PGSE Diffusion Measurements and Overhauser NMR Studies on the Salts [Rh(1,5-COD){(*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline)}](anion) and [Rh(1,5-COD){(*S*,*S*)-2,2′-isopropylidene-bis(4-*tert*-butyl-2-oxazoline)}](anion)

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PGSE NMR diffusion measurements and Overhauser studies on the salts [Rh(1,5-COD){(S,S)-4,4′-dibenzyl-2,2′-bis(2-oxazoline)}](X), **1**, and [Rh(1,5-COD){(S,S)-2,2′-isopropylidene-bis(4-*tert*-butyl-2-oxazoline)}](X), **2**, X = (**a**) CF_3SO_3, (**b**) PF_6, (**c**) BArF, (**d**) BF_4, are reported. In THF solution, there is substantial ion pairing for the CF_3SO_3, PF_6, and BF_4, salts; however, for the two BArF salts, **1c** and **2c**, the ion pairing is minimal. Strong differences in ion pairing are observed between the two series of complexes for the same anion. This represents the first example of a dependence of the degree of ion pairing on the chiral auxiliary. The ^1H spectra for the BArF salts reveal a different ^1H spin−spin coupling pattern for the three oxazoline protons, suggesting a slight change in the conformation of the chelate ring due to the larger anion. On the basis of the intensity of the $^1H,^{19}F$ HOESY contacts, it would appear that the anions in the *tert*-butyl series, **2**, come closer to the cation than in the benzyl-substituted series, **1**.

Introduction

There is an increasing inorganic literature[1−12] concerned with ^1H and ^{19}F pulsed gradient spin−echo (PGSE) diffusion measurements. Admittedly, the diffusion literature is already quite extensive (as the technique is relatively old) and the applications range into the fields of biology[9,13,14] and polymers;[15,16] however, an increasing number of studies on organometallic systems have emerged.[17−23] Many of the papers are concerned with determining relative molecular volumes and/or aggregation states.[24,25]

Recently, a number of PGSE studies directly concerned with ion pairing have appeared.[26−33] For suitable ions of a given salt, this method provides the individual diffusion constants and thus an estimation of the amount of ion pairing in a given solvent. If PGSE results can be combined with HOESY (and or NOESY) measurements,[17,34−36] which provide an estimation of the relative

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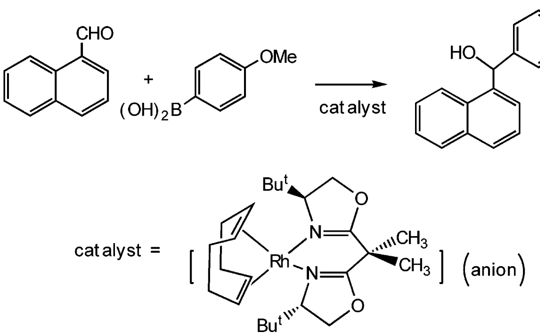
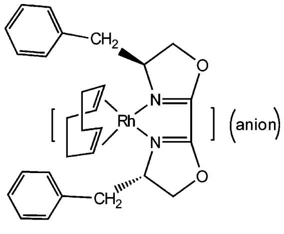
positions of the ions, one has a potent tool for probing the details of anion and cation interactions in solution. These studies are particularly timely, as the homogeneous catalysis literature contains an increasing number of examples of counterion effects on the kinetics of the catalytic reaction.[37−42] Interestingly, it would seem that larger, noncoordinating anions, such as BArF, often permit faster reactions, whereas anions such as $CF_3SO_3^-$ and PF_6^- are associated with relatively slow reactions.

Frost and co-workers[43] have recently reported an anion dependence of the kinetics for the rhodium-catalyzed aryl transfer from aryl boronic acids to aldehydes, as shown in eq 1. This reaction is reported in several ether-type solvents such as DME, dioxane, or THF. This synthetically useful addition of an aryl group to a carbon−heteroatom double bond, catalyzed by a transition metal complex, has been revived in recent years; for example, Hayashi[44,45]and Miyarau[46−50] have reported the use of large phosphine-bearing catalysts in aqueous solution for addition of aryl boronic acid to aldehydes, while Fürstner[51] has developed imidazolium-containing rhodium catalysts for related chemistry.

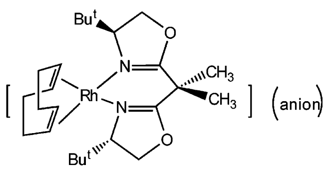


(1)

As we have previously found anion effects in rhodium 1,5-cyclooctadiene cationic complexes of bidentate phosphine ligands,[52] we were curious as to whether these or other effects exist in rhodium 1,5-cyclooctadiene bis-oxazoline complexes as well. Consequently, we have synthesized two sets of bis-oxazoline salts, [Rh(1,5-COD)((*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline))]-(anion), **1**, and [Rh(1,5-COD)((*S*,*S*)-2,2′-isopropylidenebis(4-*tert*-butyl-2-oxazoline)](anion), **2**, both with CF_3SO_3, PF_6, BF_4, and BArF as anions, and report here our results from both PGSE diffusion measurements and Overhauser NMR studies. Series **2** represents several of the salts used by Frost and co-workers.[43]



1a-d

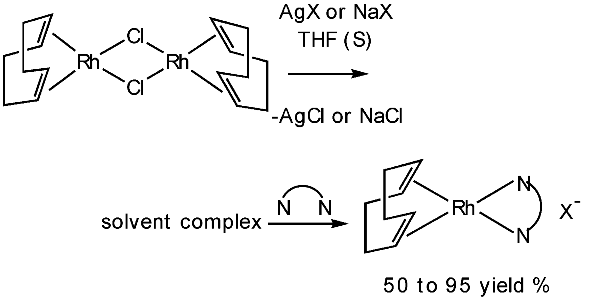


2a-d

a = CF_3SO_3, **b** = PF_6, , **c**= BAr^F, **d** = BF_4

Results and Discussion

The complexes were prepared according to literature methods.[53]Specifically, as indicated in eq 2, treatment of the known dinuclear species $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ with the appropriate amount of silver or sodium salts in THF followed by addition of the chelating ligand afforded the required rhodium complex.



(2)

The characterization was achieved by means of ^1H, ^{13}C, and ^{19}F NMR measurements and, for three representative salts, via ^{103}Rh and ^1H, ^{13}C HMQC NMR spectroscopy and mass spectrometry. The ^1H chemical shifts and ^1H, H coupling constants for the complexed 1,5-COD and oxazoline protons of both series containing the CF_3SO_3, PF_6, and BF_4 anions are comparable. However, for the BArF salts, **1c** and **2c**, one finds surprising changes (see Figure 1). The two 1,5-COD olefinic protons of the BArF salt, **2c**, are shifted to lower frequency (as are several of the aliphatic COD resonances and the oxazoline methyl groups) and, coincidently, appear at the same position. The low-frequency shift in the oxazoline methyl groups, 0.69 ppm, is even larger than that experienced by the COD olefinic protons (see Figure 1). Continuing, the ABX ($CH_2O−CHN$) spin system for the three oxazoline ring protons now appears changed.

The different olefinic 1,5-COD ^1H NMR chemical shifts might well arise from a pronounced anisotropy associated with the aromatic rings of the BArF. This is supported by the similarity of the ^{13}C NMR spectra for all four anions in both series. However, there is a marked change in one of the two vicinal coupling constants, $^3J(NCH−OCH)$, from ca. 2.5 Hz (for the three smaller anions) to ca. 8.6 Hz (for the BArF). Since one expects the usual dihedral angle dependence of this three-bond interaction,[54] these data suggest that the oxazoline ring conformation has changed. We believe this to be the first

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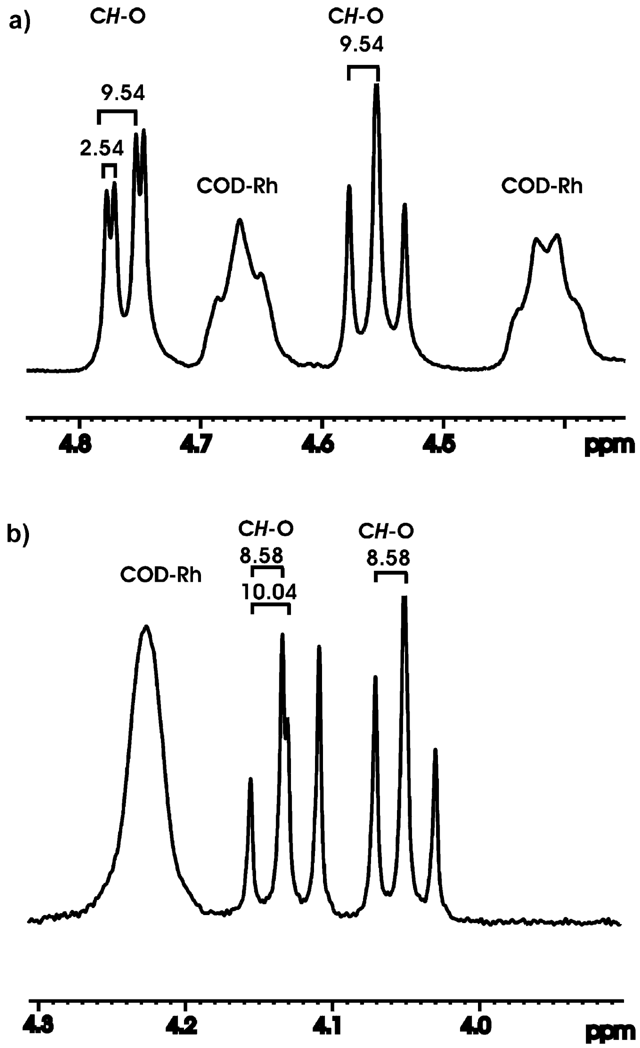

Figure 1. ^{1}H NMR spectrum for (a) **2a** (CF_3SO_3) and (b) **2c** (BArF) in THF-d_8, showing the region of the Rh-1,5-COD and the two CH_2-O protons.

reported example of such an anion effect on a chelate ring conformation.

^{1}H, ^{13}C HQMC NMR measurements provided supplementary data for the assignment of the Rh-1,5-COD, CH_2-O, and CH-N proton peaks, since this method provides a direct correlation of the ^{13}C signals to their respective protons. This was quite useful since these various ^{1}H resonances were often not well resolved (see Figure 2). The conventional ^{13}C NMR spectra for both **1** and **2** reveal the expected two Rh-1,5-COD doublets at around 80−83 ppm and two singlets for the CH_2O and CHN ^{13}C resonances at around 73−77 and 64−72 ppm, respectively (see Table 1 for a representative example). As expected, the 1,5-COD olefinic proton and carbon signals are not equivalent and are split by the ^{103}Rh, $I = 1/2$ spin, and these proton interactions can be used to determine the ^{103}Rh chemical shifts.

Diffusion Data. Diffusion constants, D, from the ^{1}H and ^{19}F PGSE diffusion measurements in THF-d_8 solution are given in Table 2. The hydrodynamic radii, r_H, are obtained from the Stokes−Einstein relation, shown in eq 3, where k is the

$$r_H = \frac{kT}{6\pi\eta D} \tag{3}$$

Boltzmann constant, η is the viscosity of the solvent, and T is the temperature. THF was chosen, as it was one of the solvents used by Frost and co-workers,[43] and we have obtained some model D-values, in earlier studies, in this solvent.[55] THF is expected to afford a substantial amount of ion pairing in most cases.[55] It is now recognized that, for salts with cations and anions of very different size (and in the absence of, for example, hydrogen bonding), when the cation and anion reveal identical D-values, one can consider this as resulting from complete ion pairing.[55−57] When the two values are different, the extent of the difference reflects the degree of ion pairing.

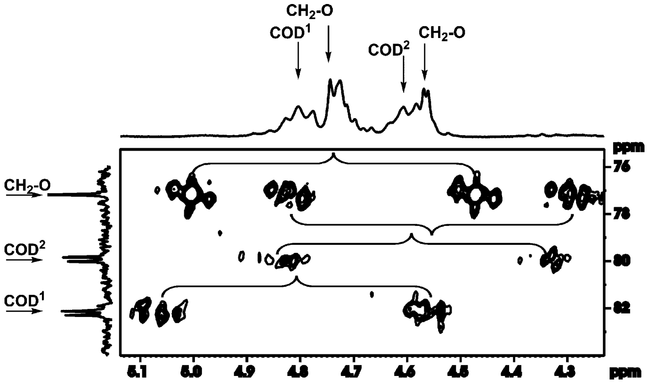

Figure 2. ^{1}H, ^{13}C HMQC for **1d** (BF_4) in THF-d_8 showing the assignment for the strongly overlapped olefinic Rh-1,5-COD, CH_2-O, and CH-N protons.

The first point to note from the data in Table 2 is that, for the anions CF_3SO_3 and PF_6, the two series reveal *different amounts of ion pairing for the same anion*; that is, there is dependence of the ion pairing on the nature of the auxiliary. We believe this to be the first example of this type of effect.

In series **1**, the derived r_H-values for the anions CF_3SO_3 and PF_6 (r_H = 5.6 and 5.5 Å, respectively) indicate that these ions are moving at not very different rates relative to the cations (r_H = 6.1 Å). This indicates very substantial but not 100% ion pairing for these salts in this solvent. The ion pairing for the BF_4 salt (r_H = 4.8 Å) is not quite so large. In methanol, a solvent where ion pairing is minimal, the sizes (r_H) of the solvated PF_6 and BF_4 anions were estimated to be about 2.5−2.8 Å, whereas for the solvated CF_3SO_3 anion the value is ca. 3.0−3.3 Å.[56]

For the BArF anion,[57] in **1c**, we find an r_H-value of 6.8 Å. In methanol solution the solvated anion is estimated to have an r_H-value of ca. 5.8−6.1 Å. This value suggests relatively little ion pairing in THF if (a) one takes into account the larger structure of the THF solvent, relative to methanol, and (b) one notices that the cation in **1c** is now considerably smaller, r_H = 5.4 Å; that is, significant ion pairing would result in a much larger r_H cation value.

In series **2** the same trend is observed as the anions are varied. For compounds **2a**, **2b**, and **2d**, on the basis of their D-values, the sizes of the anions were calculated to be 4.9, 4.5, and 4.9Å for the CF_3SO_3, PF_6, and BF_4 anions, respectively. This suggests substantial, if somewhat smaller, amounts of ion pairing in these compounds, relative to **1**. The size of the BArF anion in **2c** is, once again, ca. 6.8 Å.

The "smaller size" of the cation in the second series is a little surprising at first. However, phenyl groups are known to create

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Table 1. ^{1}H and ^{13}C NMR Data for the Salts 1a and 2a in THF-d_8[a]

1a			2a		
^{1}H	7.34	$C_6\mathit{H}_5$	^{1}H	4.67	Rh-olefin
	7.24	$C_6\mathit{H}_5$		4.75	C*H*-O
	4.78	Rh-olefin		4.41	Rh-olefin
	4.73	C*H*-O		4.55	C*H*-O
	4.60	Rh-olefin		3.90	C*H*-N
	4.56	C*H*-O		2.70	1,5-COD
	4.78−4.56	C*H*-N		2.38	1,5-COD
	3.02	$C\mathit{H}_2$-C_6H_5		2.04	1,5-COD
	2.98	1,5-COD		1.81	1,5-COD
	2.84	$C\mathit{H}_2$-C_6H_5		2.16	Me
	2.25−2.18	1,5-COD		0.95	t-Bu
	1.68	1,5-COD			
^{13}C	135.7	*ipso*-C_6H_5	^{13}C	82.7	Rh-olefin ^1J(Rh,C) 13.7
	129.4	C_6H_5		80.0	Rh-olefin ^1J(Rh,C), 13.7
	128.6	C_6H_5		73.3	CH-O
	126.8	*p*-C_6H_5		72.3	CH-N
	81.8	Rh-olefin ^1J(Rh,C), 12.5		40.8	C-Me_2
	79.8	Rh-olefin ^1J(Rh,C), 12.5		33.9	C-Me_3
	77.0	CH-O		31.0	1,5-COD
	64.3	CH-N		28.9	1,5-COD
	39.2	$C\mathit{H}_2$-C_6H_5		24.8	t-Bu
	31.9	1,5-COD		24.6	Me (overlapped with THF)
	28.9	1,5-COD			
	162.9	N═C-O		178.4	N═C-O
^{19}F	−79.1	CF_3SO_3	^{19}F	−78.9	CF_3SO_3
^{103}Rh	895		^{103}Rh	1071	

[a] ^{1}H (400 MHz), ^{13}C (75 MHz), ^{19}F (376 MHz), and ^{103}Rh (15.9 MHz) referenced to TMS at 100 MHz. *J* values in Hz.

Table 2. ^{1}H and ^{19}F NMR Diffusion Data[a] for the Rh Salts 1 and 2

		set **1**		set **2**	
anion		D^a	$r_H{}^b$	D^a	$r_H{}^b$
CF_3SO_3	cations (^{1}H)	7.81	6.1	8.41	5.7
	CF_3SO_3 ($^{19}F^c$)	8.50	5.6	9.64	4.9
PF_6	cations (^{1}H)	7.77	6.1	8.24	5.8
	PF_6 ($^{19}F^c$)	8.70	5.5	10.48	4.5
BArF	cations (^{1}H)	8.85	5.4	11.21	4.2
	BArF (^{1}H)	6.90	6.8	7.03	6.8
	BArF ($^{19}F^c$)			7.08	6.7
BF_4	cations (^{1}H)	7.69	6.2	8.27	5.7
	BF_4 ($^{19}F^c$)	9.82	4.8	9.75	4.9

[a] $\times 10^{-10}$ m^2 s^{-1}. 2 mM THF solutions. Estimated using the diffusion coefficient of HDO in D_2O as reference. [b] THF-d_8 η (299 K, kg s^{-1} m^{-1}): 0.461. [c] The values for ^{19}F were corrected to the gyromagnetic ratio relative to ^{1}H, i.e., $\gamma_F/\gamma_H = 0.8858$.

more resistance to flow and stretch out into the solution.[58] Of course the C_7 benzyl group is also simply larger than the C_4 *tert*-butyl group. As in previous reports,[57] we have estimated the cationic radii via Chem3D and find these to be 5.5 and 4.4 Å, for **1** and **2**, respectively. Both solvation and some ion pairing will increase these values and bring them closer to what we observe for the CF_3SO_3, PF_6, and BF_4 ions based on the diffusion data. The r_H-values for the cations in the two BArF salts, **1c** and **2c**, 5.4 and 4.2 Å, respectively, seem too small. Applying the correction to the "*c*" constant in eq 3, suggested by Macchioni,[22a] gives values of 5.7 and 4.6 Å. It is interesting that these are fairly close to the Chem3D values.

Overhauser Studies. ^{19}F, ^{1}H HOESY spectra were measured in order to determine the relative positions of the ions in **1** and **2**. Figure 3 shows a section of the 2-D HOESY spectrum for both PF_6 salts **1b** and **2b** in THF-d_8 solution at 299 K.

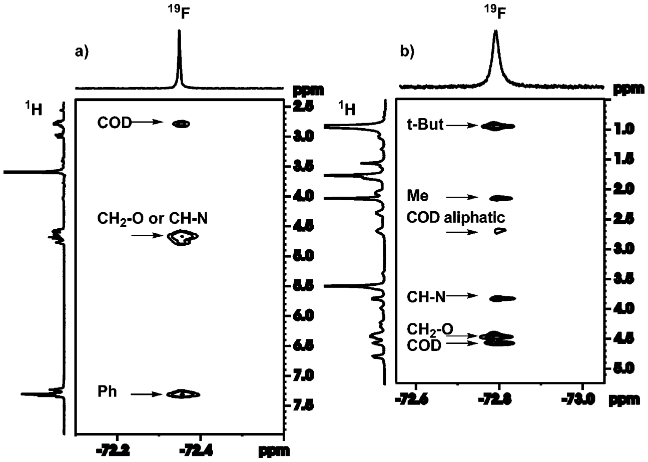

Figure 3. ^{19}F, ^{1}H HOESY for (a) **1b** (PF_6) and (b) **2b** (PF_6) showing the different contacts observed from the anion to the cation (10 mM, THF-d_8). Only one-half of the ^{19}F doublet is shown for clarity.

The benzyl salt, **1b**, in Figure 3a, reveals a series of medium-intensity cross-peaks between the PF_6 anion and the cation in **1b**. These are selective in that, for example, only one of the *aliphatic* 1,5-COD protons and not all of the phenyl resonances are involved. The remaining cross-peaks arise from one of the CH_2-O and/or the CH-N proton(s). One can say that, at most, *only one* of the two olefinic 1,5-COD resonances reveals a HOESY cross-peak.

In the compounds of series **2**, all of the cross-peaks are stronger in intensity, relative to **1**, and this can be seen for **2b** in Figure 3b. The strongest contacts occur with the *tert*-butyl groups, one olefin resonance of the 1,5-COD, and one of the CH_2-O signals. Medium-intensity contacts are observed with the CH-N proton and the methyl groups and finally a very weak contact with one of the aliphatic protons of the 1,5-COD.

The HOESY selectivity with respect to the 1,5-COD olefinic protons might arise from a rotation of the complexed diolefin. This structural distortion has been documented a number of times via X-ray diffraction measurements[59−61] and might alleviate steric repulsions between the diolefin and the *tert*-butyl groups, as suggested by the fragment below.

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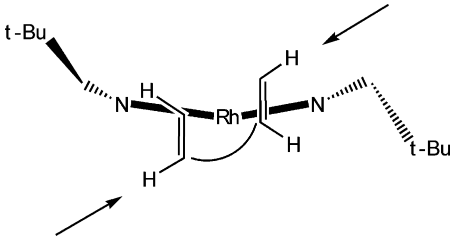
(58) Nama, D.; Anil Kumar, P. G.; Pregosin, P. S. *Magn. Reson. Chem.* **2005**, *43*, 246−250.



The two olefinic protons indicated with the arrows will be closer to the anion assuming that the latter approaches the cation from a pseudo-fifth coordination position. However, this selectivity may also be related to the direction of approach, with the anion choosing to come from the side of the oxazoline remote from the *tert*-butyl group.

The cross-peak intensity differences between **1** and **2** are interesting. The PF_6 anion seems to "come closer" to the cation in series **2**. On the surface this seems to contrast with the diffusion results, i.e., more ion pairing for **1** than **2**. However, the extent of ion pairing cannot be directly related to structure, so that it is perfectly logical that *whenever* **2** forms an ion pair, its anion comes closer to the cation, thus affording more and stronger contacts.

A ^{19}F, ^{1}H HOESY spectrum was also recorded in THF-d_8 for the compound of the BArF salt **2c**. This spectrum shows *no contacts* between the ions in **2c**. The only cross-peaks observed were due to contact between the CF_3 substituents and the proximate aryl ring protons.

Conclusions and Comments. From the PGSE studies we find differences in the ion pairing as a function of the structure of the bis-oxazoline ligand. Further, these diffusion results support previous studies,[62] in which the degree of ion pairing in a transition metal salt is markedly affected by the nature of the anion. Whereas the anions CF_3SO_3, PF_6, and BF_4 all demonstrate significant (but not always identical) ion pairing, the results from the two BArF salts suggest little or no ion pairing. It is not possible to directly extrapolate our results to the catalytic studies of Frost and other groups; however, we note, once again, that the BArF anion is (a) not involved in much ion pairing and (b) relatively remote from the cation (i.e., we find no HOESY contacts to the cation). These two points will certainly favor relatively rapid catalytic reactions, relative to other salts where the anion might well be close to—or blocking—a coordination position. Moreover, the presence of the relatively large BArF species seems, somewhat surprisingly, to have some effect on the oxazoline ring conformation, as suggested by the changes in several vicinal proton−proton coupling constants.

The significance of the various HOESY cross-peak intensities is not completely obvious. In the *tert*-butyl series, **2**, these signals are both relatively strong and numerous. The various contacts to the oxazoline confirm that the anion will tend to approach the nitrogen donors, as these will be partially positively charged. The absence of numerous 1,5-COD contacts speaks in favor of a selective anion approach; however, the unfortunate signal overlap in parts of the various ^{1}H spectra prohibit a more detailed analysis. Nevertheless, this study illustrates once again that there is much to be learned about the interactions of ions from the combined use of diffusion and ^{19}F, ^{1}H HOESY NMR studies.

Experimental Section

General Procedures (NMR). ^{1}H, ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance 300, 400, and 500 NMR spectrometers. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Deuterated solvents were dried by distillation over molecular sieves and stored under N_2.

Diffusion. All the measurements were performed on a Bruker Avance spectrometer, 400 MHz, equipped with a microprocessor-controlled gradient unit and a multinuclear inverse probe with an actively shielded Z-gradient coil. The gradient shape is rectangular, and its length was 1.75 ms. The gradient strength was increased by steps of 4% during the course of the experiment. The time between midpoints of the gradients was 167.75 ms for all experiments. The experiments were carried out at a set temperature of 299 K within the NMR probe.

As indicated in Table 2, diffusion values were measured on 2mM THF-d_8 solutions. Cation diffusion rates were measured using the ^{1}H signal from the aromatic protons or 1,5-COD protons depending on the signal separation in the ^{1}H spectrum. Anion diffusion was obtained from the ^{19}F and ^{1}H of the group attached to boron. The error in the D-values is thought to be ±0.06.

HOESY. $^{19}F-^{1}H$ HOESY spectra were measured at concentrations of 10 mM, in THF-d_8, at 299 K with a 0.8 s mixing time.

[Rh(1,5-COD)((*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline))]-(CF_3SO_3), 1a. $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and $AgCF_3SO_3$ (0.051 g, 256.9 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 1 h under N_2. The dark orange solution and the AgCl precipitate formed were then filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline) (0.0641 g, 320.39 g mol^{-1}, 0.2 mmol) and the mixture then stirred for another hour. The THF was then concentrated under vacuum. The crude solid was washed with hexane (1 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as a dark orange solid, is partially soluble in Et_2O. Yield: 64 mg, 9.41×10^{-5} mol (94.1%). MS (ESI): M^+ 531.2, $M^+ - $ 1,5-COD 423.

[Rh(1,5-COD)((*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline))]-(PF_6), 1b. $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and $AgPF_6$ (0.051 g, 253 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the atmosphere in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 45 min under N_2. The red-orange solution and the AgCl precipitate were then filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline) (0.0641 g, 320.39 g mol^{-1}, 0.2 mmol), and the mixture was stirred for another hour. Then THF was then concentrated under vacuum and the resulting crude solid washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as an orange solid, is partially soluble in Et_2O. Yield: 64 mg, 9.47×10^{-5} mol (94.7%). MS (ESI): M^+ 531.2. NMR: ^{1}H (THF-d_8, 400 MHz, 299 K) 7.34 (C_6H_5), 7.26 (C_6H_5), 4.79 (1,5-COD-Rh), 4.73−4.65 (CH-O and CH-N), 4.64 (1,5-COD-Rh), 4.59 (CH-O), 3.00 (CH_2-C_6H_5), 2.77−2.86 (CH_2-C_6H_5 and 1,5-COD), 2.2−2.4 (1,5-COD); ^{13}C (THF-d_8, 75 MHz, 299 K) 135.8 (*ipso*-C_6H_5), 129.8 (C_6H_5), 129.0 (C_6H_5), 127.4 (*p*-C_6H_5), 82.7 (d, 9.15 Hz, 1,5-COD-Rh), 80.7 (d, 9.15 Hz, 1,5-COD-Rh), 77.6 (CH-O), 64.6 (CH-N), 39.7 (CH_2-C_6H_5) 32.4 (1,5-COD), 29.3 (1,5-COD); ^{31}P −143 (septet, 714 Hz, PF_6); ^{19}F (THF-d_8, 376 MHz, 299 K) −73.3 (d, 714 Hz, PF_6).

[Rh(1,5-COD)((*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline))]-(BAr^F), 1c. $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and Na(BArF) (0.107 g, 535 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids

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(59) Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 4510−4518.

(60) Valentini, H.; Selvakumar, K.; Worle, M.; Pregosin, P. S. *J. Organomet. Chem.* **1999**, *587*, 244−251.

(61) Nishibayashi, Y.; Segawa, K.; Arikawa, Y.; Ohe, K.; Hidai, M.; Uemura, S. *J. Organomet. Chem.* **1997**, *546*, 381−398.

(62) Sirbu, D.; Consiglio, G.; Milani, B.; Kumar, P. G. A.; Pregosin, P. S.; Gischig, S. *J. Organomet. Chem.* **2005**, *690*, 2254−2262.

were dissolved and stirred in dry THF (10 mL) at room temperature over 1 h under N_2. The dark orange solution and the NaCl precipitate formed were then filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline) (0.0641 g, 320.39 g mol^{-1}, 0.2 mmol) and the mixture then stirred for another hour. Then THF was then concentrated under vacuum. The crude solid was washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as a red-orange solid, is partially soluble in Et_2O. Yield: 83 mg, 5.95 × 10^{-5} mol, 59.5%. MS (ESI): M$^+$ 531.2, M$^+$ − 1,5-COD 423. NMR: ^{1}H (THF-*d*$_8$, 400 MHz, 299 K) 7.84 and 7.61 (BArF), 7.27−7.35 (C_6H_5), 4.51−4.61 (overlapped: 1,5-COD-Rh, CH-O, CH-N, 1,5-COD-Rh, and CH-O), 3.10 and 2.75 (CH_2-C_6H_5), 2.15, 2.40, and 2.76 (1,5-COD); ^{13}C (THF-*d*$_8$, 75 MHz, 299 K) 162.0 (49.9 Hz, C-B of BArF), 135.9 (*ipso*-C_6H_5), 134.6 (BArF), 129.2 (C_6H_5), 128.6 (C_6H_5), 127.0 (*p*-C_6H_5), 124.5 (q, 270 Hz, CF_3), 117.2 (BArF), 80.8 (d br, 10.9 Hz, 1,5-COD-Rh), 79.7 (d br, 10.9 Hz, 1,5-COD-Rh), 75.0 (CH-O), 65.7 (CH-N), 40.1 (CH_2-C_6H_5), 31.6 (1,5-COD), 29.6 (1,5-COD); ^{19}F (THF-*d*$_8$, 376 MHz, 299 K) −63.4 (BArF).

[Rh(1,5-COD)((*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline))]-(BF_4), 1d. [Rh(μ-Cl)(1,5-COD)]$_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and $AgBF_4$ (0.039 g, 194.7 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 1 h under N_2. The brownish solution and the AgCl precipitate were then filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-4,4′-dibenzyl-2,2′-bis(2-oxazoline) (0.0641 g, 320.39 g mol^{-1}, 0.2 mmol) and the mixture then stirred for another hour. The THF was then concentrated under vacuum. The crude solid was washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as a yellow-brown solid, is partially soluble in Et_2O. Yield: 30 mg, 5.95 × 10^{-5} mol, 48.5%. MS (ESI): M$^+$ 531.2, M$^+$ − 1,5-COD 423. NMR: ^{1}H (THF-*d*$_8$, 400 MHz, 299 K) 7.40 (C_6H_5), 7.25 (C_6H_5), 4.80 (1,5-COD-Rh), 4.74 (CH-O), 4.60 (1,5-COD-Rh), 4.52 (CH-O (2)), 4.72 (CH-N), 3.00 (CH_2-C_6H_5), 2.83 (CH_2-C_6H_5 and 1,5-COD), 2.22 and 1.70 (1,5-COD); ^{13}C (THF-*d*$_8$, 75 MHz, 299 K) 162.8 (N=C-O), 135.6 (*ipso*-C_6H_5), 129.5 (C_6H_5), 128.5 (C_6H_5), 126.8 (*p*-C_6H_5), 82.0 (d, 12.6 Hz, 1,5-COD-Rh), 80.0 (d, 12.6 Hz, 1,5-COD-Rh), 77.2 (CH-O), 64.2 (CH-N), 39.2 (CH_2-C_6H_5), 32.0 (1,5-COD), 28.9 (1,5-COD); ^{19}F (THF-*d*$_8$, 376 MHz, 299 K) −153.9 (BF_4).

[Rh(1,5-COD)((*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline)](CF_3SO_3), 2a. [Rh(μ-Cl)(1,5-COD)]$_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and $AgCF_3SO_3$ (0.051 g, 256.9 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 1 h under N_2. The orange solution and the AgCl precipitate formed were then filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline) (0.059 g, 294 g mol^{-1}, 0.2 mmol) and the mixture then stirred for another hour. The THF was concentrated under vacuum. The crude solid was washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as a yellow solid, is partially soluble in Et_2O. Yield: 43 mg, 6.57 × 10^{-5} mol, 65.7%. MS (ESI): M$^+$ 505.2.

[Rh(1,5-COD)((*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline)](PF_6), 2b. [Rh(μ-Cl)(1,5-COD)]$_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and $AgPF_6$ (0.051 g, 253 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 45 min under N_2. The dark orange solution and the AgCl precipitate formed were then filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline) (0.059 g, 294 g mol^{-1}, 0.2 mmol), and the mixture was stirred for another hour. The THF was then concentrated under vacuum. The crude solid was washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as a dark yellow solid, is partially soluble in Et_2O. Yield: 41 mg, 6.31 × 10^{-5} mol, 63.1%. MS (ESI): M$^+$ 505.2, M$^+$ − 1,5-COD 397.2. NMR: ^{1}H (THF-*d*$_8$, 400 MHz, 299 K) 4.55 (b, 1,5-COD-Rh), 4.79 (dd, 2.4 and 9.9 Hz, CH-O), 4.37−4.50 (m, 1,5-COD-Rh and CH-O), 3.82 (dd, 2.4 and 8.7 Hz, CH-N), 2.69, 2.38, 2.06, and 1.80 (m, 1,5-COD), 2.15 (s, C-(C*H*$_3$)$_2$), 0.95 (s, C-(C*H*$_3$)$_3$); ^{13}C (THF-*d*$_8$, 75 MHz, 299 K) 178.4 (N=C-O), 82.6 (d, 13.0 Hz, 1,5-COD-Rh), 80.0 (d, 13.0 Hz, 1,5-COD-Rh), 73.2 (CH-O), 72.2 (CH-N), 40.7 (*C*-(CH_3)$_3$), 33.9 (s, *C*-(CH_3)$_2$), 31.0 (1,5-COD backbone), 28.9 (1,5-COD backbone), 24.8 (C-(*C*H$_3$)$_3$, 24.6 C-(*C*H$_3$)$_2$); ^{31}P −143 (septet, 752 Hz, PF_6); ^{19}F (THF-*d*$_8$, 376 MHz, 299 K) −73.6 (d, 752 Hz, PF_6).

[Rh(1,5-COD)((*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline)](BAr^F), 2c. [Rh(μ-Cl)(1,5-COD)]$_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and NaBAr^F (0.107 g, 535 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 1 h under N_2. The yellow-orange solution was reduced, and the NaCl precipitate formed was filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline) (0.059 g, 294 g mol^{-1}, 0.2 mmol), and the mixture was stirred for another hour. The THF was then concentrated under vacuum. The crude solid was washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, a pale yellow solid, is partially soluble in Et_2O. Yield: 126 mg, 9.25 × 10^{-}5 mol, 92.5%. MS (ESI): M$^+$ 505.2, M$^+$ − 1,5-COD 397.2. NMR: ^{1}H (THF-*d*$_8$, 400 MHz, 299 K) 7.82 and 7.60 (b, BArF), 4.23 (b, 1,5-COD-Rh), 4.13 (dd, 8.58 and 10.04 Hz, CH-O), 4.05 (t, 8.58 Hz, CH-O), 3.80 (dd, 7.69 and 10.04 Hz, CH-N), 2.70 and 1.80 (m, 1,5-COD), 1.46 (s, C-(C*H*$_3$)$_2$), 0.89 (s, C-(C*H*$_3$)$_3$); ^{13}C (THF-*d*$_8$, 75 MHz, 299 K) 168.4 (N=C−O), 162.4 (50 Hz, C-B of BArF), 135.0 (BArF), 117.6 (BArF), 129.4 (q, *C*-CF_3), 125.0 (q, 270 Hz, CF_3), 78.3 (d, 13.7 Hz, 1,5-COD-Rh (1and 2)), 75.9 (CH-O), 68.9 (CH-N), 31.6 (1,5-COD backbone), 38.9 (*C*-(CH_3)$_2$), 33.8 (s, *C*-(CH_3)$_3$), 25.6 ((*C*-(CH_3)$_2$ and 33.8 *C*-(CH_3)$_3$); ^{19}F (THF-*d*$_8$, 376 MHz, 299 K) 63.4 (BArF); ^{103}Rh (THF-*d*$_8$, 15.9 MHz, 299 K) 1070.

[Rh(1,5-COD)((*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline)](BF_4), 2d. [Rh(μ-Cl)(1,5-COD)]$_2$ (0.050 g, 493 g mol^{-1}, 0.1 mmol) and $AgBF_4$ (0.039 g, 194.7 g mol^{-1}, 0.2 mmol) were placed under vacuum, and the air in the flask was then replaced by N_2. The solids were then dissolved and stirred in dry THF (10 mL) at room temperature over 1 h under N_2. The brownish solution and the AgCl precipitate formed were filtered over Celite under N_2. To the filtrate was added (*S*,*S*)-2,2′-isopropylidenebis(4-terbutyl-2-oxazoline) (0.059 g, 294 g mol^{-1}, 0.2 mmol), and the mixture was stirred for another hour. The volume of THF was concentrated under vacuum. The solid was washed with hexane (2 × 5 mL) and Et_2O (3 × 1 mL) and then dried in vacuo. The product, as a yellow-brown solid, is partially soluble in Et_2O. Yield: 32 mg, 5.40 × 10^{-5} mol, 54.0%. MS (ESI): M$^+$ 505.2, M$^+$ − 1,5-COD 397.2. NMR: ^{1}H (THF-*d*$_8$, 400 MHz, 299 K) 4.65 (b, 1,5-COD-Rh), 4.44 (b, 1,5-COD-Rh) 4.77 (dd, 2.49 and 9.75 Hz, CH-O), 4.54 (dd, 8.67, 9.63 Hz, CH-O), 3.86 (dd, 2.49 and 8.63 Hz, CH-N), 2.70, 2.38, 2.07, and 1.80 (m, 1,5-COD), 2.15 (s, C-(C*H*$_3$)$_2$), 0.95 (s, C-(C*H*$_3$)$_3$); ^{13}C (THF-*d*$_8$, 100.6 MHz, 299 K) 179 (N=C-O), 83.2 (d, 13.5 Hz, 1,5-COD-Rh), 80.3 (d, 13.0 Hz, 1,5-COD-Rh), 73.7 (CH-O), 72.6 (CH-N), 34.3 (s, *C*-(CH_3)$_2$), 31.5 (1,5-COD backbone), 29.3 (1,5-COD backbone), 25.9 (C-(*C*H$_3$)$_3$, 25.3 C-(*C*H$_3$)$_2$); ^{19}F (THF-*d*$_8$, 376 MHz, 299 K) −153.5 (BF_4).

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