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Synthesis, Reactivity, Spectroscopic Characterization, X-ray Structures, PGSE, and NOE NMR Studies of (η^5-C_5Me_5)-Rhodium and -Iridium Derivatives Containing Bis(pyrazolyl)alkane Ligands

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Rhodium(III) and iridium(III) complexes containing bis(pyrazolyl)methane ligands (pz = pyrazole, L′ in general; specifically, $L^1 = H_2C(pz)_2$, $L^2 = H_2C(pz^{Me2})_2$, $L^3 = H_2C(pz^{4Me})_2$, $L^4 = Me_2C(pz)_2$), have been prepared in a study exploring the reactivity of these ligands toward $[Cp^*MCl(\mu\text{-}Cl)]_2$ dimers (M = Rh, Ir; Cp* = pentamethylcyclopentadienyl). When the reaction was carried out in acetone solution, complexes of the type [Cp*M(L′)Cl]Cl were obtained. However, when L^1 and L^2 ligands have been employed with excess $[Cp^*MCl(\mu\text{-}Cl)]_2$, the formation of [Cp*M(L′)-Cl][Cp^*MCl_3] species has been observed. PGSE NMR measurements have been carried out for these complexes, in which the counterion is a cyclopentadienyl metal complex, in CD_2Cl_2 as a function of the concentration. The hydrodynamic radius (r_H) and, consequently, the hydrodynamic volume (V_H) of all the species have been determined from the measured translational self-diffusion coefficients (D_t), indicating the predominance of ion pairs in solution. NOE measurements and X-ray single-crystal studies suggest that the $[Cp^*MCl_3]^-$ approaches the cation, orienting the three Cl-legs of the "piano-stool" toward the CH_2 moieties of the bis(pyrazolyl)methane ligands. The reaction of 1 equiv of [Cp*M(L′)Cl]Cl or [Cp*M(L′)Cl][Cp^*MCl_3] with 1 equiv of AgX (X = ClO_4 or CF_3SO_3) in CH_2Cl_2 allows the generation of [Cp*M(L′)Cl]X, whereas the reaction of 1 equiv of [Cp*M(L′)Cl] with 2 equiv of AgX yields the dicationic complexes $[Cp^*M(L')(H_2O)][X]_2$, where single water molecules are directly bonded to the metal atoms. The solid-state structures of a number of complexes were confirmed by X-ray crystallographic studies. The reaction of $[Cp^*Ir(L')(H_2O)][X]_2$ with ammonium formate in water or acetone solution allows the generation of the hydride species [Cp*Ir(L′)H][X].

Introduction

Since the first syntheses of poly(pyrazolyl)borates by Trofimenko in 1966,[1] over two thousand publications have appeared describing the syntheses and applications of bis-(pyrazolyl)borate ligands in various areas of chemistry.[2] Adducts of bis(pyrazolyl)alkanes remain less studied because of greater difficulties encountered in the preparation of large quantities of these N_2-donor species.[3] These bidentate ligands are less rigid than some other bidentate ligands such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline. In addition, because of the aromatic rings, they are likely to give more stable adducts than the most commonly used aliphatic diamines such as ethylenediamine. In the literature, the first rhodium-(I) complexes containing the ligand $H_2C(pz)_2$ were reported by Oro and co-workers.[4] Rh(I) derivatives containing H_2C-$(pz^{Me2})_2$ can be used as catalysts in the hydroformylation and hydroaminomethylation of olefins.[5] Ir(1,5-cyclooctadiene) and $Ir(CO)_2$ derivatives containing L^1 and L^2 have been

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synthesized, characterized, and demonstrated to be effective catalysts for the alcoholysis of a range of alcohols and hydrosilanes, including secondary and tertiary hydrosilanes, under mild conditions.[6]

As an extension of our previous work on Cp*Rh(III)- and Cp*Ir(III)-scorpionates,[7] we have undertaken a systematic study of the reactions between $[Cp^*MCl(\mu\text{-}Cl)]_2$ dimers (M = Rh, Ir) and bis(pyrazolyl)alkane $(R_2C)_n(pz')_2$ ligands. Several studies have been reported describing the molecular structures of $[Cp^*Rh(N{-}N)X]^{n+}$ systems, as interesting catalytic precursors, and it has been proposed that catalytic activity depends on the chelate ring conformation, metal−ligand bond distances, and interbond angles. However, to date, structural information is limited to complexes containing bipyridine-type ligands that generate five-membered chelate rings.[8]

$[Cp^*Rh(bpy)(H_2O)]^{2+}$ has been demonstrated to be a versatile tool for efficient nonenzymatic regeneration of oxidoreductase coenzymes such as NAD(P)H, $NAD(P)^+$, and $FADH_2$.[9] $[Cp^*Rh(bpy)H]^+$, generated in situ from $[Cp^*Rh(bpy)(H_2O)]^{2+}$ and sodium formate,[10,11] can be considered to be a biomimetic enzymatic hydride via its ability to bind and regioselectively transfer a hydride in the 4-ring-position of the NAD^+ model.[12] Here we report the syntheses and spectral and structural characterization of a number of complexes containing the Cp*M synthons (M = Rh and Ir) with various bis(pyrazolyl)alkanes which are able to form six-membered chelate rings. The reactivity of some species toward PPh_3 and ammonium formate has been investigated. $[Cp^*Ir(L')H]^+$ hydride formation has been found be independent of the pH value and solvent employed.

Since it is well-recognized that ion-pairing drastically affects the reactivity and structure of ionic organometallics,[13] we also considered it to be of interest to investigate the interionic solution structures of the complexes $[Cp^*M(L^1)Cl]^+$-$[Cp^*MCl_3]^-$, which possess an unusual organometallic counterion. (By "interionic structure", we mean both the relative anion−cation position, determined by NOE (nuclear Overhauser effect) NMR experiments,[14−16] and the level of aggregation, estimated by the PGSE (pulsed-field gradient spin echo) NMR technique).[17,18] This work is reported herein.

Results and Discussion

Synthesis and Spectroscopic Characterization of Complexes 1−21. The complexes $[Cp^*M(L')Cl][Cp^*MCl_3]$ (**1** M = Rh, $L' = L^1$; **3** M = Ir, $L' = L^1$; **5** M = Rh, $L' = L^2$; **7** M = Ir, $L' = L^2$) have been prepared from the reactions of equimolar quantities of $[Cp^*MCl(\mu\text{-}Cl)]_2$ dimers and bis(pyrazolyl)methane ligands L^1 and L^2, in THF, under N_2 streams (Chart 1). The formation of the anion $[Cp^*MCl_3]^-$ is rather unusual, as recently described by Severin and coworkers, who attribute the formation of the anion in $[Cp^*Ru(C_6H_6)][Cp^*RhCl_3]$ to the generation of the cationic $[Cp^*Ru(C_6H_6)]^+$ moiety.[19] In contrast, in our compounds, the driving force is more likely to be the ligand conformation and the number and nature of the substituents on the heterocyclic ligands. Analogous $[Cp^*M(bpy)Cl][Cp^*MCl_3]$ bpy-containing species have not yet been reported. Under the same conditions analogous compounds cannot be obtained by using L^3 and L^4, even if a large excess of $[Cp^*MCl(\mu\text{-}Cl)]_2$ is employed. On the other hand, when L^1, L^2, L^3, and L^4 react with $[Cp^*MCl(\mu\text{-}Cl)]_2$ in acetone, $[Cp^*M(L')Cl]Cl$ complexes (**2** M = Rh, $L' = L^1$; **4** M = Ir, $L' = L^1$; **6** M = Rh, $L' = L^2$; **8** M = Ir, $L' = L^2$; **9** M = Rh, $L' = L^3$; **10** M = Ir, $L' = L^3$; **11** M = Ir, $L' = L^4$) have been prepared (Chart 1). In this solvent, no evidence of $[Cp^*MCl_3]^-$ formation, as in **1**, **3**, **5**, and **7**, is found.

Complexes **1**−**11** are stable both in the solid and solution states. Under an inert atmosphere, their solutions are stable indefinitely. IR (nujol) and NMR solution data ($CDCl_3$) are consistent with the η^5-Cp* and κ^2-L coordinations confirmed by single-crystal X-ray studies, with a doublet in the $^{13}C\{^1H\}$ NMR spectra of the rhodium derivatives in the range of 88−97 ppm ($J(^{13}C{-}^{103}Rh) \approx 8$ Hz), indicative of η^5-Cp* binding. In the IR spectra, ν(M−Cl) fall between 260 and 280 cm^{-1}, in accordance with the presence of single M−Cl bonds. Two sets of signals in the ^1H spectra, attributable to the Cp* protons, are always detected in the spectra of **1**, **3**, **5**, and **7**, in accordance with the existence in solution of the two ionic forms. When the ^1H NMR spectra of $[Cp^*M(L')Cl][Cp^*MCl_3]$ were measured in acetone, the immediate formation of $[Cp^*M(L')Cl]Cl$ was observed.

It is interesting to note that the $[Cp^*M(L')Cl]Cl$ compounds can be obtained by the reaction of $[Cp^*M(L')Cl][Cp^*MCl_3]$ with excess L′ ($L' = L^1$ or L^2, solvent = THF) (eq 1). On the other hand, the addition of the dimer

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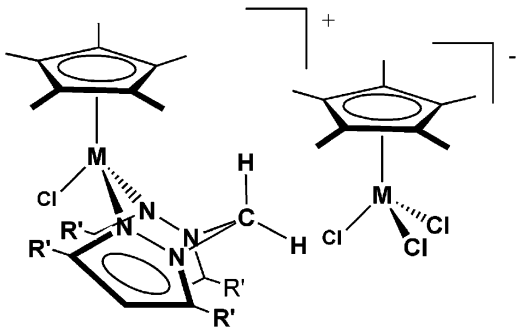
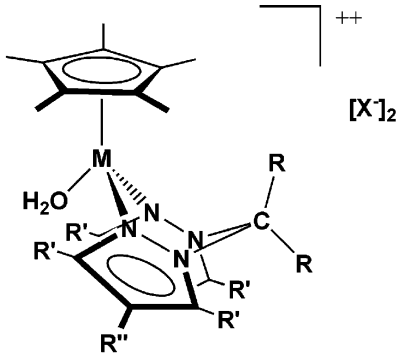
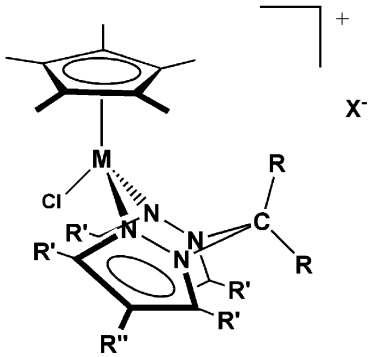
Chart 1



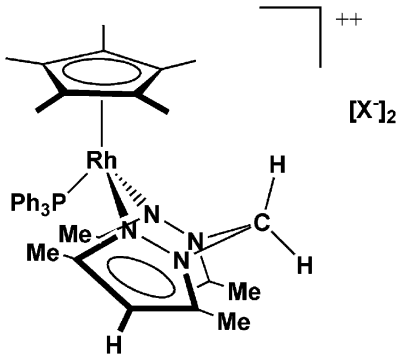
1: M = Rh, R' = H
3: M = Ir, R' = H
5: M = Rh, R' = Me
7: M = Ir, R' = Me



16: M = Rh, R = R' = R'' = H, X = O_3SCF_3
17: M = Ir, R' = Me, R = R'' = H, X = O_3SCF_3
18: M = Rh, R = Me, R' = R'' = H, X = O_3SCF_3
19: M = Ir, R = Me, R' = R'' = H, X = O_3SCF_3
20: M = Rh, R = R' = R'' = H, X = ClO_4



2: M = Rh, R = R' = R'' = H, X = Cl
4: M = Ir, R = R' = R'' = H, X = Cl
6: M = Rh, R = R'' = H, R' = Me, X = Cl
8: M = Ir, R = R'' = H, R' = Me, X = Cl
9: M = Rh, R = R' = H, R'' = Me, X = Cl
10: M = Ir, R = R' = H, R'' = Me, X = Cl
11: M = Ir, R' = R'' = H, R = Me, X = Cl
12: M = Rh, R = R' = R'' = H, X = O_3SCF_3
13: M = Rh, R = Me, R' = R'' = H, X = O_3SCF_3
14: M = Rh, R = Me, R' = R'' = H, X = O_3SCF_3
15: M = Ir, R = Me, R' = R'' = H, X = O_3SCF_3



21: [X^-] = Cl, O_3SCF_3

[Cp*MCl(μ-Cl)]$_2$ to [Cp*M(L′)Cl]Cl yields [Cp*M(L′)Cl]-[Cp*MCl_3] (L′ = L^1 or L^2, solvent = THF) (eq 2)

$$[Cp^*M(L')Cl][Cp^*MCl_3] + L \rightarrow 2[Cp^*M(L')Cl]Cl \quad (1)$$

$$[Cp^*M(L')Cl]Cl + {}^1/_2[Cp^*MCl(\mu\text{-}Cl)]_2 \rightarrow [Cp^*M(L')Cl][Cp^*MCl_3] \quad (2)$$

Compounds **12**−**15** [Cp*M(L′)Cl][CF_3SO_3] (**12** M = Rh, L′ = L^1; **13** M = Rh, L′ = L^2; **14** M = Rh, L′ = L^4; **15** M = Ir, L′ = L^4) have been prepared in one-pot syntheses by mixing equimolar quantities of the [Cp*MCl(μ-Cl)]$_2$ dimers and the N_2-donor ligand L^4, followed by the addition of the silver salt. Compounds **12**−**15** can also be prepared by the reaction between equimolar quantities of the [Cp*M(L′)Cl]-Cl species and silver triflate. These species, which are air and solution stable, are readily soluble in polar solvents. The substitution of only one chloride group is supported by the presence of the M−Cl stretching frequency in their IR spectra and by the characteristic absorption in the 1200−1000 cm^{-1} regions, attributable to an ionic SO_3CF_3 group.

In the ^{1}H−NMR spectra of **1**−**10**, **12**, and **13**, the bridging geminal methylene protons (L^1, L^2, and L^3 derivatives) are diastereotopic and appear as two doublets arising from a well-resolved AX system. In addition, in the spectra of **11**, **14**, and **15** (L^4 derivatives), the two anisochronous methyl groups appear as two singlets.

The ^{1}H-NOESY spectrum of complex **5** (Figure 1) shows strong dipolar interactions between the CH^{up} and Me^{Cp*} protons and between CH^{down} and Me^5 protons, with intensities comparable to those of the interactions between Me^5 (or Me^3) with H^4. By contrast, no dipolar interactions are present between the CH^{up} and Me^5 protons and between the CH^{down} and Me^{Cp*} protons. These observations are consistent with the preferential presence in solution of the boat conformer shown in Figure 1. In this conformation, the pyrazolyl rings

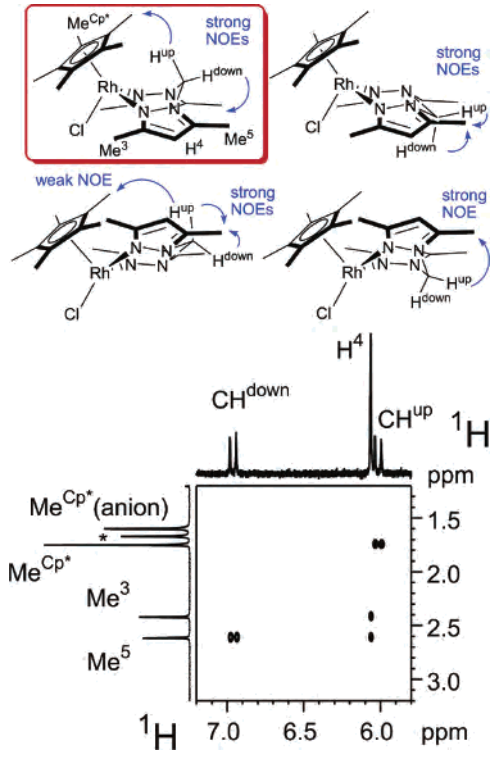


Figure 1. Section of ^{1}H-NOESY NMR spectrum (400.13 MHz, 296 K, CD_2Cl_2, mixing time = 800 ms) of complex **5**. On the top, the two boat and chair conformations of the metallacycle M(N−N)$_2$C are depicted with the expected NOEs between CH^{up} (and CH^{down}) and Me^5 (and Me^{Cp*}). The asterisk (*) denotes the resonance of H_2O.

are positioned far away from the encumbered Cp*. The same conformation of the metallacycle M(N−N)$_2$C is observed in the solid state for all complexes studied.

Upon warming of methanol or chloroform solutions of complexes **1**−**15** to 331 K, no changes were observed in the ^{1}H−NMR spectra, suggesting that they are very rigid molecules[20,21] in which the inversion of the metal center is very slow on the NMR scale.[22]

Finally, compounds **16**−**19**, [Cp*M(L′)(H$_2$O)][CF$_3$SO$_3$]$_2$ (**16** M = Rh, L′ = L^1; **17** M = Ir, L′ = L^2; **18** M = Rh, L′ = L^4; **19** M = Ir, L′ = L^4), which contain two triflate ions and one water molecule bonded to the Cp*M moiety (confirmed by X-ray and IR data), can be obtained in two different ways: (i) by mixing 1 equiv of [Cp*MCl(μ-Cl)]$_2$ with 2 equiv of N$_2$-donor ligands and 4 equiv of the silver salt and (ii) by the reaction of compounds **12**, **14**, and **15** with excess of the silver triflate. The presence of adventitious water can be attributed to the not rigorously anhydrous solvents employed for the recrystallization of **16**−**19**.

Compound **20** has been prepared with the same procedure reported for **16**−**19**, but with silver(I) perchlorate.

It is interesting to note that in **16** and **18**−**20**, the CH_3 or CH_2 protons of the methylene chain appear at room temperature as sharp singlets, suggesting that the inversion of the metal center for the dicationic water complexes is fast on the NMR scale, in accordance with the literature.[23] However, when the acetone solutions of **16** and **20** are cooled down to 210 K, two doublets from the resolved AB system appear, whereas in the case of **18** and **19**, two sharp signals are evident at 253 K. No change has been observed until 213 K.

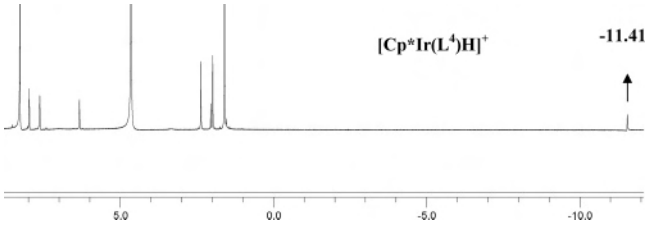


Figure 2. ^{1}H NMR spectrum (D_2O solution) of a mixture of **19** and $HCOONH_4$ in 1:3 molar ratio at 296 K (pH ≈ 7).

We have also observed that compounds **17** and **19**, soluble in water, react with ammonium formate, in the absence of reducible substrates, in water or acetone solution indifferently, yielding the hydride complex [Cp*Ir(L′)H]$^+$ (Figure 2), presumably through a β-hydrogen elimination with evolution of CO_2, in accordance with the literature.[11,12] It is interesting to note that in our case hydride generation occurs in the pH range of 3−7, independently of the solvent choice, whereas the amount of hydride formation depends on the ligand choice, the higher quantity being formed when the L^4 derivative **19** is employed.

When **13** reacts with an equimolar quantity of PPh_3, displacement of the chloride ligand from the Rh coordination sphere is observed, with the formation of the dicationic [Cp*Rh(L^2)PPh$_3$][Cl][SO$_3$CF$_3$] compound **21**. The ^{31}P NMR spectrum of **21** indicates coordination in solution of the P donor, the Rh−P coupling constant being similar to those reported for analogous Rh(III) species.[24]

NOE and PGSE NMR Measurements. The interionic structures in solutions of compounds **5** and **13** were studied by combining the information derived from NOE (nuclear Overhauser effect)[25] and PGSE (pulsed-field gradient spin−echo)[26] NMR experiments.

The relative anion−cation orientations in solution for complexes **5** and **13** ([Cp*Rh(L^2)Cl][X]) were investigated by recording ^{19}F,^{1}H-HOESY (X$^-$ = CF$_3$SO$_3^-$) and ^{1}H-NOESY (X$^-$ = [Cp*RhCl$_3$]$^-$) NMR spectra at room temperature (296 K) in CD_2Cl_2.

For complex **13**, strong interionic NOE contacts were observed between the fluorine atoms of $CF_3SO_3^-$ and the

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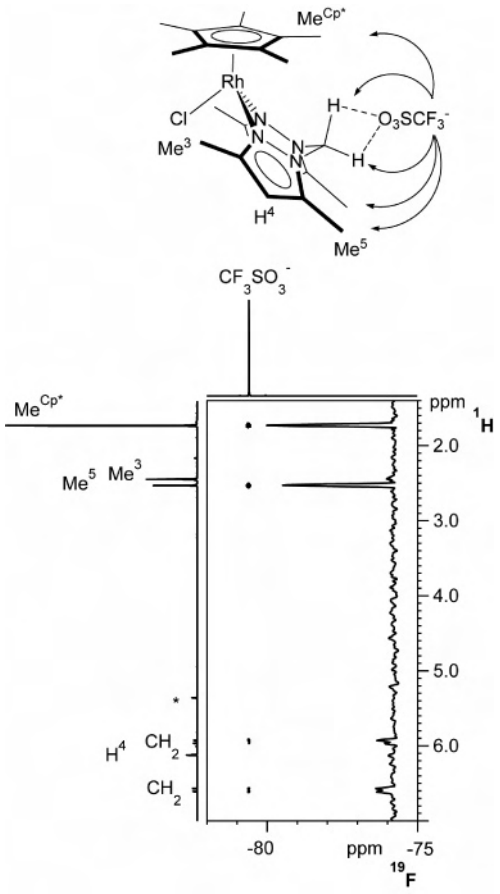

Figure 3. Section of ^{19}F-^{1}H-HOESY NMR spectrum (400.13 MHz, 296 K, CD_2Cl_2, mixing time = 800 ms) of complex **13**. The asterisk (*) denotes the resonance due to a residue of non-deuterated solvent.

Me^5 protons (Figure 3). Medium-sized NOEs were also detected with the Me^{Cp*} resonance, while weak NOEs were observed with the CH_2 resonance. The anion did not show any interaction with Me^3 and H^4. All these observations indicate that the $CF_3SO_3^-$ group lies close to the CH_2 moiety, between the two methyl groups in position 5 (Figure 3), as previously observed for octahedral Ru(II)[27] and square-planar Pd(II) and Pt(II)[28] complexes. In this position, the anion also has a dipolar interaction with the methyl groups of Cp* (Figure 3).

This single cation−anion orientation in solution deduced by NOE studies is consistent with that in the solid state. X-ray investigations of complexes containing Cl^- as counterion indicate that the cation lies close to two anions in the solid state (see below). Both anions are adjacent to the bis-(pyrazolyl)methane ligands, near to the CH_2-moiety and well removed from the chlorine ligand. The distances between the chloride anions and the methylene carbons are calculated

Table 1. Diffusion Coefficients (D_t, $\times 10^{10}$ m^2 s^{-1}), Hydrodynamic Radii (r_H, Å), Hydrodynamic Volumes (V_H, $Å^3$), and Aggregation Numbers (N) for Compounds **5** and **13** in CD_2Cl_2 as a Function of Concentration (C, mM)

entry	D_t^+	D_t^-	r_H^+	r_H^-	V_H^+	V_H^-	N^+	N^-	C
				5					
1	10.7	11.0	5.2	5.0	575	533	1.0	0.9	0.008
2	10.6	10.6	5.3	5.3	600	600	1.0	1.0	0.1
3	9.6	10.3	5.6	5.3	720	610	1.2	1.0	1.4
4	9.3	9.7	5.6	5.4	720	649	1.2	1.1	4.2
5	9.0	9.5	5.7	5.4	755	670	1.3	1.1	8.5
6	8.5	9.0	5.7	5.5	771	694	1.3	1.2	31
				13					
7	10.7	12.7	5.0	4.4	540	364	1.2	0.8	0.05
8	10.3	11.3	5.3	4.9	627	502	1.4	1.1	0.6
9	10.1	10.2	5.4	5.3	652	630	1.5	1.4	3.5
10	9.8	10.2	5.5	5.3	681	623	1.6	1.4	7.2
11	9.6	10.0	5.5	5.3	674	616	1.6	1.4	30.0

to lie in the range of 3.3−3.7 Å and indicate the presence of electrostatic $C-H^{\delta+}\cdots Cl^{\delta-}$ interactions[29] (cf. the X-ray work, below). For complex **5**, containing the $[Cp^*RhCl_3]^-$ counterion, the ^{1}H-NOESY NMR spectrum does not show any interionic dipolar interactions between the Me^{Cp*} resonance of the anion and the cationic protons. This suggests that the $[Cp^*RhCl_3]^-$ species approaches the cation orienting the three Cl legs of the "piano-stool" toward the cation and, plausibly, toward the CH_2-moiety of the cation where the positive charge is mainly accumulated.[27,28] Again, this orientation is consistent with that found in the solid state where the organometallic anion that is closest to the cation orients the three chlorines toward the methylene carbon (Figure 4). The distances between the chlorine legs and the methylene carbons are in the range of 3.3−4.0 Å, establishing in this case also the $C-H^{\delta+}\cdots Cl^{\delta-}$ interaction.

^{1}H- and ^{19}F-PGSE NMR experiments were carried out for complexes **5** and **13** in CD_2Cl_2 using TMSS as internal standard (TMSS = [tetrakis-(trimethylsilyl)silane]). PGSE measurements allowed the translational self-diffusion coefficients (D_t) for both cationic (D_t^+) and anionic (D_t^-) moieties (Table 1) to be determined. By applying (see the Experimental Section) the Stokes−Einstein equation $D_t = kT/c\pi\eta r_H$, where k is the Boltzman constant, T is the temperature, c is a numerical factor,[18] and η is the solution viscosity, the average hydrodynamic radii for the anionic (r_H^+) and cationic (r_H^-) moieties were measured (Table 1). Their hydrodynamic volumes (V_H) were obtained from r_H, assuming the aggregates to have a spherical shape. From the ratio between V_H and the Van der Waals (V_{VdW}) volumes of the ion pairs, known from the solid state (Experimental Section), the cationic (N^+) and anionic (N^-) aggregation numbers were evaluated (Table 1). Because, a distribution of ionic species is present in solution, N^+ and N^- indicate the apparent average aggregation number of the ionic moieties. For example, if they are both equal to 1 or 2, this means that either ion pairs or ion quadruples, that is, $(Ru^+X^-)_2$, are the predominant species in solution, respectively. On the other hand, if N^+, N^-, or both are lower than 1, then free ions are

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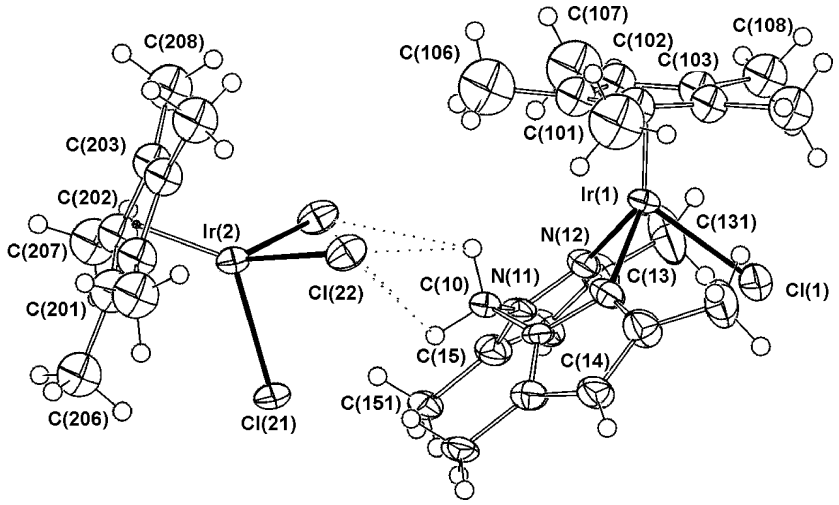

Figure 4. Anion−cation orientations in the solid state for compound **7** (Projection quasi-normal to the crystallographic mirror plane).

Table 2. Metal Atom Environments (bond distances, Å, and angles, deg)

atom/M/X	**4**/Ir/Cl	**6**·2H₂O/Rh/Cl	**15**/Ir/Cl	**16**/Rh/OH₂	**18**/Rh/OH₂
M−N(12)	2.053(7)	2.131(2)	2.083(5)	2.115(2)	2.118(4)
M−N(22)	2.073(7)	2.124(2)	2.083(6)	2.118(1)	2.114(3)
M−Ar(cp)	2.108(8)	2.155(2)	2.138(7)	2.127(2)	2.138(4)
	−2.172(8)	−2.176(2)	−2.168(8)	−2.172(2)	−2.159(3)
⟨ ⟩	2.14(2)	2.167(9)	2.153(11)	2.15(2)	2.150(9)
M−Ar(0)	1.76_9	1.78_4	1.77_9	1.76_3	1.76_8
M−X	2.383(2)	2.4136(6)	2.401(2)	2.185(1)	2.172(3)
X−M−N(12)	85.9(2)	87.57(4)	83.8(2)	83.88(5)	81.0(1)
X−M−N(22)	87.0(2)	87.86(6)	84.2(2)	81.54(5)	81.7(1)
X−M−Ar(0)	$128._4$	$124._5$	$123._6$	$129._2$	$127._7$
N(12)−M−N(22)	82.9(3)	86.49(7)	86.1(2)	87.31(5)	86.3(1)
N(12)−M−Ar(0)	$126._9$	$128._5$	$131._8$	$129._1$	$131._5$
N(22)−M−Ar(0)	$130._3$	$128._4$	$130._9$	$129._3$	$130._6$

present in solution. If only free ions were present in solution, N^+ and N^- should be 0.60 and 0.40 for **5** and 0.84 and 0.16 for **13**. PGSE NMR data reported in Table 1 clearly indicate that complexes **5** and **13** are mainly present in CD_2Cl_2 as ion pairs even at micromolar concentration (entries 1 and 7). These findings suggest that, in addition to the electrostatic forces, specific $C-H^{\delta+}\cdots X^{\delta-}$ (X = O for complex **13** and Cl for complex **5**) interactions occur in solution as previously described.[28] In addition, an increase of the salt concentration causes further aggregation with the formation of aggregates higher than that of ion pairs (entries 6 and 9−11);[16] the tendency seems less in compound **5**, compared to compound **13**.

Crystal Structures. A number of the present molecular geometries for all complexes studied, except **5**, **7**, and the dichloromethane solvate of **6** (which, for the cations, may be regarded as represented by more precisely determined similar (or identical) species), are presented in Table 3. In **5**, in the $[Cp^*RhCl_3]^-$ counterion, which, like the cation, lies on a crystallographic mirror plane, Rh−Cl distances are 2.421(4) and 2.428(3) (×2) Å with the Rh−Cp (centroid) being 1.76_5 Å; the Cp (centroid)−Rh−Cl angles range between 121.73(7) and 126.3(1)°, with Cl−Rh−Cl being 90.0(1) (×2) and 92.8(1)°, harmonious with the values of ref 19. In **7**, in the anion, the Ir−Cl distances are 2.427(6) and 2.427(5) (×2) Å, with Ir−Cp (centroid) being 1.76_3 Å; the Cp (centroid)−Ir−Cl angles range between 125.75(9) and 127.5(2)° with Cl−Ir−Cl being 89.4(2) and 87.8(2)° (×2). For the most precisely determined $[Cp^*M(L')Cl]^+$ cations of **6** and **15**, the values of Table 3 differ little from those of the neutral counterpart molecules of the scorpionates of ref 7; in **16** and **18**, where the X ligand is aqua, the exchange appears to have little impact on the remainder of the coordination environment. In **16**, in particular, there are interesting hydrogen-bonding interactions with the oxygen atoms of the triflate anions (Figure 5).

In **4**, **6**·2H₂O, **15**, **16**, and **18**·3H₂O, a single formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. In **4**, with water molecule hydrogen atoms postulated from difference map evidence, we find that in projection down *a*, as set, the anions and solvent molecules comprise a well-defined ribbon down the center of the cell (Cl(2)···O(1), H(1a); O(1), H(1a)($\bar{x}$, $\bar{y}$, $\bar{z}$) 3.170(7), 2.7 (est (estimated); 3.216(7), 2.7 Å (est)) bounded by columns of cations. There are contacts to the CH_2 hydrogen atoms of the L′ ligands (Cl(2)···C(0), H(0a), H(0b) ($\bar{x}$, $\bar{y}$, $\bar{z}$) 3.565(9), 2.7 Å (×2)), although there are stronger interactions to either side with the pyrazole ring hydrogen atoms. Compounds **5** and **7** are "isomorphous", with "disorder" being resolvable in the former but not the latter. Cations and anions approach each other pairwise as depicted in Figure 4; for **7**, the Cl_3 component of the anion embraces the CH_2 bridge of the cation. In the better-defined Ir complex, **7**, C(10), H(101,102)···Cl(22) are 3.35(2), 3.0,

Table 3. Crystal/refinement Data

	4·H_2O[a]	**5**	**6**·$2H_2O$[b]	**6**·$^1/_2CH_2Cl_2$	**7**	**15**	**18**·$3H_2O$	**16***
formula	$C_{17}H_{25}Cl_2IrN_4O$	$C_{31}H_{46}C_{l4}N_4Rh_2$	$C_{21}H_{35}Cl_2N_4O_2Rh$	$C_{21.5}H_{32}Cl_3N_4Rh$	$C_{31}H_{46}Cl_4Ir_2N_4$	$C_{20}H_{27}ClF_3IrN_4O_3$	$C_{21}H_{35}F_6N_4O_{10}RhS2$	$C_{19}H_{25}F_6N_4O_7RhS_2$
M_r (Da)	564.6	822.4	549.3	555.8	1000.9	688.2	784.6	702.5
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/m$ (No. 11)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/m$ (No. 11)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	Cc (No. 19)
a (Å)	7.542(3)	9.623(3)	15.765(2)	12.602(4)	9.6379(8)	22.596(5)	11.184(3)	18.293(3)
b (Å)	8.536(3	14.176(4)	8.3050(10)	13.993(5)	14.1369(9))	8.570(2)	23.044(6)	10.2940(10)
c (Å)	15.912(6)	13.315(4)	18.554(2)	17.467(6)	14.047(2)	23.910(5)	13.132(3)	14.626(4)
β (deg)	99.460(6)	99.136(5)	90.261(9)	82.048(5)	110.073(8)	91.232(4)	113.902(4)	105.891(7)
V (Å^3)	972.8	1793	2429	2652	1798	4624	3094	2649
T (K)	153	153	100	153	100	153	153	100
D_c (g cm^{-3})	1.927	1.244	1.502	1.392	1.849	1.977	1.684	1.76_1
Z	2	2	4	4	2	8	4	4
μ_{Mo} (mm^{-1})	7.2	1.24	0.95	0.91	7.7	6.0	0.78	0.89
specimen (mm^3)	0.07 × 0.05 × 0.03	0.35 × 0.25 × 0.03	0.38 × 0.24 × 0.12	0.28 × 0.17 × 0.06	0.28 × 0.21 × 0.055	0.08 × 0.07 × 0.03	0.24 × 0.13 × 0.12	0.28 × 0.26 × 0.19
$T_{min/max}$	0.57	0.60	0.85	0.57	0.37	0.58	0.85	0.93
N_t	8815	16 722	71 975	22 725	9406	21 808	28 712	44 821
$2\theta_{max}$ (deg)	55	52.5	70	50	50	52.5	58	76
N	4298	3782	10 706	9126	3265	4690	7818	13 535
R_{int}	0.052	0.096	0.036	0.075	0.071	0.064	0.045	0.030
N_o ($I > 2\sigma(I)$)	4298	2516	8169	9126	2635	3385	6128	11410
R1	0.052	0.10	0.037	0.10	0.084	0.060	0.043	0.034
wR2	0.12	0.12	0.103	0.12	0.22	0.093	0.12	0.060
GOF	1.14	1.13	1.10	1.17	1.09	1.14	1.09	1.010

[a] α, γ = 102.563(6), 97.057(6)°. [b] α, γ = 74.662(5), 63.242(5)°.

2.9 Å (est). Compound **6** is described in two phases. In the better defined form, modeled as a dihydrate, the anions and solvent molecules are modeled with a considerable degree of disorder, forming a ribbon, seen at the center of the cell in projection down *b* contained to either side by the planes of the Cp* ligands, the bridging CH group of the cation interacting with the chloride of an adjacent cation (Cl(1)···C(10), H(10B) (x, 1 + y, z) 3.659(3), 2.7 Å (est). In the other phase, modeled as a dichloromethane hemisolvate, two ion pairs plus a disordered solvent molecule make up the asymmetric unit of the structure; one of the anions (Cl(01/03), is also disordered. Contacts are found from C(10), H(10B) of cation 1 to Cl(01) ($\bar{x}$, 1 − y, $\bar{z}$) 3.711(9), 2.8 (est) and from C(10), H(10A) to component Cl(02) (1 + x, y, z) (3.30(1), 2.7 Å (est)), the CH_2 group of cation 2 interacting more strongly with a solvent fragment.

In **15**, where the anion is triflate, the closest interactions arise from the oxygen atoms to peripheral pyrazole hydrogen atoms: O(11)···C, H(23) (1/2 + x, 1/2 + y, z) 3.20(1), 2.3 (est); O(12)···C, H(25) (1/2 − x, 1/2 + y, $\bar{z}$) 3.05(1), 2.2 Å (est). In **16** and **18**, unsurprisingly, the coordinated water molecules are found to interact strongly with the anions, triflates in both cases. In **16**, as noted above, these are straightforward (Figure 5): O(1), H(1B)···O(11) 2.689(2), 1.8 (est); O(1), H(1A)···O(22) 2.715(2), 1.8 Å (est)). In **18** (which is hydrated), a more extended network is found, the hydrogen atoms of the coordinated water molecule hydrogen bonding to other uncoordinated water molecule oxygen atoms: O(1), H(1a)···O(2) 2.658(5), 1.7 (est); O(1), H(1b)···O(3) 2.658(6), 1.8 Å (est). The hydrogen atoms of the latter (O(2,3)) in turn then hydrogen bond further afield, one to a residue assigned as a water molecule oxygen atom O(4) (for which no hydrogen atoms were located, although plausible interactions could be postulated with triflate oxygen atoms: O(4)···O(21), O(21) ($\bar{x}$, $\bar{y}$, $\bar{z}$) 2.88(1) (×2) Å) and the two triflate anions, one linking the residues into a polymer.

Experimental Section

Materials and Methods. All chemicals and reagents were of reagent grade quality and were used as received without further purification. All solvents were distilled prior to use. THF and light petroleum (310−333 K) were dried by refluxing over freshly cut sodium. Dichloromethane was freshly distilled from CaH_2. Other solvents were dried and purified by standard procedures. The samples were dried in vacuo to constant weight (293 K, 0.1 Torr). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNSO-elemental analyzer. IR spectra from 4000 to 150 cm^{-1} were recorded with a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H and ^{13}C{^{1}H} NMR solution spectra were recorded on a VXR-300 Varian spectrometer (300 for ^{1}H and 75 MHz for ^{13}C, respectively). One- and two-dimensional ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were measured on Bruker DRX 400 spectrometers. Referencing is relative to TMS (^{1}H and ^{13}C), CCl_3F(^{19}F), and 85% H_3PO_4 (^{31}P). NMR samples were prepared by dissolving a suitable amount of compound in 0.5 mL of solvent.

Syntheses. [Cp*Rh(L^1)Cl][Cp*RhCl$_3$] (1). A THF solution containing [Cp*RhCl(μ-Cl)]$_2$ (0.182 g, 0.294 mmol) and L^1 (0.087 g, 0.588 mmol) was stirred for 48 h under N_2 at room temperature. The resulting orange precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of THF and recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C) and shown to be compound **1** (0.200 g, 0.261 mmol, yield 89%). mp: 208−210 °C. Anal. Calcd for $C_{27}H_{38}Cl_4Rh_2N_4$: C, 42.32; H, 5.00; N, 7.31. Found: C, 41.96; H, 4.92; N, 7.27. IR (nujol, cm^{-1}): 3098w, 1768w, 1631s, 1508w ν(C···C, C···N), 450w, 398w, 277s ν(Rh−Cl). ^{1}H NMR (CD_3OD, 293 K): δ 1.57 (s, 15H, CH_{3Cp*}), 1.64 (s, 15H, CH_{3Cp*}), 6.26, 6.87 (d, 2H$_{gem}$, CH_2(pz)$_2$, ^2J = 14.3 Hz), 7.28 (s, 2H, *H4*), 7.48 (d, 2H, *H5*), 9.37 (s, 2H, *H*3). ^{1}H NMR (DMSO, 293 K): δ 1.50 (s, 15H, CH_{3Cp*}), 1.63 (s, 15H, CH_{3Cp*}), 6.26, 6.68 (d, 2H, CH_2, $^2J_{gem}$ = 14.3 Hz), 7.15 (s, 2H, *H4*), 7.63 (d, 2H, *H5*), 9.78 (s, 2H, *H3*). ^{13}C NMR (CD_3OD, 293 K): δ, 8.74 (s, *C*H$_{3Cp*}$), 8.90 (s, *C*H$_{3Cp*}$), 57.61 (s, *C*H$_2$), 94.60 (dbr, C$_{Cp*}$),

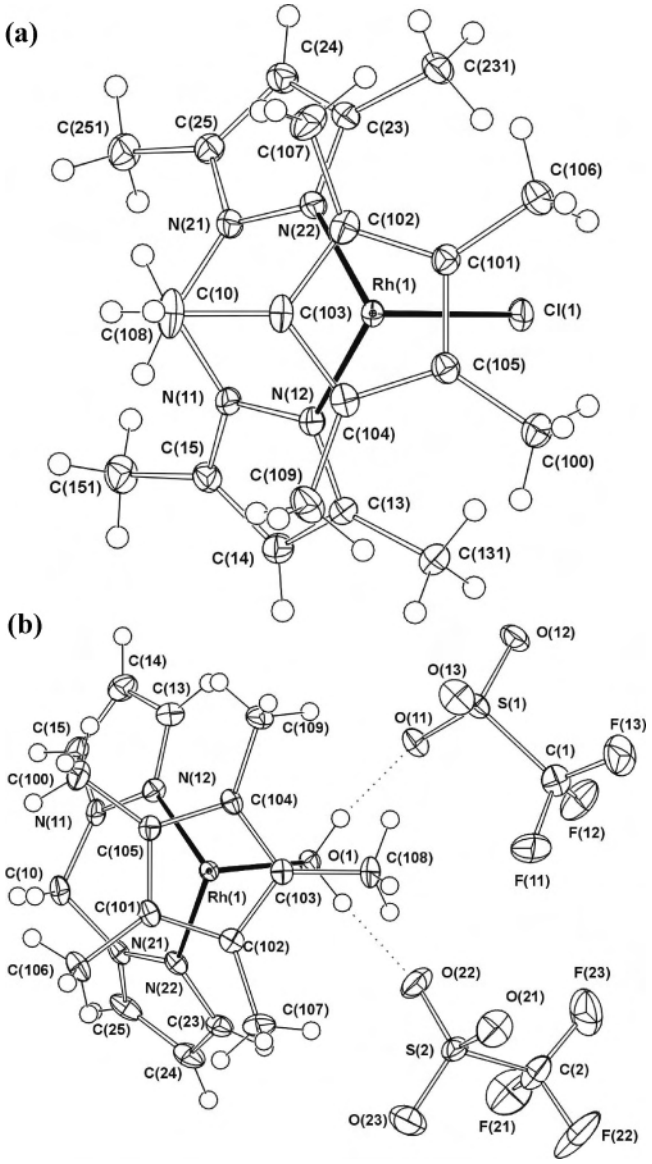

Figure 5. Projections of individual molecules (ions) of (a) **6a** and (b) **16**.

97.30 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C) = 8.5$ Hz), 121.36(s, *C4*), 131.81 (s, *C5*), 140.84 (s, *C3*).

[Cp*Rh(L¹)Cl][Cl]·H₂O (2). An acetone solution (10 mL) containing $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.182 g, 0.294 mmol) and L^1 (0.087 g, 0.588 mmol) was stirred for 6 h under N_2 at room temperature. The resulting orange precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of acetone and recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C) and shown to be compound **2** (0.095 g, 68% yield). mp: 217−219 °C. Anal. Calcd for $C_{17}H_{25}Cl_2N_4ORh$: C, 42.32; H, 5.39; N, 11.00. Found: C, 42.69; H, 5.30; N, 11.19. IR (nujol, cm^{-1}): 3380wbr, 1530w, 1507w ν(C⋯C, C⋯N), 274s ν(Rh−Cl). ^{1}H NMR (CD_3OD, 293 K): δ 1.74 (s, 15H, C*H*$_{3Cp^*}$), 6.06, 6.98 (d, 2H$_{gem}$, C*H*$_2$, $^2J_{gem} = 14.7$ Hz), 6.62 (t, 2H, *H4*), 7.92 (d, 2H, *H5*), 8.17 (d, 2H, *H3*). ^{1}H NMR (CD_3OD, 331K): δ 1.74 (s, 15H, C*H*$_{3Cp^*}$), 6.06, 6.98 (d, 2H, C*H*$_2$, $^2J_{gem} = 14.7$ Hz), 6.59 (t, 2H, *H4*), 7.89 (d, 2H, *H5*), 8.14 (d, 2H, *H3*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.70 (s, *C*H$_{3Cp^*}$), 64.38 (s, *C*H$_2$), 97.04 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C) = 8.5$ Hz), 108.45 (s, *C4*), 137.20 (s, *C5*), 144.29 (s, *C3*).

[Cp*Ir(L¹)Cl][Cp*IrCl₃] (3). Compound **3** (0.236 g, 0.249 mmol, yield 85%) was prepared following a procedure similar to that reported for **1** using $[Cp^*IrCl(\mu\text{-}Cl)]_2$ and L^1. mp: 258−260 °C. Anal. Calcd for $C_{27}H_{38}Cl_4N_4Ir_2$: C, 34.32; H, 4.05; N, 5.93. Found: C, 34.26; H, 4.24; N, 5.82. IR (nujol, cm^{-1}): 3114w, 1515w, ν(C⋯C, C⋯N), 279s ν(Ir−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.66 (s, 15H, C*H*$_{3Cp^*}$), 1.71 (s, 15H, C*H*$_{3Cp^*}$), 5.68, 9.05 (d, 2H, C*H*$_2$, $^2J_{gem} = 14.0$ Hz), 6.46 (t, 2H, *H4*), 7.64 (d, 2H, *H5*), 9.37 (d, 2H, *H3*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.18 (s, *C*H$_{3Cp^*}$), 9.41 (s, *C*H$_{3Cp^*}$), 63.22 (s, *C*H$_2$), 88.92 (s, C_{Cp^*}), 108.80 (s, *C4*), 136.40 (s, *C5*), 144.35 (s, *C3*).

[Cp*Ir(L¹)Cl][Cl]·H₂O (4). Compound **4** (0.112 g, 0.198 mmol, yield 67%) was prepared following a procedure similar to that reported for **2** using $[Cp^*IrCl(\mu\text{-}Cl)]_2$ and L^1. mp: 214−215 °C. Anal. Calcd for $C_{17}H_{25}Cl_2IrN_4O$: C, 36.17; H, 4.46; N, 9.92. Found: C, 35.75; H, 4.48; N, 9.65. IR (nujol, cm^{-1}): 3400br, 3111w, 1514 m, ν(C⋯C, C⋯N), 275s ν(Ir−Cl). ^{1}H NMR (CD_3OD, 293 K): δ 1.71 (s, 15H, C*H*$_{3Cp^*}$), 5.88, 7.03 (d, 2H, C*H*$_2$, $^2J_{gem} = 14.6$ Hz), 6.65 (t, 2H, *H4*), 7.88 (d, 2H, *H5*), 8.15 (d, 2H, *H3*). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.70 (s, 15H, C*H*$_{3Cp^*}$), 5.77, 9.07 (d, 2H, C*H*$_2$, $^2J_{gem} = 14.6$ Hz), 6.48 (t, 2H, *H4*), 7.65 (d, 2H, *H5*), 8.71 (d, 2H, *H3*). ^{13}C NMR (CD_3OD, 293 K): δ 9.18 (s, *C*H$_{3Cp^*}$), 64.31 (s, *C*H$_2$), 90.71 (s, C_{Cp^*}), 110.13 (s, *C4*), 135.92 (s, *C5*), 147.06 (s, *C3*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.38 (s, *C*H$_{3Cp^*}$), 62.89 (s, *C*H$_2$),88.95 (s, C_{Cp^*}), 108.85 (s, *C4*), 136.29 (s, *C5*), 144.49 (s, *C3*).

[Cp*Rh(L²)Cl][Cp*RhCl₃] (5). Compound **5** (0.210 g, 0.279 mmol, yield 87%) was prepared following a procedure similar to that reported for **1** using $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and L^2. mp: 280−281 °C. Anal. Calcd for $C_{31}H_{46}Cl_4N_4Rh_2$: C, 43.41; H, 5.41; N, 6.53. Found: C, 43.30; H, 5.31; N, 6.60. IR (nujol, cm^{-1}): 3400br, 1556s, ν(C⋯C, C⋯N), 279s ν(Rh−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.63 (s, 15H, C*H*$_{3Cp^*}$), 1.76 (s, 15H, C*H*$_{3Cp^*}$), 2.41 (s, 6H, *5*-C*H*$_3$), 2.62 (s, 6H, *3*-C*H*$_3$), 6.09, 7.06 (d, 2H, C*H*$_2$, $^2J_{gem} = 14.3$ Hz), 5.99 (s, 2H, *H4*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.56 (s, *C*H$_{3Cp^*}$), 10.12 (s, *C*H$_{3Cp^*}$), 12.54 (s, *5*-*C*H$_3$), 15.12 (s, *3*-*C*H$_3$), 59.77 (s, *C*H$_2$), 94.10 (dbr, C_{Cp^*}), 97.03 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C) = 7.8$ Hz), 109.16 (s, *C4*), 144.61 (s, *C5*), 154.36 (s, *C3*).

[Cp*Rh(L²)Cl][Cl]·2H₂O (6). Compound **6** (0.122 g, 0.222 mmol, yield 75%) was prepared following a procedure similar to that reported for **2** using $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and L^2. mp: 281−283 °C. Anal. Calcd for $C_{21}H_{35}Cl_2N_4O_2Rh$: C, 45.92; H, 6.42; N, 10.20. Found: C, 45.64; H, 6.64; N, 10.24. IR (nujol, cm^{-1}): 3400sbr, 1560 m, 1531w, 1519w ν(C⋯C, C⋯N), 274s ν(Rh−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.73 (s, 15H, C*H*$_{3Cp^*}$), 2.38 (s, 6H, *5*-C*H*$_3$), 2.58 (s, 6H, *3*-C*H*$_3$), 6.06, 7.04 (d, 2H, C*H*$_2$, $^2J_{gem} = 16.6$ Hz), 5.98 (s, 2H, *H4*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.56 (s, *C*H$_{3Cp^*}$), 12.52 (s, *5*-*C*H$_3$), 15.24 (s, *3*-*C*H$_3$), 59.77 (s, *C*H$_2$), 96.97 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C) = 8.3$ Hz), 109.16 (s, *C4*), 144.61 (s, *C5*), 154.36 (s, *C3*).

[Cp*Ir(L²)Cl][Cp*IrCl₃] (7). Compound **7** (0.224 g, 0.223 mmol, yield 76%) was prepared following a procedure similar to that reported for **1** using $[Cp^*IrCl(\mu\text{-}Cl)]_2$ and L^2. mp: 105−106. °C. Anal. Calcd for $C_{31}H_{46}Cl_4N_4Ir_2$: C, 35.93; H, 4.47; N, 5.41. Found: C, 36.29; H, 4.76; N, 5.53. IR (nujol, cm^{-1}): 3400br, 1556s, ν(C⋯C, C⋯N), 278s ν(Ir−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.62 (s, 15H, C*H*$_{3Cp^*}$), 1.71 (s, 15H, C*H*$_{3Cp^*}$), 2.41 (s, 6H, *5*-C*H*$_3$), 2.71 (s, 6H, *3*-C*H*$_3$), 5.88, 7.20 (d, 2H, C*H*$_2$, $^2J_{gem} = 16.6$ Hz), 6.05 (s, 2H, *H4*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.07 (s, *C*H$_{3Cp^*}$), 9.83 (s, *C*H$_{3Cp^*}$), 12.58 (s, *5*-*C*H$_3$), 15.04 (s, *5*-*C*H$_3$), 61.90 (s, *C*H$_2$), 96.20 (s, C_{Cp^*}), 88.83 (s, C_{Cp^*}), 109.01 (s, *C4*), 144.25 (s, *C5*), 154.03 (s, *C3*).

[Cp*Ir(L²)Cl][Cl]·2H₂O (8). Compound **8** (0.160 g, 0.250 mmol, yield 85%) was prepared following a procedure similar to that reported for **2** using $[Cp^*IrCl(\mu\text{-}Cl)]_2$ and L^2. mp: 107−108

°C (dec). Anal. Calcd for $C_{21}H_{35}N_4Cl_2O_2Ir$: C, 39.49; H, 5.52; N, 8.77. Found: C, 39.60; H, 5.50; N, 8.45. IR (nujol, cm^{-1}): 3390br ν(O−H, H_2O), 3121w, 3083w ν(C−H), 1620br, 1556s ν(C⋯C, C⋯N), 1281s, 1029s, 453w, 362w, 278s ν(Ir−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.70 (s, 15H, CH_{3Cp^*}), 2.40 (s, 6H, *5*-CH_3), 2.67(s, 6H, *3*-CH_3), 5.90, 7.20 (d, 2H, CH_2, $^2J_{gem}$ = 16.5 Hz), 6.05 (s, 2H, *H4*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.83 (s, *C*H_{3Cp^*}), 12.58 (s, *5*-*C*H_3), 15.05 (s, *3*-*C*H_3), 61.90 (s, *C*H_2), 88.83 (s, C_{Cp^*}), 109.02 (s, *C4*), 144.26 (s, *C5*), 154.04 (s, *C3*).

[Cp*Rh(L^3)Cl][Cl] (9). A THF solution containing [Cp*RhCl(μ-Cl)]$_2$ (0.182 g, 0.294 mmol) and L^3 (0.103 g, 0.588 mmol) was stirred for 96 h at room temperature under N_2. The resulting red precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of THF and recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C) and shown to be compound **9** (0.262 g, 0.538 mmol, yield 91%). mp: 237−239 °C. Anal. Calcd for $C_{19}H_{27}Cl_2N_4Rh$: C, 47.07; H, 5.61; N, 11.45. Found: C, 46.64; H, 5.44; N, 11.24. IR (nujol, cm^{-1}): 1560w, 1541w ν(C⋯C, C⋯N), 2.92s, 279s ν(Rh−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.71 (s, 15H, CH_{3Cp^*}), 2.04 (s, 6H, *4*-CH_3), 5.80, 8.57 (d, 2H$_{gem}$, CH_2(pz)$_2$, ^2J = 14.2 Hz), 7.45 (s, 2H, H_5-pz), 8.42 (s, 2H, H_3-pz). ^{13}C NMR (CD_2Cl_2, 293 K): δ 9.16 (s, *4*-*C*H_3), 9.65 (s, *C*H_{3Cp^*}), 63.00 (s, CH_2), 96.80 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C)$ = 8.5 Hz), 119.23 (s, *C4*), 135.33 (s, C*5*), 144.74 (s, *C3*).

[Cp*Ir(L^3)Cl][Cl] (10). Compound **10** (0.288 g, 0.500 mmol, yield 85%) was prepared following a procedure similar to that reported for **4** using [Cp*IrCl(μ-Cl)]$_2$ and L^3. mp: 292−294 °C (dec). Anal. Calcd for $C_{19}H_{27}Cl_2N_4Ir$: C, 39.72; H, 4.74; N, 9.75. Found: C, 39.33; H, 4.82; N, 9.56. IR (nujol, cm^{-1}): 1569w ν(C⋯C, C⋯N), 311s, 300s, 257w, ν(Ir−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.67 (s, 15H, CH_{3Cp^*}), 2.06 (s, 6H, *4*-CH_3), 5.48, 9.06 (d, 2H, CH_2, $^2J_{gem}$ = 13.8 Hz), 7.42 (s, 2H, *H5*), 8.44 (s, 2H, *H3*). ^{13}C NMR (CD_2Cl_2, 293 K): δ 9.13 (s, *C*H_{3Cp^*}), 31.13 (s, *4*-*C*H_3), 62.49 (s, CH_2), 88.71 (s, C_{Cp^*}), 119.23 (s, *C4*), 134.67 (s, C*5*), 144.24 (s, *C3*).

[Cp*Ir(L^4)Cl][Cl] (11). Compound **11** (0.320 g, 0.560 mmol, yield 85%) was prepared following a procedure similar to that reported for **9** using [Cp*IrCl(μ-Cl)]$_2$ and an excess of L^4 (1:6). mp: 278−279 °C. Anal. Calcd for $C_{19}H_{27}Cl_2IrN_4$: C, 39.72; H, 4.74; N, 9.75. Found: C, 39.33; H, 4.72; N, 9.46. IR (nujol, cm^{-1}): 1537w, 1509sw ν(C⋯C, C⋯N), 367s, 245s ν(Ir−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.67 (s, 15H, CH_{3Cp^*}), 2.22, 2.87 (sbr, 6H, CH_{3gem}), 6.59 (sbr, 2H, *H4*), 7.70 (m, 2H, *H5*), 8.41 (sbr, 2H, *H3*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.24 (s, *C*H_{3Cp^*}), 27.60 (s, C(*C*H_3)$_2$), 79.93 (s, CH_2), 89.18 (s, C_{Cp^*}), 109.27 (s, *C4*), 133.77 (s, C*5*), 147.03 (s, *C3*).

[Cp*Rh(L^1)Cl][CF$_3$SO$_3$]·2H$_2$O (12). A CH_2Cl_2 solution containing [Cp*RhCl(μ-Cl)]$_2$ (0.182 g, 0.294 mmol) and L^3 (0.087 g, 0.588 mmol) and $AgCF_3SO_3$ (0.151 g, 0.588 mmol) was stirred at room temperature under N_2. After 2 h, a colorless precipitate formed, which was isolated by filtration and shown to be AgCl. The clear orange solution obtained was evaporated under vacuum, and the residue was washed with light petroleum and shown to be compound **12** (0.270 g, 0.444 mmol, yield 75%). It was recrystallized from CH_2Cl_2/light petroleum (40−60 °C). mp: 251−252 °C. Anal. Calcd for $C_{18}H_{27}ClF_3N_4O_5RhS$: C, 35.63; H, 4.48; N, 9.23. Found: C, 36.05; H, 4.33; N, 9.34. IR (nujol, cm^{-1}): 3535br ν(H_2O), 3117s ν(CF_3SO_3), 1524w ν(C⋯C, C⋯N), 1266s ν(CF_3SO_3), 279s ν(Rh−Cl). ^1H NMR (CD_2Cl_2, 293 K): δ 1.58 (s, 4H, H_2O), 1.73 (s, 15H, CH_{3Cp^*}), 6.03, 7.34 (d, 2H, CH_2, $^2J_{gem}$ = 14.6 Hz), 6.52 (t, 2H, *H4*), 7.75 (d, 2H, *H5*), 8.27 (d, 2H, *H3*). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.25 (s, CH_{3Cp^*}), 62.77 (s, CH_2), 97.03 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C)$ = 8.2 Hz), 108.92 (s, *C4*), 135.57 (s, *C5*), 145.64 (s, *C3*).

[Cp*Rh(L^2)Cl][CF$_3$SO$_3$] (13). Compound **13** (0.262 g, 0.442 mmol, yield 75%) was prepared following a procedure similar to that reported for **12** using [Cp*RhCl(μ-Cl)]$_2$, L^2, and $AgCF_3SO_3$. Anal. Calcd for $C_{22}H_{31}F_3N_4O_3RhS$: C, 44.68; H, 5.28; N, 9.47. Found: C, 44.60; H, 5.14; N, 9.22. IR (nujol, cm^{-1}): 3535br ν(H_2O), 3114s ν(CF_3SO_3), 1560 m, 1531w, 1519w, ν(C⋯C, C⋯N), 270s ν(Rh−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.76 (s, 15H, CH_{3Cp^*}), 2.43 (s, 6H, *5*-CH_3), 2.50 (s, 6H, *3*-CH_3), 5.95, 6.70 (d, 2H, CH_2, $^2J_{gem}$ = 15.8 Hz), 6.03 (s, 2H, *H4*).

[Cp*Rh(L^4)Cl][CF$_3$SO$_3$] (14). Compound **14** (0.232 g, 0.490 mmol, yield 70%) was prepared following a procedure similar to that reported for **12** using [Cp*RhCl(μ-Cl)]$_2$, L^4, and $AgCF_3SO_3$. Anal. Calcd for $C_{20}H_{27}F_3N_4O_3RhS$: C, 42.64; H, 4.83; N, 9.94. Found: C, 42.33; H, 5.04; N, 9.64. IR (nujol, cm^{-1}): 3114s ν(CF_3SO_3), 1536w ν(C⋯C, C⋯N), 272s ν(Rh−Cl). ^1H NMR (CD_2Cl_2, 293 K): δ 1.75 (s, 15H, CH_{3Cp^*}), 2.25, 2.58 (s, 6H, CH_{3gem}), 6.59 (t, 2H, *H4*), 7.84 (d, 2H, *H5*), 8.03 (d, 2H, *H3*). ^{13}C NMR (CD_2Cl_2, 293 K): δ 9.24 (s, *C*H_{3Cp^*}), 26.19, 29.44 (s, C(*C*H_3)$_2$), 77.10 (s, CH_2), 97.47 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C)$ = 8.5 Hz), 108.56 (s, *C4*), 132.43 (s, C*5*), 147.50 (s, *C3*).

[Cp*Ir(L^4)Cl][CF$_3$SO$_3$] (15). Compound **15** (0.220 g, 0.318 mmol, yield 54%) was prepared following a procedure similar to that reported for **12** using [Cp*IrCl(μ-Cl)]$_2$, L^4, and $AgCF_3SO_3$. Anal. Calcd for $C_{20}H_{27}ClF_3IrN_4O_3S$: C, 34.91; H, 3.95; N, 8.14. Found: C, 34.47; H, 3.80; N, 7.89. IR (nujol, cm^{-1}): 3121m, ν(CF_3SO_3), 1511sh ν(C⋯C, C⋯N), 275s ν(Ir−Cl). ^1H NMR (CD_2Cl_2, 293 K): δ 1.68 (s, 15H, CH_{3Cp^*}), 2.18, 2.64 (s, 6H, CH_{3gem}), 6.64 (t, 2H, *H4*), 7.78 (d, 2H, *H5*), 8.09 (d, 2H, *H3*). ^{13}C NMR (CD_2Cl_2, 293 K): δ 9.04 (s, *C*H_{3Cp^*}), 26.45, 28.65 (s, C(*C*H_3)$_2$), 78.24 (s, CH_2), 89.34 (s, C_{Cp^*}), 109.09 (s, *C4*), 132.40 (s, C*5*), 147.64 (s, *C3*).

[Cp*Rh(L^1)(H$_2$O)][CF$_3$SO$_3$]$_2$ (16). A CH_2Cl_2 solution containing [Cp*RhCl(μ-Cl)]$_2$ (0.077 g, 0.125 mmol), L^1 (0.037 g, 0.250 mmol), and $AgCF_3SO_3$ (0.120 g, 0.500 mmol) was stirred at room temperature under N_2. After 2 h, the precipitate formed was isolated by filtration and washed with acetone. The orange solution obtained was evaporated under vacuum, and the residue was washed with light petroleum and shown to be compound **16** (0.090 g, 0.128 mmol, 51%). It was recrystallized from CH_2Cl_2/light petroleum (40−60 °C). Anal. Calcd for $C_{19}H_{25}F_6N_4O_7RhS_2$: C, 32.49; H, 3.59; N, 7.98. Found: C, 32.60; H, 3.43; N, 7.34. ^1H NMR ($(CD_3)_2CO$, 293 K): δ 1.91 (s, 15H, CH_{3Cp^*}), 6.72 (t, 2H, *H4*), 6.70 (br, 2H, CH_2), 8.20 (d, 2H, *H5*), 8.33 (d, 2H, *H3*). ^1H NMR ($(CD_3)_2CO$, 323 K): δ 1.91 (s, 15H, CH_{3Cp^*}), 6.72 (t, 2H, *H4*), 6.70 (sbr, 2H, CH_2), 8.20 (d, 2H, *H5*), 8.34 (d, 2H, *H3*). ^1H NMR ($CD_3)_2CO$, 213 K): δ 1.92 (s, 15H, CH_{3Cp^*}), 6.26, 7.16 (d, 2H, CH_2, $^2J_{gem}$ = 15.1 Hz), 6.67 (d, 2H, *H5*), 6.76 (t, 2H, *H4*), 8.28 (d, 2H, *H3*). ^{13}C NMR ($(CD_3)_2CO$, 293 K): δ 9.40 (s, *C*H_{3Cp^*}), 63.87 (s, *C*H_2), 99.60 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C)$ = 9.4 Hz), 110.10 (s, *C4*), 137.30 (s, *C5*), 146.37 (s, *C3*).

[Cp*Ir(L^2)(H$_2$O)][CF$_3$SO$_3$]$_2$ (17). Compound **17** (0.123 g, 0.145 mmol, 58%) was prepared following a procedure similar to that reported for **16** using [Cp*IrCl(μ-Cl)]$_2$, L^2, and $AgCF_3SO_3$. mp: 219−220 °C. Anal. Calcd for $C_{23}H_{33}F_6N_4O_7IrS_2$: C, 32.58; H, 3.92; N, 6.61. Found: C, 32.40; H, 3.75; N, 6.55. IR (nujol, cm^{-1}): 3200br, 1605s, 1562s ν(C⋯C, C⋯N), 572m, 515s, 462w. ^1H NMR ($(CD_3)_2CO$, 293 K): δ 1.85 (s, 15H, CH_{3Cp^*}), 2.48 (s, 6H, *5*-CH_3), 2.61 (s, 6H, *3*-CH_3), 5.91, 6.70 (d, 2H, CH_2, $^2J_{gem}$ = 16.0 Hz), 6.41 (s, 2H, *H4*). ^1H NMR (D_2O, 293 K): δ 1.50 (s, 15H, CH_{3Cp^*}), 2.21 (s, 6H, *5*-CH_3), 2.34 (s, 6H, *3*-CH_3), 5.43, 6.25 (d, 2H, CH_2,

$^2J_{gem}$ = 15.6 Hz), 6.15 (s, 2H, *H4*). ^{13}C NMR ((CD$_3$)$_2$CO, 293 K): *δ* 9.69 (s, *C*H$_{3Cp*}$), 11.43 (s, *5-C*H$_3$), 14.72 (s, *3-C*H$_3$), 58.84 (s, *C*H$_2$), 90.39 (s, C$_{Cp*}$), 110.12 (s, *C4*), 145.49 (s, *C5*), 154.38 (s, *C3*).

[Cp*Rh(L⁴)(H₂O)][CF₃SO₃]₂·3H₂O (18). Compound **18** (0.220 g, 0.318 mmol, yield 54%) was prepared following a procedure similar to that reported for **16** using [Cp*RhCl(*μ*-Cl)]$_2$ (0.182 g, 0.294 mmol), L^4 (0.087 g, 0.588 mmol), and AgCF$_3$SO$_3$ (0.302 g, 0.588 mmol). Anal. Calcd for C$_{21}$H$_{35}$F$_6$N$_4$O$_{10}$RhS$_2$: C, 32.14; H, 4.50; N, 7.14. Found: C, 32.45; H, 4.44; N, 7.02. IR (nujol, cm^{-1}): 3500br, 3143s *ν*(CF$_3$SO$_3$), 1538w *ν*(C⋯C, C⋯N). ^{1}H NMR (CD$_3$)$_2$CO, 293 K): *δ* 1.92 (s, 15H, C*H*$_{3Cp*}$), 2.52 (sbr, 6H, CH$_{3gem}$), 6.76 (t, 2H, *H4*), 8.38 (d, 2H, *H5*), 8.49 (d, 2H, *H3*). ^{1}H NMR (CD$_3$)$_2$CO, 253 K): *δ* 1.92 (s, 15H, C*H*$_{3Cp*}$), 2.31, 2.73 (s, 6H, CH$_{3gem}$), 6.79 (t, 2H, *H4*), 8.37 (d, 2H, *H5*), 8.55 (d, 2H, *H3*). ^{1}H NMR (CD$_3$)$_2$CO, 213 K): *δ* 1.92 (s, 15H, C*H*$_{3Cp*}$), 2.29, 2.72 (s, 6H, CH$_{3gem}$), 5.95 (d, H$_2$O), 6.81 (t, 2H, *H4*), 8.35 (d, 2H, *H5*), 8.57 (d, 2H, *H3*). ^{13}C NMR ((CD$_3$)$_2$CO, 293 K): *δ* 9.45 (s, *C*H$_{3Cp*}$), 78.44 (s, CH$_2$), 99.45 (d, C$_{Cp*}$, J(^{103}Rh−^{13}C) = 9.1 Hz), 109.35 (s, *C4*), 134.50 (s, C*5*), 147.55 (s, *C3*).

[Cp*Ir(L⁴)(H₂O)][CF₃SO₃]₂ (19). Compound **19** (0.130 g, 0.158 mmol, yield 63%) was prepared following a procedure similar to that reported for **16** using [Cp*IrCl(*μ*-Cl)]$_2$, L^4, and AgCF$_3$SO$_3$. mp: 126−128 °C (dec). Anal. Calcd for C$_{21}$H$_{29}$F$_6$N$_4$O$_7$IrS$_2$: C, 30.77; H, 3.57; N, 6.83. Found: C, 30.95; H, 3.43; N, 6.62. IR (nujol, cm^{-1}): 3500s, 3142m, 1665m, 1613s, *ν*(C⋯C, C⋯N), 576m, 516m, 458w. ^{1}H NMR ((CD$_3$)$_2$CO, 293 K): *δ* 1.82 (s, 15H, C*H*$_{3Cp*}$), 2.75 (sbr, 6H, CH$_{3gem}$), 6.80 (t, 2H, *H4*), 8.34 (d, 2H, *H5*), 8.55 (d, 2H, *H3*). ^{1}H NMR (D$_2$O, 293 K): *δ* 1.51 (s, 15H, C*H*$_{3Cp*}$), 1.93, 2.45 (s, 6H, CH$_{3gem}$), 6.57 (t, 2H, *H4*), 7.94 (d, 2H, *H5*), 8.15 (d, 2H, *H3*). ^{13}C NMR ((CD$_3$)$_2$CO, 293 K): *δ* 9.28 (s, *C*H$_{3Cp*}$), 79.76 (s, CH$_2$), 90.69 (s, C$_{Cp*}$), 110.16 (s, *C4*), 134.95 (s, C*5*), 148.32 (s, *C3*).

[Cp*Rh(L¹)(H₂O)][ClO₄]₂ (20). Compound **20** (0.316 g, 0.520 mmol, yield 88%) was prepared following a procedure similar to that reported for **16** using [Cp*RhCl(*μ*-Cl)]$_2$, L^1, and AgCF$_3$SO$_3$. Anal. Calcd for C$_{17}$H$_{29}$Cl$_2$N$_4$O$_9$Rh: C, 33.66; H, 4.82; N, 9.24. Found: C, 33.20; H, 4.63; N, 9.14. IR (nujol, cm^{-1}): 1521w, *ν*(C⋯C, C⋯N), 1089s, 622m *ν*(ClO$_4$). ^{1}H NMR ((CD$_3$)$_2$CO, 293 K): *δ* 1.90 (s, 15H, C*H*$_{3Cp*}$), 6.75 (t, 2H, *H4*), 6.79 (br, 2H, CH$_2$), 8.28 (d, 2H, *H5*), 8.37 (d, 2H, *H3*). ^{1}H NMR ((CD$_3$)$_2$CO, 323 K): *δ* 1.90 (s, 15H, C*H*$_{3Cp*}$), 6.75 (t, 2H, *H4*), 6.82 (sbr, 2H, CH$_2$), 8.28 (d, 2H, *H5*), 8.37 (d, 2H, *H3*). ^{1}H NMR (CD$_3$)$_2$CO, 213 K): *δ* 1.92 (s, 15H, C*H*$_{3Cp*}$), 6.28, 7.18 (d, 2H, C*H*$_2$, $^2J_{gem}$ = 15.0 Hz), 6.69 (d, 2H, *H5*), 6.78 (t, 2H, *H4*), 8.30 (d, 2H, *H3*). ^{13}C NMR ((CD$_3$)$_2$CO, 293 K): *δ* 9.44 (s, *C*H$_{3Cp*}$), 63.96 (s, *C*H$_2$), 99.64 (d, C$_{Cp*}$, J(^{103}Rh−^{13}C) = 9.1 Hz), 110.29 (s, *C4*), 137.04 (s, *C5*), 146.27 (s, *C3*).

[Cp*Rh(L²)(PPh₃)][Cl][SO₃CF₃] (21). A CH$_2$Cl$_2$ solution containing **13** (0.080 g, 0.133 mmol) and PPh$_3$ (0.035 g, 0.133 mmol) was stirred at room temperature under N$_2$. After 6 h, the solution was isolated by filtration, and the orange solution obtained was evaporated under vacuum; the product was shown to be compound **21** (0.064 g, 0.072 mmol, yield 54%). mp: 139−140 °C. Anal. Calcd for C$_{40}$H$_{46}$ClF$_3$N$_4$O$_3$PRhS: C, 54.03; H, 5.21; N, 6.30. Found: C, 54.44; H, 5.60; N, 5.79. IR (nujol, cm^{-1}): 1521w *ν*(C⋯C, C⋯N), 1089s, 622m *ν*(ClO$_4$). ^{1}H NMR (CDCl$_3$, 273 K): *δ* 1.71 (s, 15H, C*H*$_{3Cp*}$), 2.42 (s, 6H, *5*-C*H*$_3$), 2.49 (s, 6H, *3*-C*H*$_3$), 5.99, 6.70 (d, 2H, C*H*$_2$, $^2J_{gem}$ = 15.6 Hz), 6.03 (s, 2H, *H4*) 7.32 (m, 15H, PPh$_3$). ^{13}C NMR (CDCl$_3$, 293 K): *δ* 9.83 (s, *C*H$_{3Cp*}$), 11.57 (s, *5*-*C*H$_3$), 15.25 (s, *3*-*C*H$_3$), 58.05 (s, *C*H$_2$), 97.09 (d, C$_{Cp*}$, J(^{103}Rh−^{13}C) = 8.3 Hz), 109.53 (s, *C4*), 128.75 (d, *Cm*), 129.13 (d, *Cp*), 133.90 (d, *Co*), 134.90 (d, *Ci*), 144.00 (s, *C5*), 155.04 (s, *C3*). ^{31}P NMR (CDCl$_3$, 293 K):*δ* 30.96 (d,^1J(^{31}P−Rh) = 144.0 Hz).

NOE Measurements. The ^{1}H-NOESY[30] NMR experiments were acquired by the standard three-pulse sequence or by the PFG version.[31] Two-dimensional ^{19}F,^{1}H-HOESY NMR experiments were acquired using the standard four-pulse sequence or the modified version.[32] The number of transients and the number of data points were chosen according to the sample concentration and the desired final digital resolution. Semiquantitative spectra were acquired using a 1 s relaxation delay and 800 ms mixing times.

PGSE Experiments. ^{1}H- and ^{19}F-PGSE NMR measurements were performed using the standard stimulated echo pulse sequence[33] on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil at 296 K without spinning. Me of the Cp* and fluorine resonances were usually investigated. The dependence of the resonance intensity (I) on a constant waiting time and on a varied gradient strength (G) is described by eq 3

$$\ln \frac{I}{I_0} = -(\gamma\delta)^2 D_t\left(\Delta - \frac{\delta}{3}\right)G^2 \qquad (3)$$

where I = intensity of the observed spin echo, I_0 = intensity of the spin echo without gradients, D_t = diffusion coefficient, Δ = delay between the midpoints of the gradients, δ = length of the gradient pulse, and γ = magnetogyric ratio.

The shape of the gradients was rectangular; their duration (δ) was 4−5 ms, and their strength (G) was varied during the experiments. All the spectra were acquired using 32 K points with a spectral width of 5000 Hz and were processed with a line broadening of 1.0 Hz. The semilogarithmic plots of ln(I/I_0) versus G^2 were fitted using a standard linear regression algorithm; the R factor was always higher than 0.99. Different values of Δ, nt (number of transients), and number of different gradient strengths (G) were used for different samples.

PGSE data were treated[18] taking advantage of an internal standard (TMSS [tetrakis-(trimethylsilyl)silane], the dimension of which is known from the literature[34]), and introducing into the Stokes−Einstein equation the semiempirical estimation of the c factor that can be obtained through eq 4[35] derived from the microfriction theory proposed by Wirtz and co-workers,[36] in which c is expressed as a function of the solute to solvent ratio of radii.

$$c = \frac{6}{\left[1 + 0.695\left(\frac{r_{solv}}{r_H}\right)^{2.234}\right]} \qquad (4)$$

From the Stokes−Einstein equation $D_t = kT/c\pi\eta r_H$ and eq 4, the ratio of the D_t values for the standard TMSS (st) and sample (sa), which is also equal to the ratio of the slopes (m) of the straight lines from the plot of log(I/I_o) versus G^2 (eq 3), is

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$$\frac{m^{sa}}{m^{st}} = \frac{D_t^{sa}}{D_t^{st}} = \frac{c^{st}r_H^{st}}{c^{sa}r_H^{sa}} = f(r_{solv}, r_H^{sa}, r_H^{st}) \quad (5)$$

Equation 5 circumvents the dependence of the D_t values on the temperature, solution viscosity (which changes when the concentration of the sample is varied), and gradient calibration, and allows an accurate value of the hydrodynamic radius[18] to be obtained.

The uncertainty of the measurements was estimated by determining the standard deviation of m by performing experiments with different Δ values. The standard propagation of error analysis gave a standard deviation of approximately 3−4% in hydrodynamic radii and 10−15% in hydrodynamic volumes. The Van der Waals volume (V_{vdW})[37] was computed using the software package WebLab ViewerLite 4.0.

Structure Determinations. Full spheres of CCD area-detector diffractometer data were measured (ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections; these were merged to N unique (R_{int} cited) after "empirical"/multiscan absorption correction, N_o with $I > 2\sigma(I)$ being considered to be observed. All reflections were used in the full-matrix least-squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atoms being included with parameters derivative of a riding model. Reflection weights were $(\sigma^2(F^2) + (n_wP)^2 + n_w'P)^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$). Neutral atom complex scattering factors were employed within the Xtal 3.7 and SHELXL 97 program systems.[38,39] Pertinent results are given in the tables and figures, the latter showing 50% probability amplitude envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

(Note: Initial studies on **5**, **7**, and **6**·$^1/_2CH_2Cl_2$ resulted in inferior determinations; further attempts on recrystallized samples resulted in no improvement for **5**, but for **6**, a new form was defined, **6**·$2H_2O$, yielding a superior result.)

Crystal/Refinement Data. The crystal and refinement data are given in Table 3.

4·H_2O. A difference map residue was modeled and refined as a water molecule oxygen atom. Reflection weights were $(\sigma^2(F^2) + 33F^2)^{-1}$.

6·$2H_2O$. Difference map residues were modeled in terms of major and minor components of uncoordinated chlorine atoms and oxygen atoms in concert, associated hydrogen atoms not being located, component site occupancies refining to 0.761(4) and complement.

6·$^1/_2CH_2Cl_2$. The solvent component was modeled as disordered CH_2Cl_2, geometries constrained to estimated values, site occupancies 0.5.

7. The compound is quasi-isomorphous with **5**. In **5**, the cp rings were modeled as disordered over two sets of sites; in the present, such disorder was not resolvable, although refinement of the atoms as single components resulted in unacceptable ellipsoids with the isotropic forms ultimately being adopted. Attempted refinement in lower symmetry in both cases was unfruitful.

15. Reflections weight were $(\sigma^2(F^2) + 193F^2)^{-1}$.

16. "Friedel" data were preserved distinct; x_{abs} refined to 0.00(4).

18·$3H_2O$. Difference map residues were modeled as water molecule oxygen atoms. No associated hydrogen atoms were located. Reflection weights were $(\sigma^2(F^2) + 33F^2)^{-1}$.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **4**, **5**, **6** (two forms), **7**, **15**, **16** and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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