, C.M. Gordon, I.R. Dunkin, J. Chem. Soc., Perkin Trans. 2 (2001) 433–435.
[12] S.N.V.K. Aki, J.F. Brennecke, A. Samanta, Chem. Commun. (2001) 413–414.
[13] K.A. Fletcher, I.A. Storey, A.E. Hendricks, S. Pandey, S. Pandey, Green Chem. 3 (2001) 210–215.
[14] S.N. Baker, G.A. Baker, F.V. Bright, Green Chem. 4 (2002) 165–169.
[15] R. Karmakar, A. Samanta, J. Phys. Chem. A 106 (2002) 4447–4452.
[16] R. Karmakar, A. Samanta, J. Phys. Chem. A 106 (2002) 6670–6675.
[17] S.V. Dzyuba, R.A. Bartsch, Tetrahedron Lett. 43 (2002) 4657–4659.
[18] H. Chen, D.C. Kwait, Z.S. Gönen, B.T. Wesloski, D.J. Adballah, R.G. Weiss, Chem. Mater. 14 (2002) 4063–4072.
[19] J.L. Anderson, J. Ding, T. Welton, D.W. Armstrong, J. Am. Chem. Soc. 124 (2002) 14247–14254.
[20] S. Carda-Broch, A. Berthod, D.W. Armstrong, Anal. Bioanal. Chem. 375 (2003) 191–199.
[21] C.F. Poole, J. Chromatogr. A 1037 (2004) 49–82.
[22] D. Behar, C. Gonzalez, P. Neta, J. Phys. Chem. A 105 (2001) 7607–7614.
[23] M.J. Earle, B.S. Engel, K.R. Seddon, Aust. J. Chem. 57 (2004) 149–150.
[24] Y. Chauvin, S. Einloft, H. Olivier, Ind. Eng. Chem. Res. 34 (1995) 1149–1155.
[25] M.A. Klingshirn, G.A. Broker, J.D. Holbrey, K.H. Shaughnessy, R.D. Rogers, Chem. Commun. (2002) 1394–1395.
[26] J. Zimmermann, P. Wasserscheid, I. Tkatchenko, S. Stutzmann, Chem. Commun. (2002) 760–761.
[27] K.H. Shaughnessy, M.A. Klingshirn, S.J. P'Pool, J.D. Holbrey, R.D. Rogers, in: R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, American Chemical Society, Washington, DC, 2003, pp. 300–313.
[28] S. Csihony, H. Mehdi, I.T. Horváth, Green Chem. 3 (2001) 307–309.
[29] C. Chiappe, V. Conte, D. Pieraccini, Eur. J. Org. Chem. (2002) 2831–2837.
[30] A. Durazo, M.M. Abu-Omar, Chem. Commun. (2002) 66–67.
[31] G.S. Owens, A. Durazo, M.M. Abu-Omar, Chem. Eur. J. 8 (2002) 3053–3059.
[32] G.S. Owens, M.M. Abu-Omar, J. Mol. Catal. A: Chem. 187 (2002) 215–225.
[33] N.L. Lancaster, T. Welton, G.B. Young Soc., J. Chem. Perkin Trans. 2 (2001) 2267–2270.
[34] N.L. Lancaster, P.A. Salter, T. Welton, G.B. Young, J. Org. Chem. 67 (2002) 8855–8861.
[35] N.L. Lancaster, T. Welton, J. Org. Chem. 69 (2004) 5986–5992.
[36] K. Swiderski, A. McLean, C.M. Gordon, D.H. Vaughan, Chem. Commun. (2004) 590–591.
[37] D.M. Branan, N.W. Hoffman, E.A. McElroy, N. Prokopuk, A.B. Salazar, M.J. Robbins, W.E. Hill, T.R. Webb, Inorg. Chem. 30 (1991) 1200–1207.
[38] F. Araghizadeh, D.M. Branan, N.W. Hoffman, J.H. Jones, E.A. McElroy, N.C. Miller, D.L. Ramage, A.B. Salazar, S.H. Young, Inorg. Chem. 27 (1988) 3752–3755.
[39] Ligand substitution is generally rapid for square-planar Rh(I) complexes. J.D. Atwood, Inorganic and Organometallic Reaction Mechanisms, second ed., Wiley, New York, 1997.
[40] C. Cappas, N.W. Hoffman, J. Jones, S.H. Young, J. Chem. Ed. 68 (1991) 300–303.
[41] (a) pK_a data taken from F.A. Walker, J. Am. Chem. Soc. 95 (1973) 1150–1153;
(b) B.G. Tehan, E.J. Lloyd, M.G. Wong, W.R. Pitt, E. Gancia, D.T. Manallack, Quant. Struct.-Act. Relat. 21 (2002) 473–485;
(c) M. Berthelot, C. Laurence, M. Safar, F. Besseau, J. Chem. Soc., Perkin Trans. 2 (1998) 283–290.
[42] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, fourth ed., Butterworth-Heinemann, 1996.
[43] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156–164.