Enhanced Hydrogenation Activity and Recycling of Cationic Rhodium Diphosphine Complexes through the Use of Highly Fluorous and Weakly-Coordinating Tetraphenylborate Anions

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Abstract: The effect of the nature of the anion on the performance of ionic rhodium catalysts has received little attention. Herein it is shown that the use of highly fluorous tetraphenylborate anions can enhance catalyst activity in both conventional and fluorous media. For hydrogenation catalysts of the type [Rh(COD)(dppb)][X] {COD = 1,5-*cis*,*cis*-cyclooctadiene; dppb = 1,4-bis(diphenylphosphino)butane; X = BF_4^- (**1a**), $[BPh_4]^-$ (**1b**), $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ (**1c**), $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$ (**1d**), $[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]^-$ (**1e**), $[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$ (**1f**) and $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$ (**1 g**)} the activity towards the hydrogenation of 1-octene in acetone increased in the order **1c** < **1b** < **1e** < **1a** < **1d** ~ **1f** < **1g** with **1g** being twice as active as the commonly applied **1a**. Despite the fluorophilic character introduced by the substituted tetraarylborate anions, the presence of some perfluoroalkyl-substituents in the cation was still required for achieving high partition coefficients. Therefore, $[Rh(COD)(Ar_2PCH_2CH_2PAr_2)][X]$ {Ar = $C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-4, X = $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$ (**3f**); Ar = $C_6H_4(SiMe(CH_2CH_2C_6F_{13})_2)$-4 and X = $[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$ (**2g**)} were prepared, which were active in the hydrogenation of 1-octene, **2g** even more so than **3f**. Both these highly fluorous catalysts could be recycled with 99% efficiency through fluorous biphasic separation, whereas the corresponding BF_4^- complex of **2g** (**2a**) did not show any affinity for the fluorous phase.

Keywords: fluorinated ligands; fluorous biphasic catalyst separation; fluorous borate anions; homogeneous catalysis; P ligands; phosphine; rhodium

Introduction

The use of the unique properties of perfluorinated solvents for catalyst separation and recycling has been demonstrated successfully.[1] ***F***luorous ***b***iphasic ***c***atalyst ***s***eparation (FBCS) techniques have been employed in the immobilisation of a diverse range of transition-metal complexes allowing their recovery with high efficiency, the extent of catalyst leaching often being on the ppm level.[2] The key to this success has been the introduction of perfluoroalkyl substituents in the ligands surrounding the metal centre.[1–3] Although this approach has proved highly effective, it requires the design of a new fluorous ligand for each new catalyst that is to be adapted for FBCS. As the introduction of perfluoro substituents is far from a trivial exercise,[4] the development of a large library of fluorous catalysts entails a huge synthetic effort. In ionic catalysts an additional site for the introduction of fluorous character exists, namely the anion. As these counterions are less specific for particular catalysts or catalytic processes,[5] the development of a highly fluorous anion could enable the use of a broad range of ionic catalysts in fluorous (biphasic) catalysis.

A further point to be considered is the often-observed reduction in catalyst activity under fluorous biphasic conditions in comparison with identical catalysts in conventional solvents.[2a, c,6] In the case of ionic catalysts, this is likely the result of the low polarity of the perfluorinated solvent. This hampers dissociation of the catalysts' ion pairs, since the separate charges cannot be stabilised through solvation. As the formation of separated ion pairs is often essential for the creation of a vacant coordination site,[5a, b] which allows the substrate to bind to the catalytically active centre, this reduces the availability of the catalyst for substrate binding and consequently its activity. The introduction of a highly fluorous anion could enhance ion-separation in these apolar solvents, thereby improving catalyst performance.

The use of perfluoroalkyl-substituted tetraarylborates as solubilising moieties for transition-metal catalysts in

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apolar solvents has been reported,[7] with $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$ (TFPB) being a well-known example.[5a, b,7a] This anion has successfully been applied in catalysis in supercritical carbon dioxide, where its highly lipophilic character was used to solubilise ionic catalysts.[8] The use of tetrakis(perfluoroaryl)borates in α-olefin polymerisation has also been well documented.[9] In this type of catalysis the borate anions are employed because of their weakly-coordinating nature, which helps in the creation of vacant coordination sites, and for their lipophilic character.[7d,8c] TFPB, however, is not fluorous enough to induce sufficient fluorous character for fluorous biphasic separation strategies (*vide infra*).

Keeping these considerations in mind, we have developed a range of highly fluorous tetraphenylborate anions.[10] Herein we report the use of these anions as counterions in ionic rhodium-catalysts in combination with both fluorous and non-fluorous diphosphine ligands. The partition behaviour of these complexes, and their application in the hydrogenation of olefins in both conventional and perfluorinated solvents, was studied. Furthermore, the recovery and recycling of these complexes using FBCS is described.

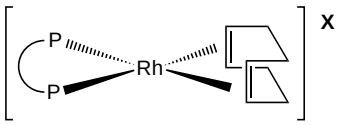
Results and Discussion

Anion Effects in 1-Octene Hydrogenation Catalysed by Rhodium Diphosphine Complexes

To investigate the influence of silyl- and perfluoroalkyl-substitution in tetraarylborate anions on catalyst performance, complexes of the type [Rh(COD)(dppb)][X] {COD = 1,5-*cis*,*cis*-cyclooctadiene, dppb = 1,4-bis(diphenylphosphino)butane, $X = [B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ (**1c**), TFPB (**1d**), $[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]^-$ (**1e**), $[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$ (**1f**) and $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$ (**1g**)} were prepared (Figure 1). Analysis of these complexes by $^{31}P\{^1H\}$ NMR spectroscopy revealed no significant variations between [Rh(COD)(dppb)][BPh_4] and **1c – g**, which indicates that the introduction of the substituents does not affect the structural and electronic properties of the cation. Using hydrogenation of 1-octene in acetone as a model reaction, the effects of the various substituents on the performance of the catalyst were assessed (Table 1).

The use of complexes **1a – 1g** as pre-catalysts in the hydrogenation of 1-octene revealed a major influence of anion variation on the activity. Compared to BF_4^-, a reduction in catalyst activity was observed when $[BPh_4]^-$ was used. The introduction of a trimethylsilyl substituent in the tetraphenylborate anion (**1c**) even resulted in an inactive catalyst, whereas the presence of $-SiMe_2CH_2CH_2C_6F_{13}$ substituents in **1e** yields a slightly enhanced activity compared with that of **1b**. The reason for the inactivity of **1c** was not investigated further. The introduction of electron-withdrawing substituents without spacer moieties in **1d**, **1f** and **1g** results in significantly enhanced hydrogenation activities, with the highly fluorous complex **1g** being over ten times more active than **1b** and twice as active as **1a**.[11–15]

It is well known that the activity of cationic rhodium diphosphine complexes in the hydrogenation of alkenes is highly dependent on the coordinating behaviour of their anions.[16] As the coordinating strength of the anion diminishes, dissociation of the complexes into solvent-separated ion pairs will become more pronounced, which increases the availability of the catalytic centre for substrate binding. The low activity observed for **1b**, relative to **1a**, is the result of the tendency of $[BPh_4]^-$ to act as a η^6-coordinating ligand through one or more of its phenyl groups.[5b,17] The low activity of **1b** corresponds with earlier reports,[18] where it was shown that a zwitterionic species is formed that exhibits low activity as a catalyst under similar, mild, reaction conditions. The introduction of a large $-SiMe_2CH_2CH_2C_6F_{13}$ substituent (Figure 2) on the tetraarylborate anion increases the activity of the corresponding catalyst (**1e**). This rate enhancement is most probably the result of the steric bulk of the perfluoro tail, because the electronic effect of this substituent is negligible as its Hammett parameter is identical to that for a proton (Table 1).[13] According to electrostatic models describing ion association, an



1a: X = BF_4^-
1b: X = $[BPh_4]^-$
1c: X = $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$
1d: X = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$
1e: X = $[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]^-$
1f: X = $[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$
1g: X = $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$

P
P = 1,4-bis(diphenylphosphino)butane

Figure 1. Rhodium diphosphine complexes used as catalysts in 1-octene hydrogenation in acetone.

Table 1. Hydrogenation of 1-octene with [Rh(COD)(dppb)]BF_4 (**1a**) and [Rh(COD)(dppb)][BAr_4] (**1b – 1g**) in acetone.[a]

Pre-catalyst	Ar	r (nm)[b]	σ[c]	TOF_{50}[d]
1c	$-C_6H_4(SiMe_3)$-4	0.8	– 0.02	–
1b	$-C_6H_5$	0.5	0.00	12
1e	$-C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-4	1.6	0.00[e]	20
1a	–	0.2	–	67
1f	$-C_6H_4(C_6F_{13})$-4	1.3	0.52[f]	75
1d	$-C_6H_3(CF_3)_2$-3,5	0.6	0.92[g]	80
1g	$-C_6H_3(C_6F_{13})_2$-3,5	1.3	0.94[f, g]	140

[a] Reaction conditions: 5 mL of acetone and 0.4 mL of *n*-decane, 2.12 mM [Rh], catalyst:1-octene = 1:200; $T = 42\,^{\circ}C$; $pH_2 = 1.1$ bar.
[b] Anion radius, Figure 2 and ref.[11]
[c] Hammett parameter, taken from ref.[12]
[d] Average turn over frequency (h^{-1}) at 50% yield of octane.
[e] Taken from ref.[13]
[f] The Hammett parameters for $-C_2F_5$ were used for $-C_6F_{13}$, ref.[2a] and ref.[14]
[g] The electronic effect of multiple substituents may be added up linearly, ref.[15] The value denoted here is $2 \times \sigma_m$.

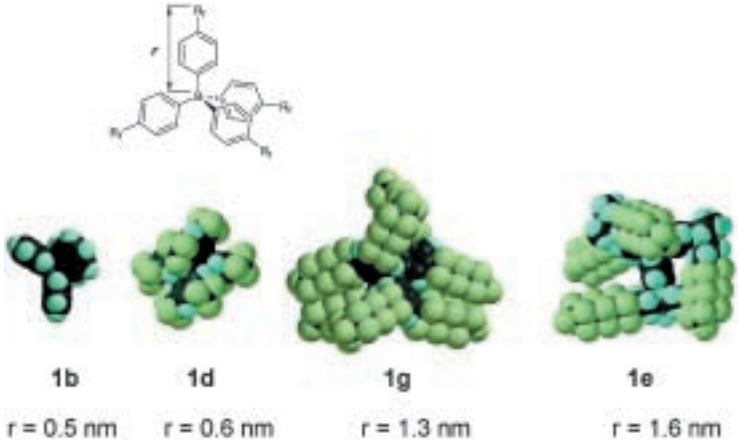
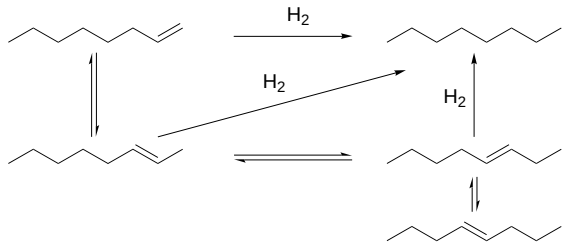


Figure 2. Influence of perfluoro substitution on the radius (r) of the anions.

increase in the distance between the two charges leads to a weakening of the electrostatic interaction.[19] Therefore, a reduced degree of association of the cation and anion will result due to the increased anion size upon introduction of perfluoroalkyl substituents.[20] Obviously, this leads to an enhanced hydrogenation activity of **1e** compared to non-substituted **1b**, because the cationic rhodium site has less and weaker interaction with the borate anion.[21]

The introduction of electron-withdrawing substituents which are directly connected to the phenyl groups of the tetraarylborate helps to reduce its η^6-coordinating ability through delocalisation of the negative charge.[17a] This will result in a reduction in the strength of the ion-pairing, which in turn could explain the enhanced activity of the corresponding catalysts. For example, the radius of the anion in **1d** is only slightly larger than that of $[BPh_4]^-$ in **1b**. Nevertheless, **1d** is a much more active hydrogenation catalyst. This indicates that the increase in hydrogenation rate observed for **1d** is most likely connected to the electron-withdrawing properties of the two CF_3-substituents in the anion. Furthermore, **1d** is four times as active as **1e**, which contains a much bulkier anion in which the perfluoro substituents cannot affect its electronic properties. This indicates that charge delocalisation is a more effective method for decreasing the ion-pairing properties of a tetraarylborate than increasing its steric bulk.

An indication for the efficiency of the combination of steric and electronic effects of perfluoroalkyl-substitution within a single anion is provided when **1f** and **1g** are compared with **1d**. In **1f** and **1g** the size of the anion is significantly larger than in the CF_3-substituted anion in **1d** (Figure 2). As a C_6F_{13}-substituent is electronically similar to a CF_3-substituent (Table 1),[12] the enhanced catalytic activity of **1g** in comparison with **1d** is the result of the bulky perfluorohexyl substituents. The 2- to 3-fold increase in the radius of the anion is accompanied by an increase in the catalytic activity by a factor two,[20] an effect similar in magnitude to that observed for **1b** and **1e**. In **1f** the number of fluorous tails is halved in comparison with **1d**, nevertheless, very similar activities are observed. Apparently, the increase in anion size by a factor of two compensates for the electronic consequen-



Scheme 1.

ces of the reduction in the number of perfluoroalkyl substituents. Thus, it can be concluded that both the electronic and steric aspects of introducing substituents in the tetraphenylborate anion have a significant impact on its ion-pairing behaviour. A combination of these two effects is the most efficient in enhancing cation-anion pair separation, and results in a more than 10-fold increase in catalytic activity (**1g**) in comparison with the corresponding $[BPh_4]^-$-equipped catalyst.

For all catalysts investigated a reaction sequence involving direct hydrogenation of 1-octene to *n*-octane, as well as isomerisation to internal octenes followed by hydrogenation to *n*-octane was observed (Scheme 1).[3,16] The initial products of this isomerisation were *cis*- and *trans*-2-octene, the *trans*-isomer being the major component (Figure 3). After full conversion of 1-octene to a mixture of 2-octenes and *n*-octane, the concentration of 2-octene in the reaction mixture declined steadily and the formation of 3- and 4-octenes was detected. Ultimately, all internal octenes were hydrogenated to octane when the reaction was allowed to proceed for a sufficiently long period of time. For **1a** – **1f** no effect of the anion on the product distribution was observed, all catalysts exhibiting reaction profiles as shown in Figure 3a. The highest concentration of 2-octenes, 50 – 60% with respect to the initial concentration of 1-octene, was observed at the moment that 1-octene was depleted. The combined concentration of 3- and 4-octenes peaked at a level of approximately 10% relative to the initial octene concentration. In contrast, for **1g** the formation of 3- and 4-octenes started before all 1-octene had been consumed and the maximum concentration of 2-octenes achieved was lower (45%) with respect to the initial 1-octene concentration. Otherwise, the product distribution was similar to that observed for **1a** – **1f**.

Synthesis and Fluorous Biphasic Separation of Rhodium Complexes Containing Fluorous Ligands and Fluorous Borate Anions

After it had been observed that the introduction of perfluoroalkyl substituents in the tetraphenylborate anion affords catalysts with similar or enhanced hydrogenation activity compared to the corresponding BF_4^--based catalyst, their use in FBCS was investigated. As all rhodium complexes, except **1g**, proved insoluble in perfluorinated solvents, they were initially tested in the lightly fluorous solvent α,α,α-trifluorotoluene (BTF).[22] Although all catalysts were found to be soluble in BTF, no hydrogenation activity was observed. The non-coordinating nature of this solvent is most likely responsible for this inactivity, as solvent coordination is required to allow solvent-separated ion-pair formation and to stabilise the cationic reaction intermediates.[16,23] Addition of 0.05 mL of THF to 2.12 mM catalyst solutions in 5.0 mL of BTF did not lead to hydrogenation activity.

Catalyst **1g** was then tested in perfluoro-α-butyltetrahydrofuran (FC-75), a fluorous solvent with an ether functionality that is potentially coordinating. The solubility of **1g** in this solvent was 0.21 mmol/L (at 25 °C), which is only one order of magnitude below the catalyst concentration we employed for the hydrogenations in acetone. Despite this reasonable solubility and the possibility for ion-separation through solvent coordination, again no activity was observed towards the hydrogenation of 1-octene.[24] It was then decided to prepare complexes containing a fluorous diphosphine ligand in addition to a fluorous tetraarylborate. This combination

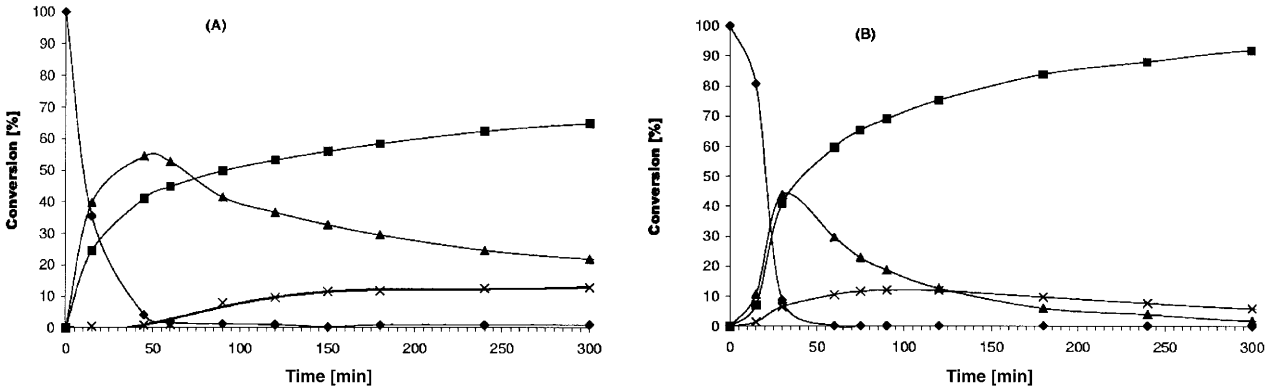


Figure 3. Conversion *vs.* time plots of the hydrogenation of 1-octene using **1a** (**A**) or **1g** (**B**). Legend: ◆ = 1-octene; ■ = *n*-octane; ▲ = 2-octenes; × = 3- and 4-octenes.

$$\left[\,[(LL)Rh]^{\cdots}[BAr_4]\,\right] \underset{-2\,S}{\overset{+2\,S}{\rightleftharpoons}} [(LL)RhS_2]^+ + [BAr_4]^- \underset{-\,Olefin}{\overset{+\,Olefin}{\rightleftharpoons}} [(LL)Rh(Olefin)S]^+[BAr_4]^- \quad (1)$$

close contact ion-pair *solvent separated ion-pair*

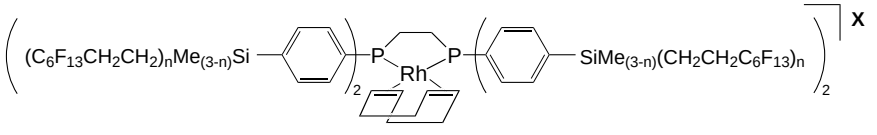
LL = diphosphine
S = solvent molecule
BAr_4 = tetraarylborate anion
Olefin = *e.g.* 1-octene

of a fluorous cation and a fluorous anion was expected to facilitate the formation of solvent-separated ion-pairs in perfluorinated solvents (cf. Equation 1). This approach did indeed prove successful (*vide infra*).

Using a procedure similar to that described for the synthesis of [Rh(dppb)(COD)][X], fluorous dppe complexes **2g** and **3f** were prepared (Figure 4) as well as the corresponding BF_4^- complexes **3a** and **4a**.[3] Analysis of **2g** and **3f** by ^{31}P NMR spectroscopy showed chemical shifts identical to those observed for **3a** and **4a**.[25] Attempts to prepare highly fluorous [Rh(COD)-$(Ar_2PCH_2CH_2Ar_2)$][X] {$Ar = C_6H_4\{SiMe(CH_2CH_2$-$C_6F_{13})_2\}$-4, $X = [B\{C_6H_3(C_6F_{13})_2$-3,5$\}_4]^-$} from [Rh(COD)-(acac)] and $Na[B\{C_6H_3(C_6F_{13})_2$-3,5$\}_4]$ were unsuccessful as mixtures of [Rh(LL)(COD)][X] and $[Rh(LL)_2][X]$ (LL = diphosphine) were obtained. Isolation of the former complex from these mixtures proved impossible. The use of $[Rh(COD)_2][X]$ (X = fluorous borate anion) as an alternative starting compound[3,26] was not feasible, as decomposition of the borate anions was observed during attempts to prepare bis-cyclooctadiene complexes from $[Rh(COD)Cl]_2$, cyclooctadiene and Na[X] or Ag[X].

To get a general idea of the fluorophilicity of the complexes **1f**, **1g**, **2 g** and **3f** also in comparison with literature data,[1–3] their partitioning in two typical fluorous biphasic solvent systems THF/perfluoromethylcyclohexane (PFMCH) and toluene/PFMCH was examined and compared with that of the tetrafluoroborate complexes **2a**, **3a** and **4a** (Table 2). The solubility of **1f** and **2a** in PFMCH was extremely low, which made the collection of relevant partitioning data impossible. The effect of a more fluorous anion became immediately clear, however, when the partitioning of **1g** and **2g** is compared with that of **1f** and **2a**, respectively. But although **1g** exhibits substantial affinity for the fluorous phase in a toluene/PFMCH biphasic system, its almost equal distribution over the two phases is still not sufficient for efficient catalyst recovery. For these ionic rhodium diphosphine complexes the introduction of a highly fluorous anion alone is clearly insufficient to obtain pronounced fluorophilicity. Its high aromatic character, especially in comparison with the BF_4^- complexes, may be held responsible for the moderate partitioning of **1g** as the presence of aryl groups is known to have an adverse effect on fluorous phase solubility.[23a,27] However, the introduction of a lightly fluorous diphosphine ligand (as in **2g**) is sufficient to increase the partition coefficient by more than an order of magnitude, despite the fact that the volume percentage of fluorine remains similar in comparison with **1g**. The contribution from the fluorous borate anion in **2g** becomes clear by comparison with BF_4^- complex **2a**, which shows no solubility in the biphasic solvent systems. Significant preference for the fluorous phase can be achieved when at least, on average, 1.5 perfluoroalkyl groups are present per aromatic moiety in the complex. To reach this level of fluorous character, the use of a perfluoroalkyl-functionalised diphosphine, containing a minimum of four fluorous tails, is required. Once a sufficient level of fluorous character has been reached, the distribution of the perfluoralkyl substituents throughout the cation and the anion as well as the nature of the anion are relatively unimportant, as evidenced by the comparable partition coefficients for **2g**, **3a** and **3f**. Nevertheless, the presence of perfluorinated substituents in both the cation and anion will enhance ion-pair separation in fluorous solvents and result in increased catalyst performance.

The partition coefficients of **2g**, **3a**, **3f** and **4a** are very similar, the only discrepancy being the high partitioning displayed by **4a** in the THF/PFMCH biphasic system. This high partition coefficient could be the result of the significantly higher fluorous volume of **4a**, as this volume fraction is the determining factor for the extent of partitioning in fluorous biphasic systems.[28] However, a



2g: n = 1, X = $[B\{C_6H_3(C_6F_{13})_2$-3,5$\}_4]^-$
3a: n = 2, X = BF_4^-
3f: n = 2, X = $[B\{C_6H_4(C_6F_{13})$-4$\}_4]^-$
4a: n = 3, X = BF_4^-

Figure 4. Rhodium-diphosphine-complexes with fluorous ligands and fluorous borate counterions.

Table 2. Partition coefficients of fluorous rhodium diphosphine complexes.

Compound	Anion	Vol % F	No. of tails	P[b]	
				PFMCH/THF	PFMCH/toluene
1f	$[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$	22	4	–[c]	–[c]
2a	BF_4^-	25	4	–[c]	–[c]
1g	$[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$	31	8	$<1\times10^{-2}$	0.7
2g	$[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$	32	12	2.1	34
3a	BF_4^-	32	8	8.1	61
3f	$[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$	33	12	6.4	65
4a	BF_4^-	37	12	34	66

[a] Volume percentage of fluorine in the molecule, calculated from semi-empirical (PM3$^{(tm)}$) optimised structures using the Spartan 5.1.1 (SGI) molecular modelling software package.
[b] Partition coefficients in a 1:1 (v/v) mixture of PFMCH and organic solvent at 0 °C ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$) determined by gravimetric methods and ICP/AAS for [Rh]. The average of these measurements is given here. The estimated error is ± 1 in the last digit.
[c] No partition coefficient could be determined due to poor solubility of the complex in PFMCH.

Table 3. Hydrogenation of 1-octene using pre-catalysts **2g** and **3f**.[a]

Catalyst precursor	Anion	Turn Over Frequency[b]		
		Acetone	*n*-Hexane/FC-75 (2:1)[c]	*n*-Hexane/FC-75 (1:1)[d]
3f	$[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$	4.2	1.2	0.7
2g	$[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$	19	5	2

[a] Reaction conditions: 5 mL of acetone or FC-75 and 0.4 mL of *n*-decane, 2.12 mM catalyst with 200 equiv. of 1-octene; $T = 42$ °C; $pH_2 = 1.1$ bar. In the 1:1 (v/v) and 1:2 (v/v) systems, 5 mL and 10 mL hexane are added, respectively.
[b] Average turn over frequency (h^{-1}) for the conversion of 1-octene to octane after 24 h.
[c] Monophasic under reaction conditions.
[d] Biphasic under reaction conditions.

similar effect on the partition coefficient of **4a** in the toluene/PFMCH biphasic system was not observed. In the toluene/PFMCH biphasic system, the partition coefficients for all complexes were found to be superior to those observed for the THF/PFMCH solvent system. The lower partition coefficients in the latter biphase system could originate from the fact that THF is capable of solvating the rhodium cation, whereas for toluene this is more difficult. The solvation makes dissolution of the complexes in THF more favourable, thus hampering partitioning into the fluorous phase. As choosing an apolar organic solvent eliminates the favourable solvent-solute interactions, preference for the fluorous phase increases.

Complexes **2g** and **3f** were tested for catalytic performance under fluorous conditions towards the hydrogenation of 1-octene. The THF/perfluoromethylcyclohexane (PFMCH) and toluene/PFMCH biphasic solvent systems that were used to determine the fluorophilicity of the complexes were found to be unsuitable. However, in mixtures of FC-75 and hexane, **2g** and **3f** were indeed found to be active catalysts (Table 3). Furthermore, their catalytic performance in acetone was determined for comparison with the other fluorous catalytic species (*vide supra*). Whereas **1g** displayed no activity in FC-75, probably due to the fluorophobic nature of the $[Rh(COD)(dppb)]^+$ cation, fluorous dppe derivatives in **2g** and **3f** displayed modest hydrogenation activity in 2:1 hexane/FC-75 mixtures (v/v). This indicates that the use of a fluorous ligand facilitates ion separation in a reaction medium with low polarity. When a 1:1 ratio of hexane and FC-75 is used, the reaction is performed under biphasic conditions. This leads to a decrease in activity, possibly due to mass transfer limitations between the two phases. When the relative activity of **2g** and **3f** is compared, the complex with 3,5-substituted borate anion (**2g**) was found to be more active, as was also observed for the rhodium complexes **1f** and **1g** with a non-fluorous diphosphine ligand. Interestingly, **2g** and **3f** were less active than their dppb-analogues **1f** and **1g** in acetone. This is in agreement with earlier reports that showed that increased catalyst activity can be expected when the chelate ring size increases from five to seven atoms.[16] This rate enhancement for the diphosphines with a longer alkane bridge can be explained by an increase in flexibility of the dichelating ligand, which lowers the relevant transition state energies.

Both **2g** and **3f** could be recycled efficiently through biphasic separation at 0 °C (Table 4). Complex **3f** could be recycled three times without loss of activity using both 1:1 (v/v) and 2:1 (v/v) mixtures of hexane and FC-75. Leaching of the catalyst into the organic phase was

Table 4. Efficiency of catalyst recycling for **2g** and **3f** in the hydrogenation of 1-octene in hexane/FC-75 biphasic systems.[a]

Catalyst precursor	Cycle	Turn Over Frequency[b]	
		n-Hexane/FC-75 (1:1)[c]	*n*-Hexane/FC-75 (1:2)[d]
3f	1	0.7	1.2
	2	0.7	1.4
	3	0.7	1.5
	5[e]	0.5	
Rh leaching[f]		0.5% (4 ppm)	0.5% (2 ppm)
2g	1	2.0	5.0
	2	2.0	6.0
Rh leaching[f]		1% (4 ppm)	1% (2 ppm)

[a] For reaction conditions, see Table 3. Phase separation performed at 0 °C.
[b] Average turn over frequency (h^{-1}) for the conversion of 1-octene to octane over 24 h.
[c] Biphasic under reaction conditions.
[d] Monophasic under reaction conditions.
[e] Catalyst present as an oil, FC-75 had leached into the organic phase during the previous cycles.
[f] Average leaching of Rh into the organic phase per cycle, determined by ICP-AAS.

investigated by ICP-AAS analysis which revealed a loss of 0.5% of catalyst per cycle. Complex **2g** was recycled once without loss of activity, catalyst leaching into the organic phase amounting to 1.0% per cycle. For the 1:1 hexene/FC-75 system, all fluorous solvent had been extracted after four recycles.[2d,3] Nevertheless, **3f** remained active in the absence of fluorous solvent, albeit at a somewhat lower level, the catalyst being present as an emulsified oil. When the fluorous solvent was replenished after the last cycle the catalyst did not regain its initial activity, presumably because it had partly decomposed in the absence of a coordinating solvent.

Conclusions

As demonstrated explicitly in polymerisation catalysis, the nature of the weakly-coordinating counterion can have a major impact on the activity and selectivity of a cationic catalyst. However, for rhodium-catalysed hydrogenation the role of the anion has hardly been investigated. The results described show that cation-anion separation plays a significant role in determining activity of rhodium-diphosphine-complexes in the hydrogenation of 1-octene in acetone. These studies indicate that the electronic properties of substituents of a tetraarylborate anion exert a stronger effect on the performance of the catalyst than their steric properties. The use of highly fluorous tetraarylborate anions enhances the solubility of rhodium diphosphine complexes in apolar solvents. Furthermore, the use of $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$ resulted in enhanced hydrogenation activity in acetone as well as in fluorous media in comparison with catalysts equipped with less fluorous borate anions. Significant affinity for perfluorinated solvents was only achieved by the use of $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$ in combination with a lightly fluorous diphosphine ligand. This allowed efficient catalyst recycling through fluorous biphasic separation, whereas the corresponding BF_4^- complex did not show any affinity for fluorous solvents.

Experimental Section

General

All reactions were performed under a dry N_2 atmosphere using standard Schlenk techniques. Hexane, tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, CH_2Cl_2 from CaH_2, acetone from $CaCl_2$ and toluene from sodium. FC-75 and α,α,α-trifluorotoluene were degassed and stored over molecular sieves (3 Å). *p*-Bromo-(tridecafluorohexyl)benzene,[4b] $Ar_2PCH_2CH_2PAr_2$ {Ar = C_6H_4-($SiMe_2CH_2CH_2C_6F_{13}$)-4 or $C_6H_4[SiMe(CH_2CH_2C_6F_{13})_2]$-4},[4a] $Na[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$,[29] $Na[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$[10a] and $Na[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]$,[10a] $Na[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]$,[10a] $Na[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]$,[10b] $[Rh(COD)_2]BF_4$,[26] [Rh(COD)(acac)],[30] [Rh(COD)(dppb)]BF_4 (**1a**),[31] [Rh(COD)(dppb)][BPh_4] (**1b**),[17c] $[Rh(COD)(Ar_2PCH_2CH_2PAr_2)]BF_4$ {Ar = $C_6H_4[SiMe(CH_2CH_2C_6F_{13})_2]$-4 (**3a**) or $C_6H_4[Si(CH_2CH_2C_6F_{13})_3]$-4 (**4a**)}[3] were prepared according to literature procedures. All other chemicals were used as received. NMR spectra were recorded on Varian Mercury 200 (^{31}P) and Varian Inova 300 (^1H and ^{13}C) spectrometers with TMS (^1H, ^{13}C) and H_3PO_4 (85%) (^{31}P) as external references. Gas chromatography was performed using a Perkin Elmer Autosystem XL equipped with a 30 m PE-17 column. Elemental analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr.

Sodium Tetrakis[4-(perfluorohexyl)phenyl]borate

To *p*-bromo(perfluorohexyl)benzene (7.77 g, 16.3 mmol) in Et_2O (100 mL) at −78 °C was slowly added *n*-BuLi (9.7 mL, 1.6 M in hexanes, 15.5 mmol). The resulting solution was stirred for 1.5 h at −78 °C. $BF_3 \cdot Et_2O$ (0.34 mL, 2.7 mmol) was then added and the solution was allowed to reach room temperature over a period of 16 h. The solution was poured into H_2O and saturated with NaCl. After extraction of the aqueous layer with Et_2O (3 × 50 mL), the combined organic layers were washed with H_2O (50 mL) and dried over $MgSO_4$. Removal of the solvent and washing with hexane afforded a white solid; yield: 3.69 g (84%); ^{1}H NMR (acetone-d_6, 300.1 MHz): δ = 7.48 (m, 8H, Ar_o), 7.35 (d, $^3J_{HH}$ = 8.1 Hz, 8H, Ar_m); ^{13}C{^{1}H} NMR (acetone-d_6, 75.5 MHz): δ = 167.7 (q, $^1J_{BC}$ = 49.3 Hz, Ar_i), 136.0 (Ar_o), 124.0 (Ar_m), 122.6 (m, Ar_p), 120.5 (m), 117.7 (m), 113.0 (m), 112.6 (m), 112.1 (m), 110.6 (m); anal. calcd. for $C_{48}H_{16}BF_{52}Na$: C 35.71, H 1.00, Na 1.42; found: C 35.58, H 0.88, Na 1.57.

[Rh(COD)(dppb)][B{$C_6H_4(SiMe_3)$-4}$_4$] (1c)

Preparation of **1c** was carried out using a procedure similar to that employed for the preparation of **1d**. Starting from 55 mg (0.18 mmol) [Rh(COD)(acac)], 122 mg (0.19 mmol) Na[B{$C_6H_4(SiMe_3)$-4}$_4$] and 76 mg (0.18 mmol) dppb this afforded an orange solid; yield: 0.17 g (77%); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.51 (m, 20H), 7.41 (m, 8H), 7.15 (d, $^3J_{HH}$ = 6.3 Hz, 8H), 4.39 (s, 4H), 2.35 (s, 4H), 2,17 (m, 8H), 1.54 (s, 4H), 0.13 (s, 36H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 166.2 (q, $^1J_{BC}$ = 53.4 Hz, B-*C*), 137.0 (s), 136.2 (s), 135.0 (s), 134.1 (s), 133.0 (s), 131.8 (s), 131.2 (m), 130.8 (s), 129.4 (s), 115.6 (s), 100.6 (s), 74.7 (d), 31.0 (m), 30.2 (s), 28.5 (s), 24.6 (s), 1.2 (s), −0.8 (m, Si-CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ = 25.3 (d, $^1J_{RhP}$ = 143.4 Hz); anal. calcd. for $C_{100}H_{96}BF_{52}P_2RhSi_4$: C 69.43, H 7.45, P 4.97, Si 9.02; found: C 69.26, H 7.41, P 4.96, Si 9.61.

[Rh(COD)(dppb)][B{$C_6H_3(CF_3)_2$-3,5}$_4$] (1d)

To a solution of 51 mg (0.16 mmol) [Rh(COD)(acac)] and 181 mg (0.21 mmol) Na[B{$C_6H_3(CF_3)_2$-3,5}$_4$] in THF (25 mL) at 0 °C was dropwise added 70 mg (0.16 mmol) dppb in THF (10 mL) over 15 min. After stirring the solution for an additional 15 min, the solvent was removed under vacuum. Toluene was added and solids were filtered off using a glass sinter. The resulting solution was evaporated to dryness affording a yellow solid; yield: 0.09 g (62%); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.72 (m, 8H), 7.52 (m, 24H), 4.42 (s, 4H), 2.42 (s, 4H), 2.22 (s, 8H), 1.62 (s, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 161.9 (q, $^1J_{BC}$ = 49.9 Hz, B-*C*), 135.6 (s), 134.4 (s), 133.8 (m), 132.6 (m), 130.2 (s), 129.3 (s), 128.9 (s), 128.5 (s), 126.6 (s), 123.0 (s), 118.2 (s), 117.1 (s), 101.8 (s), 100.1 (s), 31.8 (s), 30.5 (t), 24.9 (s); ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ = 25.4 (d, $^1J_{RhP}$ = 143.0 Hz); anal. calcd. for $C_{68}H_{52}BF_{24}P_2Rh$: C 54.42, H 3.49, P 4.13; found: C 54.15, H 3.74, P 4.37.

[Rh(COD)(dppb)][B{$C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-4}$_4$] (1e)

Preparation of **1e** was carried out using a procedure similar to that employed for the preparation of **1c**. Starting from 137 mg (0.44 mmol) [Rh(COD)(acac)], 0.94 g (0.48 mmol) Na[B{$C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-4}$_4$] and 188 mg (0.44 mmol) dppb this afforded an orange solid; yield: 0.82 g (73%); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.53 (m, 20H), 7.42 (m, 8H), 7.19 (d, $^3J_{HH}$ = 7.5 Hz, 8H), 4.44 (s, 4H), 2.40 (s, 4H), 2,23 (m, 8H), 2.03 (m, 8H, CH_2CF_2), 1.61 (s, 4H), 0.87 (m, 8H, $SiCH_2$), 0.21 (s, 24H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 166.7 (q, $^1J_{BC}$ = 48.8 Hz, B-*C*), 137.1 (s), 137.0 (s), 133.5 (s), 132.9 (s), 132.4 (s), 132.1 (s), 131.7 (s), 131.3 (s), 130.6 (m), 129.4 (s), 123.8 (m), 122.3 (m), 119.1 (m), 115.7 (s), 111.9 (m), 110.3 (m), 100.6 (s), 76.1 (d), 31.3 (m), 30.1 (s), 26.4 (t), 24.6 (s), 5.7 (s, $SiCH_2$), 1.3 (s), −3.3 (s, Si-CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ = 25.2 (d, $^1J_{RhP}$ = 143.4 Hz); anal. calcd. for $C_{100}H_{96}BF_{52}P_2RhSi_4$: C 46.67, H 3.76, F 38.38, P 2.41; found: C 46.82, H 4.79, F 38.26, P 2.49.

[Rh(COD)(dppb)][B{$C_6H_4(C_6F_{13})$-4}$_4$] (1f)

Preparation of **1f** was carried out using a procedure similar to that employed for the preparation of **1c**. Starting from 72 mg (0.23 mmol) [Rh(COD)(acac)], 384 mg (0.24 mmol) Na[B{$C_6H_4(C_6F_{13})$-4}$_4$] and 138 mg (0.23 mmol) dppb this afforded an orange solid; yield: 0.40 g (77%); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.49 (m, 12H), 7.42 (m, 8H), 7.24 (d, $^3J_{HH}$ = 8.0 Hz, 8H), 7.16 (m, 5H), 7.06 (m, 3H), 4.40 (s, 4H), 2.36 (s, 4H), 2.19 (m, 8H), 1.57 (s, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 167.5 (q, $^1J_{BC}$ = 49.3 Hz, B-*C*), 135.9 (s), 133.1 (s), 132.1 (s), 129.7 (s), 129.0 (s), 124.2 (s), 122.7 (s), 121.4 (m) 118.8 (m), 115.4 (m), 114.8 (m), 110.4 (m), 107.5 (m), 100.9 (s), 31.8 (m), 30.5 (s), 24.9 (s); ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ = 25.7 (d, $^1J_{RhP}$ = 142.4 Hz); anal. calcd. for $C_{84}H_{56}BF_{52}P_2Rh$: C 45.26, H 2.53, F 44.32, P 2.78; found: C 45.10, H 2.58, F 44.28, P 2.71.

[Rh(COD)(dppb)][B{$C_6H_3(C_6F_{13})_2$-3,5}$_4$] (1g)

Preparation of **1g** was carried out using a procedure similar to that employed for the preparation of **1c**. Starting from 56 mg (0.18 mmol) [Rh(COD)(acac)], 0.58 g (0.20 mmol) Na[B{$C_6H_3(C_6F_{13})_2$-3,5}$_4$] and 77 mg (0.18 mmol) dppb this afforded an orange oil; yield: 0.5 g (76%); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.62 (bs, 8H, B-Ar_o), 7.52 (m, 20H, P-Ar), 7.42 (s, 4H, B-Ar_p), 4.42 (bs, 4H), 2.42 (bs, 4H), 2,23 (m, 8H), 1.58 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 167.5 (q, $^1J_{BC}$ = 49.3 Hz, B-*C*), 137.5 (s), 135.3 (s), 133.7 (s), 132.9 (s), 131.6 (s), 130.2 (s), 127.9 (s), 127.0 (s), 119.3 (s), 117.0 (s), 115.8 (m), 115.2 (m), 110.9 (m), 110.5 (m), 110.0 (m), 108.2 (m), 100.0 (s), 31.8 (m), 30.5 (s), 24.9 (s); ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ = 25.4 (d, $^1J_{RhP}$ = 142.4 Hz); anal. calcd. for $C_{108}H_{52}BF_{104}P_2Rh$: C 37.05, H 1.50, F 56.43, P 1.77; found: C 36.91, H 1.41, F 56.46, P 1.77.

[Rh(COD)($Ar_2PCH_2CH_2PAr_2$)][B{$C_6H_3(C_6F_{13})_2$-3,5}$_4$] {Ar = $C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-4} (2g)

Preparation of **2g** was carried out using a procedure similar to that employed for the preparation of **1c**. Starting from 40 mg (0.13 mmol) [Rh(COD)(acac)], 0.38 g (0.13 mmol) Na[B{$C_6H_3(C_6F_{13})_2$-3,5}$_4$] and 0.26 g (0.13 mmol) $Ar_2PCH_2CH_2PAr_2$ {Ar = $C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-4} this yielded a red oil. This was dissolved in MeOH (5 mL) and

extracted with FC-75 (3 × 5 mL). The FC-75 fractions were combined and all volatiles removed under vacuum, leaving a red oil; yield: 0.34 g (49%); ^{1}H NMR [C_6D_6:FC-75 (1:1), 300.1 MHz]: δ = 7.90 (m, 8H), 7.54 (m, 4H), 7.40 (m, 16H), 4.72 (s, 4H), 1.95 (m, 16H), 1.00 (m, 12H), 0.16 (s, 24H); ^{31}P{^{1}H} NMR [C_6D_6:FC-75 (1:1), 81.0 MHz]: δ = 56.2 (d, $^1J_{RhP}$ = 148.4 Hz); anal. calcd. for $C_{138}H_{72}BF_{156}P_2RhSi_4$: C 34.45, H 1.66, F 58.23, P 1.22; found: C 34.52, H 1.78, F 58.16, P, 1.25.

[Rh(COD)(Ar$_2$PCH$_2$CH$_2$PAr$_2$)][B{C$_6$H$_4$(C$_6$F$_{13}$)-4}$_4$] {Ar = C$_6$H$_4$(SiMe(CH$_2$CH$_2$C$_6$F$_{13}$)$_2$)-4} (3f)

Preparation of **3f** was carried out using a procedure similar to that employed for the preparation of **1c**. Starting from 29.4 mg (0.095 mmol) [Rh(COD)(acac)], 153 mg (0.095 mmol) Na[B{$C_6H_4(C_6F_{13})$-4}$_4$] and 317 mg (0.095 mmol) $Ar_2PCH_2CH_2PAr_2$ (Ar = $C_6H_4(SiMe(CH_2CH_2C_6F_{13})_2)$-4) this yielded a red oil. This was dissolved in MeOH (5 mL) and extracted with FC-75 (3 × 5 mL). The FC-75 fractions were combined and all volatiles removed under vacuum, leaving a red oil; yield: 0.58 g (71%); ^{1}H NMR [C_6D_6:FC-75 (1:1), 300.1 MHz]: δ = 7.72 (m, 8H), 7.52 (m, 24H), 4.42 (s, 4H), 2.42 (s, 4H), 2.22 (s, 8H), 1.62 (s, 4H); ^{31}P{^{1}H} NMR [C_6D_6:FC-75 (1:1), 81.0 MHz]: δ = 56.2 (d, $^1J_{RhP}$ = 148.1 Hz); anal. calcd. for $C_{150}H_{92}BF_{156}P_2RhSi_4$: C 35.01, H 1.80, F 57.59; found: C 34.88, H 1.71, F 57.42.

Hydrogenation of 1-Octene in Acetone

Hydrogenation reactions were carried out under the following conditions: 5 mL of catalyst solution (2.1 mM [Rh]) were vigorously stirred (using a cross-shaped Spinplus magnetic stirring bar at 1250 rpm) at 42 °C under 1.1 bars of H_2 for 30 min. Then, 1-octene (0.40 mL, 0.49 M) was added and the progress of the reaction was followed using GC by taking samples after regular intervals. *n*-Decane (0.40 mL) was added at the start of the reaction as internal reference for GC analysis.

Hydrogenation of 1-Octene under Fluorous Biphasic Conditions

Hydrogenation reactions were carried out under the following conditions: to a solution of catalyst in FC-75 (5 mL, 2.1 mM [Rh]) was added 1-octene (0.40 mL, 0.49 M) and *n*-decane (0.40 mL). This was followed by the addition of *n*-hexane (5 mL or 10 mL) and the resulting mixture was vigorously stirred (using a cross-shaped Spinplus magnetic stirring bar at 1250 rpm) at 42 °C under 1.1 bars of H_2. The progress of the reaction was followed using GC by taking samples after regular intervals. When *n*-hexane (5 mL) was added the reaction was run in emulsion, whereas the addition of 10 mL resulted in a homogeneous system under the reaction conditions. After 24 h the reaction mixture was cooled to 0 °C, the upper layer removed and new batches of 1-octene, *n*-decane and *n*-hexane were added and the reaction was continued.

Determination of Partitioning Coefficients

A known amount of rhodium complex was dissolved in PFMCH (2.00 mL). A biphasic system was created by the addition of toluene (2.00 mL) or THF (2.00 mL). The mixture was stirred and then allowed to equilibrate at 0 °C. When two clear layers were obtained, an aliquot of 0.5 mL was removed from each layer, and its weight was determined (± 0.5 mg). After removal of all volatiles under vacuum, the weight of the residue was determined (± 0.5 mg). Furthermore, for each layer examined this way, a sample was analysed by ICP-AAS.

References and Notes

[1] a) E. de Wolf, G. van Koten, B.-J. Deelman, *Chem. Soc. Rev.* **1999**, *28*, 37 – 41; b) E. G. Hope, A. M. Stuart, *J. Fluorine Chem.* **1999**, *100*, 75 – 83; c) I. T. Horváth, *Acc. Chem. Res.* **1998**, *31*, 641 – 650; d) D. P. Curran, *Angew. Chem. Int. Ed.* **1998**, *37*, 1175 – 1196; e) B. Cornils, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2057 – 2059.

[2] a) I. T. Horváth, G. Kiss, R. A. Cook, J. E. Bond, R. A. Stevens, J. Rábai, E. J. Mozeleski, *J. Am. Chem. Soc.* **1998**, *120*, 3133 – 3143; b) J. J. J. Juliette, D. Rutherford, I. T. Horváth, J. A. Gladysz, *J. Am. Chem. Soc.* **1999**, *121*, 2696 – 2704; c) E. G. Hope, R. D. W. Kemmit, D. R. Paige, A. M. Stuart, *J. Fluorine Chem.* **1999**, *99*, 197 – 200; d) B. Richter, A. L. Spek, G. van Koten, B.-J. Deelman, *J. Am. Chem. Soc.* **2000**, *122*, 3945 – 3951; e) T. Nishimura, Y. Maeda, N. Kakiuchi, S. Uemura, *J. Chem. Soc. Perkin Trans. 1* **2000**, 4301 – 4305.

[3] E. de Wolf, A. L. Spek, B. W. M. Kuipers, A. P. Philipse, J. D. Meeldijk, P. H. H. Bomans, P. M. Frederik, B.-J. Deelman, G. van Koten, *Tetrahedron* **2002**, *58*, 3911 – 3922.

[4] For various procedures for introducing perfluoroalkyl substituents, see: a) E. de Wolf, B. Richter, B.-J. Deelman, G. van Koten, *J. Org. Chem.* **2000**, *65*, 5424 – 5427; b) P. Bhattacharyya, D. Gudmunsen, E. G. Hope, R. D. W. Kemmitt, D. R. Paige, A. M. Stuart, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3609 – 3612; c) T. Mathivet, E. Monflier, Y. Castanet, A. Mortreux, J.-L. Couturtier, *Tetrahedron Lett.* **1999**, *40*, 3885 – 3888; d) W. Chen, L. Xu, J. Xiao, *Tetrahedron Lett.* **2001**, *42*, 4275 – 4278; e) S. Darses, M. Pucheault, J.-P. Genêt, *Eur. J. Org. Chem.* **2001**, 1121 – 1128.

[5] a) *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. Herrmann), Wiley-VCH, Weinheim, **1996**; b) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927 – 942; c) A. J. Lupinetti, S. H. Strauss, *Chemtracts – Inorg. Chem.* **1998**, *11*, 565 – 595.

[6] a) D. Rutherford, J. J. J. Juliette, C. Rocaboy, I. T. Horváth, J. A. Gladysz, *Catal. Today* **1998**, *42*, 381 – 388; b) L. V. Dinh, J. A. Gladysz, *Tetrahedron Lett.* **1999**, *40*, 8995 – 8998; c) I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72 – 75; d) D. C. Smith, E. D. Stevens, S. P. Nolan, *Inorg. Chem.* **1999**, *38*, 5277 – 5281; e) S. Saito, Y. Chounan, T. Nogami, O. Ohmori, Y. Yamamoto, *Chem. Lett.* **2001**, 444 – 445.

[7] a) H. Kobayashi, *J. Fluorine Chem.* **2000**, *105*, 201 – 203; b) K. Fujiki, M. Kashiwagi, H. Miyamoto, A. Sonoda, J. Ichikawa, H. Kobayashi, T. Sonoda, *J. Fluorine Chem.* **1992**, *57*, 307 – 321; c) K. Fujiki, J. Ichikawa, H. Kobayashi, A. Sonoda, T. Sonoda, *J. Fluorine Chem.* **2000**, *102*, 293 – 300; d) L. Jia, X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1995**, *14*, 3135 – 3137.

[8] a) S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, *J. Am. Chem. Soc.* **1999**, *121*, 6421 – 6429; b) M. J. Burk, S. Feng, M. F. Gross, W. Tumas, *J. Am. Chem. Soc.* **1995**, *117*, 8277 – 8278; c) T. J. de Vries, R. Duchateau, M. A. G. Vorstman, J. T. F. Keurentjes, *Chem. Commun.* **2000**, 263 – 264.

[9] a) E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391 – 1434; b) F. A. R. Kaul, G. T. Puchta, H. Schneider, M. Grosche, D. Mihalios, W. A. Herrmann, *J. Organomet. Chem.* **2001**, *621*, 177 – 183; c) J. Zhou, S. J. Lancaster, D. A.; Walker, S. Beck, M. Thornton-Pett, M. Bochmann, *J. Am. Chem. Soc.* **2001**, *123*, 223 – 237; d) R. Taube, J. Langlotz, J. Sieler, T. Gelbrich, K. Tittes, *J. Organomet. Chem.* **2000**, *597*, 92 – 104; e) S. D. Ittel, L. K. Johnson, M. Brookhart, C*hem. Rev.* **2000**, *100*, 1169 – 1203; f) L. Li, M. V. Metz, T. J. Marks, L. Liable-Sands, A. L. Rheingold, *Polymer Preprints* **2000**, *41*, 1912 – 1913.

[10] a) J. van den Broeke, M. Lutz, H. Kooijman, A. L. Spek, B.-J. Deelman, G. van Koten, *Organometallics* **2001**, *20*, 2114 – 2117; b) J. van den Broeke, B.-J. Deelman, G. van Koten, *Tetrahedron Lett.* **2001**, *42*, 8085 – 8087.

[11] The ion radius *r* denotes the longest distance from the boron atom to the periphery of the anion: TFPB taken from J. H. Golden, P. F. Mutolo, E. B. Lokovsky, F. J. DiSalvo, *Inorg. Chem.* **1994**, *33*, 5374 – 5375; BF_4^-, $[BPh_4]^-$, $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$, $[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]^-$, $[B\{C_6H_4(C_6F_{13})\text{-}4\}_4]^-$ and $[B\{C_6H_3(C_6F_{13})_2\text{-}3,5\}_4]^-$ calculated for semi-empirical (PM3™) optimised structures using the Spartan 5.1.1 (SGI) molecular modelling software package.

[12] C. Hansch, A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, John Wiley & Sons, New York, **1979**.

[13] E. de Wolf, A. J. M. Mens, O. L. J. Gijzemans, J. H. van Lenthe, L. W. Jenneskens, B.-J. Deelman, G. van Koten, *Inorg. Chem.*, accepted.

[14] H. Jiao, S. Le Stang, T. Soós, R. Meier, K. Kowski, P. Rademacher, L. Jafarpour, J.-B. Hamard, S. P. Nolan, J. A. Gladysz, *J. Am. Chem. Soc.* **2002**, *124*, 1516 – 1523.

[15] J. A. S. Howell, N. Fey, J. D. Lovatt, P. C. Yates, P. McArdle, D. Cunningham, E. Sadeh, H. E. Gottlieb, Z. Goldschmidt, M. B. Hursthouse, M. E. Loght, *J. Chem. Soc. Dalton Trans.* **1999**, 3015 – 3028.

[16] a) C. R. Landis, J. Halpern, *J. Organomet. Chem.* **1983**, *250*, 485 – 490; b) J. Reiss, J. Hetflejs, *React. Kinet. Catal. Lett.* **1986**, *31*, 309 – 313.

[17] a) M. Aresta, E. Quaranta, I. Tommasi, *New J. Chem.* **1997**, *21*, 595 – 613; b) Z. Zhou, G. Facey, B. R. James, H. Alper, *Organometallics* **1996**, *15*, 2496 – 2503.

[18] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 2134 – 2143.

[19] The Eigen–Denison−Ramsey–Fuoss Model describes the association of an ion pair in solution as follows: $K_{ass} = [4\pi N_A r^3/3000]e^b$, where $b = (|z^+z^-|e^2)/4\pi r\varepsilon\varepsilon_0 kT$, r = the centre to centre distance of the ions in contact, ε is the dielectric constant of the solvent, see: J. E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, (Ed.: G. A. Olah), Wiley, New-York, **1975**, p. 372.

[20] From semi-empirical (PM3™) optimised $[Rh(dppb)(COD)]^+$ using the Spartan 5.1.1 (SGI) molecular modelling software package, the shortest radius from Rh to the periphery of the cation was estimated at 4 Å. Using the Eigen–Denison−Ramsey–Fuoss model the difference in ion association between the complexes can be estimated. For example, in acetone $K_{ass\ 1b}/K_{ass\ 1e} = 1.5$ and $K_{ass\ 1c}/K_{ass\ 1g} = 1.7$.

[21] A similar reduction of cation-anion interactions was observed for $[BPh_4]^-$ and TFPB in cationic palladium catalysts active in co-polymerisation of CO and styrene. Enhanced catalyst activity for TFPB was supported by HOESY and NOESY NMR which confirmed a weakening of the inter-ionic interactions: A. Macchioni, G. Bellachioma, G. Cardaci, M. Travaglia, C. Zuccacia, *Organometallics* **1999**, *18*, 3061 – 3069.

[22] This solvent has a polarity similar to that of CH_2Cl_2: A. Ogawa, D. P. Curran, *J. Org. Chem.* **1997**, *62*, 450 – 451.

[23] a) L. P. Barthel-Rosa, J. A. Gladysz, *Coo. Chem. Rev.* **1999**, *190 – 192*, 587 – 605; b) B. Betzemeier, P. Knochel, *Topics in Current Chemistry* **1999**, *206*, 61 – 78.

[24] Reaction conditions: 3.7 mg (1.0 μmol) **1g** was dissolved in 5 mL FC-75. To this solution 0.02 mL (0.2 mmol) 1-octene was added and the resulting homogeneous solution was stirred for 24 h under 1 bar of H_2 at 40 °C.

[25] ^{31}P NMR chemical shifts in $CDCl_3$ for $[Rh(dppe)(COD)]BF_4$ ($\delta = 56.5$), $[Rh(dppe)(COD)][BPh_4]$ ($\delta = 56.2$), **3a** ($\delta = 56.5$) and in $C_6D_6/CF_3C_6H_5$ 1:1 (v/v) for **4a** ($\delta = 56.8$) are reported in ref.[3] **3f** ($\delta = 56.2$) and **2g** ($\delta = 56.2$) were measured in C_6D_6:FC-75 1:1 (v/v).

[26] T. G. Schenk, J. M. Downes, C. R. C. Milne, P. B. Mackenzie, H. Boucher, *Inorg. Chem.* **1985**, *24*, 2334 – 2337.

[27] As indicated by the significantly lower partition coefficients observed for **1g** in comparison with **3a**, despite the fact that both have a comparable fluorous volume.

[28] a) L. E. Kiss, I. Kövesdi, J. Rábai, *J. Fluorine Chem.* **2001**, *108*, 95 – 109; b) E. de Wolf, *PhD Thesis*, Utrecht University, **2002**, Chapter 7.

[29] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920 – 3922.

[30] R. Cramer, *J. Am. Chem. Soc.* **1964**, *86*, 217 – 219.

[31] Adapted from $[Rh(COD)(dppe)]BF_4$: M. Green, T. A. Kuc, S. H. Taylor, *J. Chem. Soc. A* **1971**, 2334 – 2337.

