Solution Structure Investigation of Ru(II) Complex Ion Pairs: Quantitative NOE Measurements and Determination of Average Interionic Distances

Cristiano Zuccaccia, Gianfranco Bellachioma, Giuseppe Cardaci, and Alceo Macchioni*

Contribution from the Department of Chemistry, University of Perugia, Via Elce di Sotto, 8 - 06123 Perugia, Italy

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Abstract: The structure of the Ru(II) ion pairs *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]X (X$^-$ = BPh$_4^-$, **1a**; BPh$_3$Me$^-$, **1b**; BPh$_3$(*n*-Bu)$^-$, **1c**; BPh$_3$(*n*-Hex)$^-$, **1d**; B(3, 5-(CF$_3$)$_2$(C$_6$H$_3$))$_4^-$, **1e**; PF$_6^-$, **1f**; and BF$_4^-$, **1g**; pz = pyrazol-1-yl-ring) was investigated in solution from both a qualitative (chloroform-*d*, methylene chloride-*d*$_2$, nithromethane-*d*$_3$) and quantitative (methylene chloride-*d*$_2$) point of view by performing 1D- and 2D-NOE NMR experiments. In particular, the relative anion−cation localization (interionic structure) was qualitatively determined by ^{1}H-NOESY and ^{19}F, ^{1}H-HOESY (heteronuclear Overhauser effect spectroscopy) NMR experiments. The counteranion locates close to the peripheral protons of the bispyrazolyl ligand independent of its nature and that of the solvent. In complexes **1c** and **1d** bearing unsymmetrical counteranions, the aliphatic chain points away from the metal center as indicated by the absence of NOE between the terminal Me group and any cationic protons. An estimation of the average interionic distances in solution was obtained by the quantification of the NOE build-up versus the mixing time under the assumption that the interionic and intramolecular correlation times (τ_c) are the same. Such an assumption was checked by the experimental measurements of τ_c from both the dipolar contribution to the carbon-13 longitudinal relaxation time (T_1^{DD}) and the comparison of the intramolecular and interionic cross relaxation rate constant (σ) dependence on the temperature. Both the methodologies indicate that anion and cation have comparable τ_c values. The determined correlation time values were compared with those obtained for the neutral *trans*-[Ru(COMe){(pz$_2$)BH$_2$}(CO)(PMe$_3$)$_2$] complex (**2**), isosteric with the cation of **1**. They were significantly shorter (~3.8 times), indicating that the main contribution to dipolar relaxation processes comes from the overall ion pair rotation. As a consequence, the determined average interionic distances appear to be accurate. By using such interionic distances, it was possible to verify that the counteranion in complex **1b** also orients the BMe group far away from the metal center.

Introduction

The importance of the ion pairing phenomenon in chemistry is long-standing. Its effects on the reactivity of organic substrates have been realized for several decades.[1] The chemistry of coordination and organometallic compounds[2] is also strongly affected by ion−counterion interactions, and most of the reactions catalyzed by transition metal complexes involve cationic compounds where the counteranion has a significant role.[2] Olefin polymerizations or copolymerizations catalyzed by both first transition metallocene[3] and late transition[4] metal complexes, for instance, always involve cationic complexes working in low dielectric constant solvents where they are mainly present as intimate ion pairs. Although many experimental[5] and theoretical[6] studies have been done to understand the behavior of transition metal ion pairs in different reactions as a function of solvent, temperature, size of substituents on catalysts and substrates, very little is known about their structure in solution. Most of the structural features of transition metal complex ion pairs in solution have been deduced either from X-ray solid-state investigations or theoretical considerations. Owing to the small amount of energy involved in ion pair formation, dissociation, and eventual reorganization, the deductions may not always be true.

In the mid 1980s, it was found that NOE (nuclear Overhauser effect) NMR experiments can be successfully applied to investigate the structure of ion pairs in solution when intermo-

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* E-mail for corresponding author: alceo@unipg.it.

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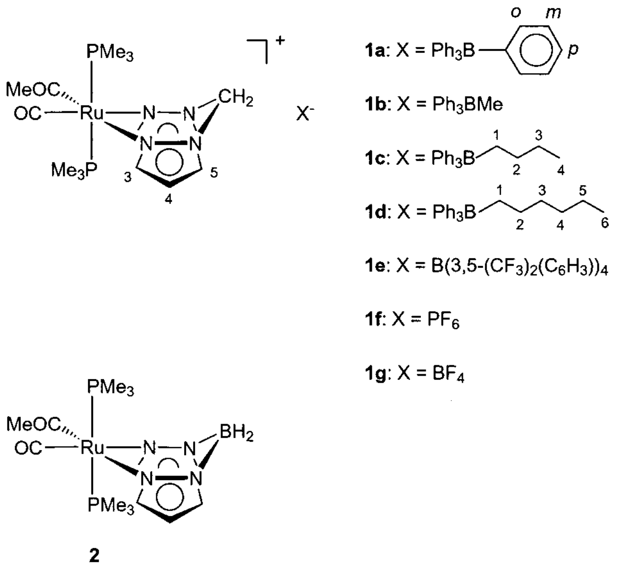
lecular interactions are strong enough to stabilize a particular anion−cation orientation so that other conformations, or dissociated ions, are negligibly populated.[7,8] Detailed investigations were carried out on organic closed shell ion pairs that are important for phase-transfer catalysis[7] and organolithium ion pairs.[8] We decided to apply this methodology for investigating transition metal complex ion pairs.[9] Several Fe(II),[9b,c] Ru(II),[9a−d,9h] Os(II),[10] Pd(II),[9f] Pt(II),[9e,g,i] Ir(III),[11] and Ag(I)[12] complex ion pairs were qualitatively investigated by ^{1}H-NOESY and ^{19}F, ^{1}H-HOESY (heteronuclear Overhauser effect spectroscopy) NMR experiments in solvents with low dielectric constants, and the interionic structure was always well-defined. The reason for the specificity in the cation−anion interactions, which was generally higher than that found in other types of ion pairs, was attributed to the noncentrosymmetric electron density distribution[7d,11] and/or formation of a dipolar moment in the cationic moiety facilitated by the high polarizability of the d-metal orbitals.

Chart 1



Encouraged by the results from the qualitative NOE studies, we recently started the quantification of the NOEs in order to estimate the average interionic distances in solution.[13] Despite the fact that the subject needs many precautions, especially because interionic distances refer, by definition, to distances between two noncovalently bonded nuclei which are, reasonably, in motion relative to each other, we decided to attempt such measurements because (1) the main presence of only one type of intimate ion pair in solution should limit the types of motions and (2) the estimations of average interionic distances could be very precious to investigate transition metal catalysts in the environment where they really "work".

In this paper, we report the synthesis and the qualitative interionic investigation in solution of *trans*-[Ru(COMe){(pz$_2$)-CH$_2$}(CO)(PMe$_3$)$_2$]X (X$^-$ = BPh$_4^-$, **1a**; BPh$_3$Me$^-$, **1b**; BPh$_3$-(*n*-Bu)$^-$, **1c**; BPh$_3$(*n*-Hex)$^-$, **1d**; B(3,5-(CF$_3$)$_2$(C$_6$H$_3$))$_4^-$, **1e**; PF$_6^-$, **1f**; and BF$_4^-$, **1g**; pz = pyrazol-1-yl-ring), complexes bearing both symmetric and unsymmetric counteranions. Preliminary results were already communicated.[13] The results of our efforts to determine the average interionic distances in solution for complexes **1a**,**b** by using the measurements of the complete kinetic of NOE build-up are described. Furthermore, two methodologies were used to determine the rotational correlation times for complex **1a** and for the neutral isosteric *trans*-[Ru(COMe){(pz$_2$)BH$_2$}(CO)(PMe$_3$)$_2$] (**2**) complex. The results are presented to validate average interionic distance values obtained.

The twofold aim of this study was (1) to test both the qualitative and quantitative NOE NMR methodologies for ion pair investigations in solution by (2) determining the relative cation−anion position for complexes **1a**−**g** as a function of anion nature, solvent, and temperature. Even if the chemistry of such complexes is not affected by ion pairing, they have been chosen as "model" compounds for developing and checking the NMR investigation methodologies, because they are relatively easy to synthesize and present all the suitable NMR properties. The methodologies validated in this study have already been used[9f,g] and will be further applied to chemical systems whose reactivity or catalysis is affected by cation−anion interactions.

Results and Discussion

Synthesis. Complexes **1b**,**c** (Chart 1) were synthesized by the reaction of *cis,trans*-RuI(Me)(CO)$_2$(PMe$_3$)$_2$ with pz$_2$(CH$_2$) in methanol in the presence of a large excess of K[BPh$_3$R] (R = Me (**1b**), *n*-Bu (**1c**)). Because of (a) the migration of the methyl onto a cis carbonyl group, (b) the ionization of the Ru−I bond, and (c) the coordination of the bidentate N,N-ligand (pz$_2$(CH$_2$)), the acetyl ionic complex *trans*-[Ru(COMe){(pz$_2$)-CH$_2$}(CO)(PMe$_3$)$_2$]I forms that exchanges the I$^-$ counteranion with BPh$_3$R$^-$, affording the precipitation of the desired product. The preparation of complex **1d** (Chart 1) was similar, but owing

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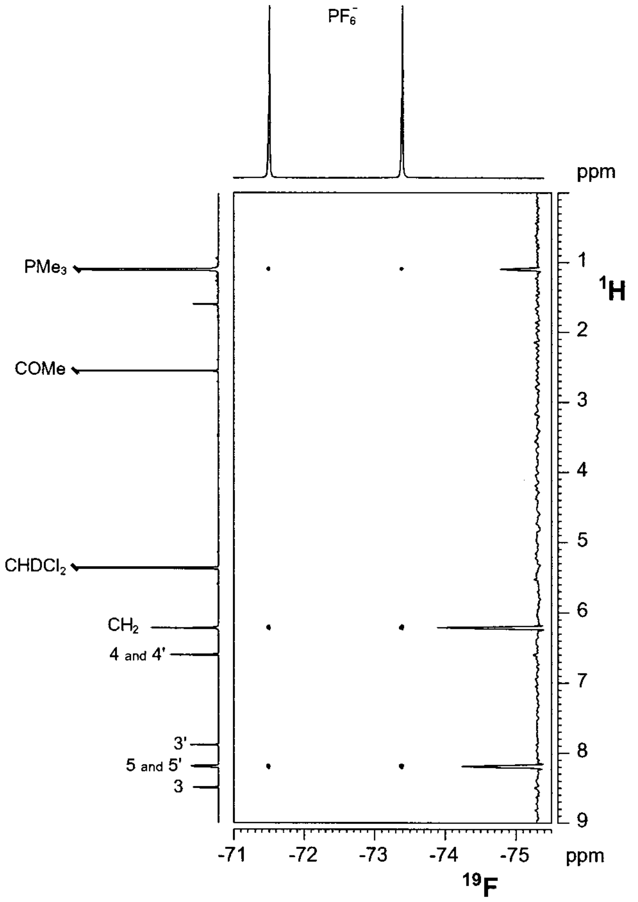

Figure 1. ^{19}F, ^1H-HOESY spectrum of complex **1f** showing the "heteronuclear interionic contacts". The F1 trace (indirect dimension) relative to one component of the fluorine doublet is reported on the right (376.65 MHz, 298 K, methylene chloride-d_2).

to the insolubility of K[BPh$_3$(*n*-Hex)] in methanol, the reaction was carried out in nitromethane and complex **1d** was then precipitated from a methanol/water mixture. Complex **1e** (Chart 1) was obtained in methanol and precipitated by the addition of water. The synthesis of complex **1f** was carried out in methylene chloride similarly to those of complexes **1a**,**b** with the only difference being that the ionization of the Ru−I bond was induced by TlPF$_6$, with the consequent precipitation of TlI that was then filtered off. The product was precipitated by adding *n*-hexane to the solution.

Qualitative NOE Measurements. The relative anion−cation position in solution (methylene chloride-d_2) was previously investigated for complexes **1a** and **1g**; only preliminary results concerning complexes **1b**−**d** were communicated.[13] In all cases, the counteranion showed very specific interionic interactions and preferred to locate close to the 5/5′ and CH$_2$ protons (Chart 1) as illustrated for complex **1f** in Figure 1. A weak interionic contact between the fluorine nuclei of the counterion and PMe$_3$ protons can be observed in Figure 1, but its intensity is rather small, especially considering that the intensity of a cross-peak due to N_I equivalent spins I and N_S equivalent spins S is proportional to the ratio $N_IN_S/(N_I + N_S)$.[14] Such a ratio equals 4.5 for PMe$_3$, 1.5 for CH$_2$, and 1.5 for H5 and H5′. The intensity of the observed PMe$_3$−PF$_6^-$ peak in Figure 1 must be divided by 3.0 (4.5/1.5) to be quantitatively compared with other interionic peaks, and consequently, its intensity is very small. An explanation for the observed specific localization of the counteranion was found, with the help of quantomechanical calculations, in the noncentrosymmetric distribution of the electron density around the metal.[7d] The main energetic contribution for stabilizing the observed interionic structure is therefore of an electrostatic nature. This is also demonstrated by the fact that relative anion−cation position is independent of the counteranion nature. Both organic (in **1a**−**d** complexes) and inorganic (in **1f**,**g** complexes) counteranions essentially locate in the same position.

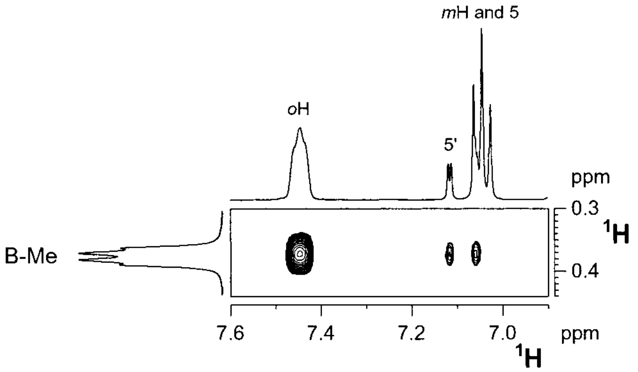

Figure 2. Section of the ^1H-NOESY spectrum of the complex **1b** showing the interionic contacts between the BMe group of the anion and H5 and H5′ protons of the cation (400.13 MHz, 298 K, methylene chloride-d_2).

Complex **1e** behaves in a particular way, because the B(3,5-(CF$_3$)$_2$(C$_6$H$_3$))$_4^-$ counterion is so weakly coordinating that it affords nonintimate ion pairs even in methylene chloride solution at room temperature and at NMR concentrations (10^{-4}−10^{-1} M solutions). Consequently, no interionic contacts were observed in methylene chloride-d_2 in either the ^{19}F, ^1H-HOESY or ^1H-NOESY NMR spectra. When these last experiments were performed for a ∼10^{-2} M solution of **1e** in chloroform-*d*, weak interionic contacts appeared in the ^{19}F, ^1H-HOESY spectrum between the anion fluorine nuclei and 5/5′ and CH$_2$ protons, again. As in the other cases, no NOE was observed between the fluorine nuclei and the COMe protons. This means that the interionic structure of complex **1e** is the same as those of the other complexes, once the experimental parameters (solvent, concentration, and temperature) allow the prevalence of intimate ion pairs in solution.

Complexes **1b**−**d** were synthesized, and their interionic structures were investigated in order to understand whether the presence of unsymmetrical counteranions could further enhance the specificity of the interionic contacts. The analysis of the results for complex **1b** did not answer our question. In fact, the ^1H-NOESY NMR spectrum recorded in methylene chloride-d_2 (at room temperature) showed interionic contacts between both the *o*H and BMe anion protons with 5/5′ and CH$_2$ cation protons (Figure 2). The qualitative approach did not solve the *dilemma* of either (a) a preferential orientation of the counteranion with the Me group that was still close enough to interact or (b) an equilibrium between different anion orientations. By increasing the aliphatic chain length of the counteranion, clearer results were obtained. The terminal methyl groups of complexes **1c**,**d** did not show NOEs with any cation protons, while *o*H anion protons continued to interact with 5/5′ and CH$_2$ cation protons. This clearly indicates that, at least in the cases of **1c**,**d**, the counteranion prefers to orient its aliphatic chain far from the cationic organometallic moiety. Interestingly, the α-CH$_2$ protons of the counterions showed interionic contacts with the cationic protons, which suggests that, for complex **1b**, there could also be a preferential orientation of the counterion while the BMe group still remains close enough to be able to give NOEs with

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[14] Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95.

some cationic protons. In any case, the results relative to complexes **1c**,**d** indicate that the favorable van der Waals interactions between the phenyl groups of the counterion and the pyrazolyl rings of the cationic organometallic moiety affect the relative anion−cation orientation. The highly specific interionic solution structure of complexes bearing unsymmetrical counteranions can be considered to be guided mainly by electrostatic energy gain and then finely modulated by "stackinglike" $\pi-\pi$ interactions.

The effect of solvent on the interionic structure was investigated for complex **1a**. The choice of solvents was based on their dielectric constants, keeping their coordination capability low. The studies were performed in methylene chloride-d_2 (ϵ = 8.93 at 298 K), acetone-d_6 (ϵ = 20.56 at 298 K), and nitromethane-d_3 (ϵ = 35.94 at 298 K). The solution concentrations were between 10^{-2}−10^{-1} M. The ^{1}H NMR spectra already indicated that the intimate ion pairs were destroyed in both acetone and nitromethane. In fact, only the resonances of the cationic moiety that are close to the counterion in methylene chloride (CH$_2$, H5, and H5′) and are shielded by the π-electron density of phenyl groups resonate at substantially higher frequencies.[15] Several ^{1}H-NOESY spectra were recorded in acetone-d_6 and nitromethane-d_3 for complex **1a** with changes in the concentration and the mixing times. In every case, very weak interionic NOEs were detected (maximum 1.2%) but with the "usual" cationic protons. This leads to the conclusion that the few ion pairs that are present in such solvents have the same interionic structure as those in methylene chloride.

Quantitative NOE Measurements. The quantitative NOE experiments were performed for complexes **1a** (2×10^{-1} M)[16] and **1b** (4×10^{-2} M) in methylene chloride-d_2 at 302 K by using the selno[17] and selnogp[18] sequences. The target resonances were chosen on the basis of the qualitative interionic structure: *o*H, H5, H4, and CH$_2$ for complex **1a** (H5′ was not selectively inverted because it was buried under the *p*H protons of the anion), and *o*H, CH$_2$, BMe, PMe$_3$ for complex **1b**. The NOEs between the inverted and all the dipolarly coupled nuclei were measured as a function of the mixing time (τ_m). The data relative to the NOE percentages as a function of τ are presented in the Supporting Information (see also Figure 3).

In the case of *complex* ***1a***, τ was varied from 10^{-4} to 10 s in each experiment, and consequently, the complete time course of the NOE enhancements was recorded. In Figure 3, the experimental time course of the NOE build-up for the dipolarly coupled nuclei after inversion of *o*H protons is illustrated. The experimental data were treated in two different ways: (a) they were fitted by eq 1,[19] valid for two isolated spins, using R (total longitudinal relaxation rate constant) and σ_{IS} as fittable parameters, and (b) the fittings were limited to the first points where the kinetic of NOE build-up is almost linear ($\tau \leq 0.4$ s).

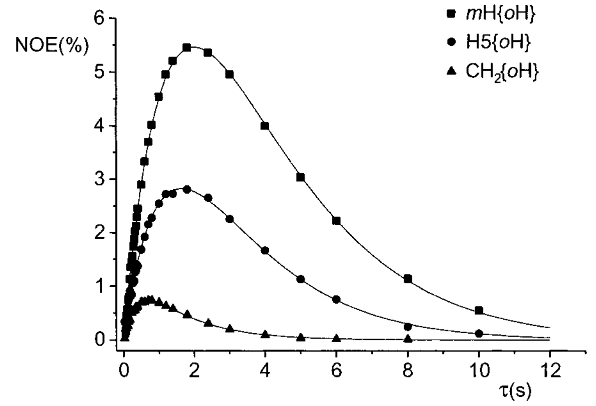

Figure 3. Experimental data relative to the % NOE as a function of τ for the irradiation of *o*H protons of the BPh$_4^-$ (T = 302 K) for complex **1a**.

Table 1. Cross Relaxation Rate Constant $\langle\sigma_{IS}\rangle$ (s^{-1})[a] and Internuclear Distance ($\langle r_{IS}\rangle$ (Å)[b]) Values for Complex **1a**

	$\langle\sigma_{IS}\rangle$ (s^{-1})	$\langle r_{IS}\rangle$ (Å)	$\langle\sigma_{IS}\rangle$ (s^{-1}) linear fitting up to 0.4 s	$\langle r_{IS}\rangle$ (Å) from linear fitting	$\langle r_{IS}\rangle$ (Å)[c]
*m*H{*o*H}	0.0743[d]	2.47[e]	0.0678	2.47[e]	2.47
H5{*o*H}	0.0058	**4.16**	0.0055	**4.13**	
CH$_2${*o*H}	0.0035	**4.52**	0.0027	**4.65**	
H4{H5}	0.0358	2.79	0.0294	2.84	2.66
CH$_2${H5}	0.0345	**3.08**	0.0256	**3.20**	
*o*H{H5}	0.0047	**4.30**	0.0046	**4.26**	
H5{H4}	0.0349	2.80	0.0293	2.84	2.66
H3{H4}	0.0356	2.79	0.0310	2.81	2.65
H5{CH$_2$}	0.0350	**3.08**	0.0254	**3.20**	2.94
*o*H{CH$_2$}	0.0036	**4.50**	0.0024	**4.74**	

[a] All the fits have R^2 values higher than 0.97, and the estimated error for a single $\langle\sigma_{IS}\rangle$ value is less than 5%. [b] The distances relative to the protons that undergo dynamic processes were increased by 10% and are reported in bold. [c] Values derived from the X-ray structure by averaging all the possible distances in the case of equivalent protons. [d] The spin *o*H−*m*H subsystem must be treated carefully. In fact, while the 8 *ortho* protons and the 8 *meta* protons are magnetically equivalent, it is not correct to divide the rate of NOE build-up by 8 (the number of irradiated spins), because each *o*H relaxes mainly with "its own" *m*H (i.e., the adjacent *m*H). [e] The *o*H−*m*H distance was calculated by averaging the data derived from neutron scattering investigations.[20]

$$\mathrm{NOE_I\{S\}}(\tau) = \frac{1}{2}e^{-(R-\sigma_{IS})\tau}(1 - e^{-2\sigma_{IS}\tau}) \qquad (1)$$

In both cases, the time-average values of the *cross relaxation* rate ($\langle\sigma_{IS}\rangle$), reported in Table 1, were determined by dividing the σ_{IS} values derived from fittings by the number of inverted protons. For the "symmetric" experiments, that is, I spin inversion and NOE detection on S and vice versa, the "symmetry" rule is satisfied; for example, the rate of NOE build-up on *o*H protons after the inversion of CH$_2$ protons is equal, within experimental error, to the rate of NOE build-up on CH$_2$ protons after the inversion of *o*H protons (Table 1).

With the assumption that $\omega_I = \omega_S = \omega$, σ_{IS} depends on the correlation time (τ_c) and the internuclear distance according to the following equation:

$$\sigma_{IS} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_I^2\,\gamma_S^2}{10} \cdot \tau_c\left(\frac{6}{1 + (2\omega\tau_c)^2} - 1\right) r_{IS}^{-6} \qquad (2)$$

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(15) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Zuccaccia, C. In preparation.

(16) It must be said that at this high concentration value ion quadrupoles are also present (Zuccaccia, C.; Bellachioma, G.; Cardaci, G.; Macchioni, A. *Organometallics* **2000**, *19*, 4663.). Despite this, the qualitative interionic structure of ion quadrupoles was found to be the same as that of ion pairs, and the quantification of NOE should not be affected. Furthermore, unlike the results reported in ref 7f, no negative NOE was observed indicating for our system a lower level of aggregation.

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(19) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.

Table 2. Cross Relaxation Rate Constant ($\langle\sigma_{IS}\rangle$ (s^{-1})^a) and Internuclear Distance ($\langle r_{IS}\rangle$ (Å)^b) (*o*H−*m*H Distance Is Used as Reference Distance) for Complex **1b**

	$\langle\sigma_{IS}\rangle$ (s^{-1})	$\langle r_{IS}\rangle$ (Å)
*m*H{*o*H}	0.0440	2.47^c
BMe{*o*H}	0.0070	3.69
CH_2{*o*H}	0.0021	**4.51**
*o*H{CH_2}	0.0021	**4.51**
H5{CH_2}	0.0220	**3.05**
BMe{CH_2}	0.0009	**5.19**
PMe_3{CH_2}	0.0024	**4.41**
*o*H{BMe}	0.0071	3.68
H5{BMe}	0.0026	4.35
*m*H{PMe_3}	0.0002	**6.67**
CH_2{PMe_3}	0.0025	**4.38**

[a] All the fits have R^2 values higher than 0.9 and the estimated error for a single $\langle\sigma_{IS}\rangle$ value is about 10%. [b] All the $\langle r_{IS}\rangle$ values, except the reference distance, were increased by 10% in order to correct for the overestimation of the short distances. [c] The *o*H−*m*H distance is calculated by averaging the data derived from neutron scattering investigations.[20]

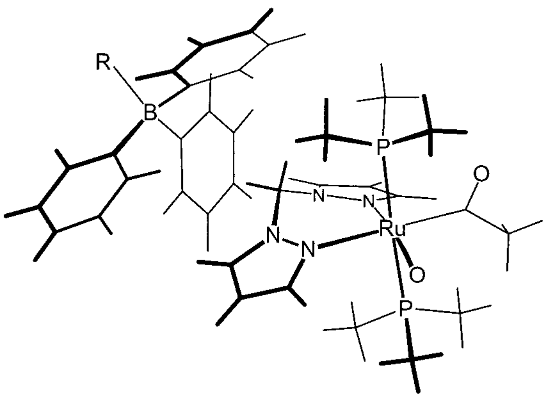

Figure 4. Three-dimensional structure of **1a**−**d** Ru(II) ion pairs derived from qualitative and quantitative interionic NOE measurements showing as the aliphatic chain (in **1b**−**d**) points away from the metal center.

The average distances, $\langle r_{IS}\rangle$, were then calculated from the obtained σ values by using eq 3 and the intramolecular reference distance (r_{AB}) *o*H−*m*H (Table 1) with the assumption that the tumbling of the system can be described by a single rotational correlation time.

$$r_{IS} = r_{AB}\sqrt[6]{\frac{\sigma_{AB}}{\sigma_{IS}}} \qquad (3)$$

The *o*H−*m*H distance (2.47 Å) was derived from experimental data available by neutron diffraction investigations.[20] The distances involving the protons of the counteranion that undergoes dynamic motions (demonstrated by the equivalence of the four phenyl groups) and those of CH_2 and H_5 protons (interested in the chair−boat inversion of the six-member Ru−N−N−CH_2−N−N ring) were increased by 10% in order to correct, at least partially, for the overestimation of the short distances and are indicated in bold in Table 1.[19]

As mentioned above, the interionic structure of *complex **1b*** bearing an unsymmetrical counteranion is not completely defined by the qualitative NOE investigation. In particular, the orientation of the BMe group with respect to the organometallic moiety is not clear. For such a complex, kinetic experiments were performed to determine the rate of the NOE build-up by using only the first linear part of the curve, ($\tau_m \leq 0.4$ s); all the experiments were performed using the PFG version of the selno sequence (selnogp).[18] The estimations of the average cross relaxation rate constants ($\langle\sigma_{IS}\rangle$) and internuclear distances ($\langle r_{IS}\rangle$) are reported in Table 2.

The 0.7 Å difference between the average distances CH_2−MeB (5.19 Å) and CH_2−*o*H (4.51 Å) indicate two possible conclusions: (1) the situation for complex **1b** is the same as that of complexes **1c**,**d**, with the methyl group pointing away from the cation; (2) two different populated ion pairs are present, one with the aliphatic tail pointing away from the cation, the other with the aliphatic tail pointing toward the cation. The latter interpretation can be excluded because the CH_2−*o*H distance for complex **1b** (4.51 Å) is very similar to that of **1a** (4.51 and 4.62 Å with total and linear fittings, respectively), and this would not be the case if **1b** were present in solution as two different ion pairs. In fact, in the hypothetical ion pair where BMe points toward the metal, the average CH_2−*o*H distance should be longer than that in the other ion pair. In conclusion, the quantitative NOE investigation of complex **1b** allows us to unambiguously understand that the BMe group points away from the cationic fragment, as in complexes **1c**,**d** as schematized in Figure 4. This is probably due to a maximization of lipophilic interactions.

Measurements of the Correlation Time. As mentioned above, the average internuclear distances were determined from kinetic NOE experiments using an intramolecular reference distance and by assuming that the tumbling of the system can be described by a single rotational correlation time. This assumption is valid if the molecular system can be reasonably approximated to a rigid spherical body tumbling in solution because of Brownian motion. On the other hand, our systems consist of two separated fragments, linked together only by noncovalent forces, and this assumption has to be verified.

For this reason, we decided to estimate the rotational correlation time (τ_c) for complex **1a** in methylene chloride-d_2 by using two different approaches: (a) ^{13}C relaxation measurements and (b) dependence of the ^{1}H−^{1}H *cross relaxation* on temperature.

(a) Carbon T_1 Determinations. It is well-known that the most important pathway of relaxation for nonquaternary carbon nuclei is dipole−dipole relaxation by the attached protons.[21] In an isotropic system, at the *extreme narrowing limit* (i.e., when the product $\omega\tau_c \ll 1$), the dipolar contribution to the total relaxation is directly proportional to the rotational correlation time:[22]

$$\frac{1}{T_1^{DD}} = R_1^{DD} = \left(\frac{\mu_0}{4\pi}\right)^2 N\frac{\gamma_H^2\,\gamma_C^2\hbar}{r_{CH}^6}\cdot\tau_C = NK\tau_c \qquad (4)$$

where the longitudinal relaxation time and relaxation rate constant refer to ^{13}C, N is the number of protons attached to a given carbon, and $K = 2.0325 \times 10^{10}$ s^{-2}, if the C−H bond lengths, r_{CH}, are assumed to be constant (1.1 Å).

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Table 3. Relaxation Times (T_1 and T_1^{DD}), NOE Factors and Rotational Correlation Times (τ_c) for Complex **1a** in Methylene Chloride-d_2

signal	NOE(^{13}C{^{1}H})	T_1 (s)	T_1^{DD} (s)	τ_c (ps)
C3	1.68	0.484	0.575	86
C3′	1.88	0.513	0.543	90
C5′	1.67	0.458	0.545	90
*o*C	1.72	0.858	0.993	49
C5	1.78	0.476	0.533	92
*m*C	1.70	0.858	1.003	49
*p*C	1.70	0.62	0.727	67
C4	1.70	0.66	0.776	63
C4′	1.87	0.661	0.704	70
CH_2	1.69	0.326	0.384	64
COMe	1.52	1.917	2.510	7
PMe_3	1.94	1.376	1.408	11

The dipolar contribution to the total relaxation can be estimated from the NOE data; in fact, if the CH_n systems relax entirely by dipole−dipole interactions, at the *extreme narrowing limit* the expected value for the NOE(^{13}C{^{1}H}) is 1.987, and we can write

$$\mathrm{NOE}(^{13}\mathrm{C}\{^1\mathrm{H}\}) = \frac{1.987 \cdot T_1}{T_1^{DD}} \qquad (5)$$

where T_1 is the total longitudinal relaxation time.

The NOE(^{13}C{^{1}H}) can be obtained by comparing the standard *gated decoupling* ^{13}C{^{1}H} spectrum, with the corresponding *inverse gated decoupling* spectrum, in which the decoupler is only switched on during the acquisition time; the T_1 value can be obtained by the standard *inversion recovery* sequence. The results concerning the measured values of NOE(^{13}C{^{1}H}), T_1, T_1^{DD}, and τ_c for complex **1a** are reported in Table 3. As expected, the correlation times of COMe and PMe_3 groups are shorter than the others because of the contribution of the fast internal rotations of the CH_3 groups around the C−C or P−C bonds, respectively. Apart from these two groups, the correlation times of the cation (64−92 ps) and those of the anion (49−67 ps) are comparable. Slightly different correlation times for the pz-cationic CH vectors were observed. Whereas the CH vectors in positions 3, 3′, 5, and 5′ reorient with the same correlation time, those in position 4 and 4′ reorient faster. On the other hand, the correlation times for the anion are also different; in particular, the *o*C−*o*H and *m*C−*m*H vectors reorient with the same correlation times (49 ps), but the *p*C−*p*H vector reorients more slowly (67 ps), with the same correlation time as those of the 4 and 4′ cation vectors.

The similar correlation time values for both anion and cation could be due to their similar size. To ascertain if the two fragments influence the motion of each other, we decided to investigate neutral complex *trans*-[Ru(COMe){(pz_2)BH_2}(CO)(PMe_3)$_2$] (**2**), which only differs from the cationic part of **1a** with the substitution of one carbon atom with a boron, and it is isostructural, isosteric, and isomass with the cation itself. The experimental results for a 2×10^{-1} M solution of complex **2** in methylene chloride-d_2 are reported in Table 4. All the C−H vectors in the bispyrazolylborate ligand have similar correlation times (∼23 ps), whereas, as expected, the correlation times for the COMe and PMe_3 groups are lower. By excluding COMe and PMe_3 groups, the average ratio between the correlation times relative to CH values of complex **1** and those of complex **2** is ∼3.8. From the Debye equation[19] that relates τ_c with the volume of the rotating particle, assumed to be spherical, we can consider 3.8 as a first approximation of the ratio of volumes. Considering all the assumptions involved, this value is in good agreement with that from previous PGSE measurements[15] (∼3) and indicates, for sure, that the τ_c values of complex **1** are governed by the overall ion pair rotation that determines similar τ_c values for anion and cation. Furthermore, the invariance of τ_c values for complex **2** indicates that it tumbles in solution like a rigid spherical body. Crystallographic inspection of the cationic moiety of complex **1** indicates that it is reasonably correct to consider **2** as spherical. The three molecular axes defined (1) from the carbon of the acetyl group to C5′ (7.41 Å), (2) from the largest distance between two carbons belonging to the different phosphine groups (7.06 Å), and (3) from C4 to C4′ (6.47 Å) are very similar. In contrast, in the case of complex **1a**, the formation of the ion pair or, eventually, higher aggregates, destroys the pseudospherical symmetry at the cation and anion. This is reflected in the different correlation time values for the internuclear vectors that form different angles with the principal axes of rotation.

Table 4. Relaxation Times (T_1 and T_1^{DD}), NOE Factors and Rotational Correlation Times (τ_c) for Complex **2** in Methylene Chloride-d_2

signal	NOE(^{13}C{^{1}H})	T_1 (s)	T_1^{DD} (s)	τ_c (ps)
C3	1.65	1.883	2.270	22
C3′	1.56	2.027	2.592	19
C5′	1.58	1.962	2.479	20
C5	1.84	1.988	2.151	23
C4	1.85	1.848	1.989	25
C4′	1.58	1.923	2.417	20
COMe	1.06	5.472	10.251	2
PMe_3	1.84	2.153	2.322	7

(b) Dependence of the Cross Relaxation Rate Constant on the Temperature. Another methodology to obtain information about the correlation time of the various internuclear vectors is to measure the *cross relaxation* rate as a function of temperature. A number of studies have shown that the rotational correlation time varies with temperature according to the following equation:[23]

$$\tau_c = \tau^0 \cdot e^{E_R/k_B T} \qquad (6)$$

where E_R is the activation energy for rotational reorientation, τ^0 is a constant, and k_b is the Boltzmann constant.

By substituting the τ_c expression (eq 6) into classical eq 2, that relates σ_{IS} with τ_c and r, the expression for the temperature dependence of σ_{IS} is obtained. Its analysis indicates that σ_{IS} reaches a maximum at the same τ_c or T value independent of the internuclear distance and it has a zero cross point for $\omega\tau_c = 1.12$.

We performed 1D-transient experiments by inverting *o*H or H5 in the 217−302 K temperature range for complex **1a** in methylene chloride-d_2 (the data are reported in Supporting Information). Because the experiments were rather time-consuming, the σ_{IS} values were estimated by using only one τ value that was set at 0.4 s as a compromise between the initial rate approximation condition and a good signal-to-noise ratio (especially for the temperature near the zero cross point, i.e., when $\omega\tau_c = 1.12$). The experimental data points were fitted setting E_R and τ^0 as fittable parameters and introducing the scaling factor P_1 ($0 < P_1 < 1$). The results of this procedure are summarized in Table 5. It is important to outline that the position of the maximum (∼285 K) and that of the zero cross

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Table 5. Values of r_{IS} (Å), E_R (kJ/mol), τ^0 (ps), and P_1 for Complex **1a** Estimated from the Best Nonlinear Least-Squares Fit of Data Points

	r_{IS} (Å)	E_R (kJ/mol)	τ^0 (ps)	P_1	τ_c (ps) (302 K)
*m*H{*o*H}[a]	2.47	10.4	1.9	0.614	120
H4{H5}	2.81	9.5	3.0	0.614	132
CH_2{H5}	2.91	7.8	7.0	0.614	156
H5{*o*H}	3.92	10.5	2.0	0.614	131
*o*H{H5}	3.80	11.1	1.4	0.614	117
*o*H{CH_2}	4.43	9.5	3.2	0.614	141

[a] In the fit of *m*H{*o*H} data points, the r_{IS} is maintained as fixed and the P_1 is varied between 0 and 1, while in the other fits the P_1 was maintained at a fixed value of 0.614 and r_{IS} was varied.

Table 6. Summarizing Table of Main Average Internuclear Distances ($\langle r_{IS} \rangle$ (Å)) for Complex **1a**

	$\langle r_{IS} \rangle$ (Å)[a]	$\langle r_{IS} \rangle$ (Å)[b]	$\langle r_{IS} \rangle$ (Å)[c]
H4/H5	2.8	2.8	2.8
H5/CH_2	3.1	3.2	2.9
H5/*o*H	4.2	4.2	3.9
CH_2/*o*H	4.5	4.7	4.4

[a] Derived by fitting the complete NOE built up with eq 2. [b] Derived from the linear fits of NOE built up with $\tau_m \leq 0.4$ s. [c] Derived from the dependence of the cross relaxation rate constant on temperature.

point (around 230 K) are very similar for all the fittings. This strongly indicates that both the intramolecular and interionic vector reorientations have the same temperature dependence.

As a general consideration, the information from the temperature variation of σ_{IS} also seems to indicate that the assumption of a single correlation time in the interionic distance estimation is acceptable. Regarding the numerical values of τ_c (Table 5), they are higher than those obtained from the ^{13}C relaxation investigations, but considering the assumptions underlying both methodologies and the experimental errors, they can be considered in good agreement. The activation energy values for rotational reorientation (E_R) amount to ~10 kJ/mol, in agreement with data previously reported in the literature.[22a] The average distances extracted from the fits are consistent with those coming from the kinetics of NOE build-up. To facilitate the comparison, the main distances are summarized in Table 6. It can be noted that the agreement is very good.

General Discussion. After having reported on the measurements of the rotational correlation times, we can now discuss the accuracy of the average interionic distance determinations, a subject strictly related to the rates of the motions present in the ion pairs that can contribute to dipolar relaxation processes. Inside the Ru(II) ion pairs here investigated, there are three types of motions: (1) overall rotation of ion pairs and/or ions constituting them, (2) ion pair dissociation and formation, and (3) internal motions (Me group rotations around single bonds and chair–boat inversion of the six-member Ru–N–N–CH_2–N–N cycle). As stated above, the use of eq 3 for the determination of both intramolecular and interionic distances assumes that the correlation times of the unknown and reference distances are the same. The τ_c measurements (with both the methodologies) clearly indicate that the cation and anion have substantially the same rotational correlation times, higher than those of complex **2** which has the same size and mass as the cation of **1**. It is reasonable to conclude that *the overall ion pair rotation makes the greatest contribution to the dipolar relaxation processes, and consequently, the "contact" time is long enough to allow rather accurate average interionic distances to be estimated.* On the other hand, the four or three phenyl groups of the **1a**,**b** anions are always equivalent, even at low temperatures (down to ~200 K), indicating that a motion that averages them does exist. There can be two possibilities: (a) relative anion–cation rotation inside the ion pair, and (b) ion pair dissociation and reassociation with different anion–cation orientation. Both possibilities have to occur in less than ~10^{-2} s in order to average the differences in chemical shift, but it is not immediately clear which is the lowest limit. In his elegant papers,[7] Pochapsky and co-workers showed that for organic closed-shell ion pairs, the "contact" time is ~10^{-5} s.[7d] Despite the fact that, in such ion pairs, the anion is compenetrated with the cation, and consequently, the dissociation could be slowed, we consider it to be reasonable to estimate our "contact" time between 10^{-6} and 10^{-7} s, because it (point (b)) must not contribute significantly to the dipolar relaxation processes. Concerning point (a), in the case of Pochapsky's ion pairs, the anion is so small (BH_4^-) that it can "freely" rotate inside the ion pair as indicated by its very short correlation time (4 ps).[7c] In our compounds, the (a) motion could be partially inhibited by steric interactions. This explains why, whatever the (a) or (b) process is that averages the phenyl groups, its rate is smaller than $1/\tau_c$ and contributes little to the dipolar relaxation processes.

Conclusions

We have shown that the interionic structure of Ru(II) complex ion pairs **1a**–**g** can be directly and deeply investigated in solution by NOE NMR measurements. Qualitative ^1H-NOESY and ^{19}F, ^1H-HOESY indicate that interionic interactions are strong enough to determine a preferential anion–cation orientation that is not affected by changing the solvent: the counteranion prefers to locate close to the peripheral protons of bispyrazolyl ligand maximizing the electrostatic and van der Waals (in the case of "organic" anions) interaction energy as indicated in Figure 4. Of course, by increasing the dielectric constant of the solvent, the percentage of intimate ion pairs decreases, and NOEs become smaller. The quantification of NOEs allowed the average interionic distances to be estimated; these were checked and found to be both precise and accurate. In fact, by using two different methodologies, it was found that the rotational correlation times of cation and anion are similar and, very importantly, higher than that of neutral complex **2** that is isosteric with the cation of **1**. Consequently, the dipolar relaxation processes are determined mainly by the overall ion pair rotation. The determination of average interionic distances may afford valuable structural information. For example, only by comparing the interionic distances between BMe/CH_2 and *o*H/CH_2 was it possible to determine that in complex **1b** the anion orients the BMe group far away from the metal center. Generally speaking, the results of this study indicate that NOE NMR spectroscopy is a promising technique for investigating transition metal complex ion pairs in solution. We are currently applying the technique to transition metal complexes whose reactivity or catalytic properties are affected by ion pairing phenomena.

Experimental Section

General Considerations. Reactions were generally carried out in a dried apparatus under a dry inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified by conventional methods prior to use.[24] $Pz_2(CH_2)$,[25] *cis*,*trans*-RuI(Me)$(CO)_2(PMe_3)_2$,[26] *trans*-[Ru-

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(COMe){(pz_2)CH_2}(CO)(PMe_3)$_2$]BPh_4 (**1a**),[7b] *trans*-[Ru(COMe){(pz_2)CH_2}(CO)(PMe_3)$_2$]BF_4 (**1g**),[7b] and *trans*-Ru(COMe){(pz_2)BH_2}(CO)(PMe_3)$_2$ (**2**)[27] were prepared according to the literature. BPh_3 was prepared by the reaction of the adduct (BPh_3·NaOH)$_{aq}$ with HCl_{aq}. MeLi, *n*-BuLi, and *n*-HexLi reagents were purchased and used without further purifications.

Characterization of Complexes. All the complexes were investigated in solution by IR spectroscopy using an FT-IR Perkin-Elmer 1725X. All the carbonyl bands are in the range 1500−2200 cm^{-1} and are diagnostic for the relative positions of different C═O groups belonging to the same complexes or for the formation of the COMe group. Elemental analyses were made on a Carlo Erba 1106 elemental microanalyzer.

All the NMR measurements were performed on a Bruker Avance DRX 400 spectrometer operating at 400.13 MHz (^1H), 376.65 MHz (^{19}F), 161.98 MHz (^{31}P), and 100.61 MHz (^{13}C). Gradient pulses, only along the *z* direction, were generated by using the Great 1/10 gradient unit. Shaped pulses were generated by the standard controls available in a Bruker Avance DRX 400 spectrometer; the shape was Gaussian with a 1% truncation. Sample temperature was controlled using the BVT 3000 variable temperature unit equipped with digital control; the value was checked using a 4% CH_3OH in CD_3OD standard tube. Proton, carbon, and phosphorus spectra were acquired using the 5 mm QNP probe or the 5 mm TBI (triple resonance broadband inverse) probe. Fluorine spectra were acquired using the QNP probe. Referencing is relative to external TMS for ^1H and ^{13}C, external H_3PO_4 for ^{31}P, and external CCl_3F for ^{19}F. All FIDs (free induction decays) for proton, fluorine, and phosphorus were acquired using 32K or 64K points; the FIDs for carbon spectra were acquired using 64K or 128K data points. Carbon and phosphorus spectra were acquired by decoupling the ^1H nucleus. In the 2D NMR experiments, the number of digital points dedicated to direct and indirect dimension was fixed according to the desired resolution and to the total experimental time. Each transient (direct dimension) was acquired using 1K, 2K, or 4K points; the number of transients (indirect dimension) was from 512 to 2K, and the number of scans was set at 16, 24, or 32, depending on solute concentration. All bidimensional spectra were transformed using the zero filling procedure in both dimensions. The longitudinal relaxation times for the ^{13}C nuclei were measured by the standard inversion recovery method with ^1H decoupling. A total of 32 experiments, having the relaxation delay ranging from 0.001 to 28 s, were acquired, each of them consisting of 512 scans. The total relaxation delay between two consecutive scans was 15 s. All single experiments were Fourier transformed by using an exponential function with line broadening of 3.0 Hz. Frequency domain spectra were processed with a standard T_1/T_2 software package available on Bruker spectrometers to extract the relaxation parameters. The ^1H,^1H monodimensional NOE experiments for the quantitative investigation were carried out using the "selno" [17] or the "selnogp" [18] sequences; both are available in the standard pulse microprogram library of the Bruker spectrometers. All kinetic experiments using the selno sequence were performed by setting the central frequency (O1) on resonance with the "target" multiplet (i.e., the multiplet that has to be excited) and increasing the spectral width until all peaks were observed. A total of 32 experiments, having the mixing time period ranging from 0.0001 to 10 s, were acquired, each of them consisting of 64 scans. The total relaxation delay between two consecutive scans was 15 s. All single FIDs were Fourier transformed by using an exponential function with line broadening of 1.5 Hz. The spectrum with the shortest mixing time value was used as a reference spectrum; the integral value of the excited resonance was set at $-n_S$·100, and the integral values of all the other spectra were in reference to the previous one. The observed integral value on a given enhanced signal, divided by the number of protons corresponding to the signal itself (n_I), directly yields the percentage of NOE. The experiments using the selnogp sequence were acquired and processed in the same way; the total scan number depended on the concentration of the sample. The pulsed field gradient strength was set accordingly to the value suggested in the Bruker microprograms.

NMR Data. All the values in Tables 1 and 2 are presented with two digits, assuming a precision of 0.01 Å; of course, this is an underestimation of the error. First, the experimental $\langle\sigma_{IS}\rangle$ data are affected by an error of about 5% due to the goodness of nonlinear regression; second the reference distance, in the case of *o*H−*m*H, is again affected by a 4% experimental error. In light of this, distances, as a rough estimation, must be considered precise within ±0.1−0.2 Å. Finally, the 10% correction due to the overestimation of short distances is rather empirical, even if it is often used in the literature.[19] In Table 1, the intramolecular solid-state distances from the X-ray investigations[9b] are also reported; they are in very good agreement with the NOE measurements. Despite $\langle\sigma\rangle$ values determined by fitting complete experimental data with eq 1 and those coming from linear fittings up to a 0.4 s mixing time which are slightly different, the derived internuclear distances are in excellent agreement within experimental error. From the comparison of both intramolecular and interionic distances of complexes **1a**,**b** reported in Tables 1 and 2, it appears that they are excellently reproduced.

Synthesis of K[BPh$_3$R] (R = Me, *n*-Bu, *n*-Hex). RLi (11 mmol, Et_2O solution) was added to a solution of BPh_3 (3 g, 10.6 mmol) in Et_2O. The resulting solution was stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure. A volume of 50 mL of H_2O was added to the residual solid, obtaining a suspension that was then filtered; the final solution was saturated with KCl and K[BPh_3R] precipitated. It was washed with H_2O and dried.

R = Me:[28] yield = 78%. Anal. calcd (found) for $C_{19}H_{18}BK$: H, 6.12 (6.07); C, 77.03 (77.45). ^1H NMR (methanol-d_4, 298 K): δ 7.22 (m, *o*H), 6.91 (t, $^3J_{HH}$ = 7.2, *m*H), 6.75 (t, $^3J_{HH}$ = 7.1, *p*H), 0.21 (q, $^2J_{BH}$ = 3.8, BMe). R = *n*-Bu: yield = 73%. Anal. calcd (found) for $C_{22}H_{24}BK$: H, 7.15 (7.07); C, 78.10 (78.54). ^1H NMR (methanol-d_4, 298 K): δ 7.35 (m, *o*H), 6.97 (t, $^3J_{HH}$ = 7.2, *m*H), 6.80 (t, $^3J_{HH}$ = 7.1, *p*H), 1.24 (q, $^3J_{HH}$ = 7.2 CH_2(3)), 0.99 (m, CH_2(1) and CH_2(2)), 0.81 (t, $^3J_{HH}$ = 7.2, Me(4)). R = *n*-Hex: yield = 54%. Anal. calcd (found) for $C_{24}H_{28}BK$: H, 7.70 (7.58); C, 78.68 (78.46). ^1H NMR (nitromethane-d_3, 298 K): δ 7.23 (m, *o*H), 6.97 (t, $^3J_{HH}$ = 7.4, *m*H), 6.69 (t, $^3J_{HH}$ = 7.2, *p*H), 1.11 (m, CH_2(2), CH_2(4), CH_2(5)), 0.87 (m, CH_2(1) and CH_2(3)), 0.81 (t, $^3J_{HH}$ = 7.3, Me(6)).

Synthesis of Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$].[29] A solution of 3,5-(CF_3)$_2C_6H_3$-Br (10.26 g, 35 mmol) in 50 mL of Et_2O was slowly added to 10 mL of Et_2O containing 1 g of Mg and some I_2 crystals. The mixture was refluxed for 1 h, and then $NaBF_4$ (0.68 g, 6 mmol) was added. The solution was stirred for 48 h, and Na_2CO_3 (15 g in 200 mL of H_2O) was added. The solution was stirred for an additional 20 min. A solid separated from the solution and was filtered off. The resulting solution was extracted with Et_2O (4 × 40 mL). The ether solution was dried under anhydrous Na_2SO_4 and treated with decolorant carbon; the solvent was then removed, and the residual solid washed with small aliquots of CH_2Cl_2. The final product Na[B(3,5-(CF_3)$_2C_6H_3$)$_4$] was recrystallized from CH_2Cl_2/*n*-hexane. Yield = 70%. Anal. calcd (found) for $C_{32}H_{12}F_{24}BNa$: H, 1.35 (1.42); C, 43.34 (43.51). ^1H NMR (acetone-d_6, 298K): δ 7.78 (m, *o*H), 7.67 (s, *p*H). ^{19}F NMR (acetone-d_6, 298 K): δ −58.5 (s).

Synthesis of *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]BPh$_3$R (R = Me (1b), *n*-Bu (1c)). *cis*,*trans*-RuI(Me)(CO)$_2$(PMe_3)$_2$ (100 mg, 0.22 mmol) and pz_2(CH_2) (53 mg, 0.30 mmol) were dissolved in 5 mL of MeOH. K[BPh_3R] (large excess) was added, and a white solid precipitated. The solid was filtered, washed with cold Et_2O, and dried. Characterization of **1b**: yield = 63%. Anal. calcd (found) for $C_{35}H_{47}BN_4O_2P_2Ru$: H, 6.48 (6.52); C, 57.61 (57.16); N, 7.68 (7.75). IR (CH_2Cl_2): ν_{CO} = 1950.0 cm^{-1}; ν_{COMe} = 1602.6 cm^{-1}. ^1H NMR (methylene chloride-d_2, 298 K): δ 8.29 (d, $^3J_{HH}$ = 2.4, H3), 7.68 (d, $^3J_{HH}$ = 2.0, H3′), 7.41 (m, *o*H), 7.07 (d, $^3J_{HH}$ = 2.6, H5′), 7.02 (d, $^3J_{HH}$ = 2.1, H5), 7.01 (t, $^3J_{HH}$ = 7.2, *m*H), 6.84 (t, $^3J_{HH}$ = 7.1, *p*H), 6.34 (m, H4 and H4′), 4.64 (s, CH_2), 2.45 (s, COMe), 0.96 (Harris t,[30] $|^2J_{PH} + {}^4J_{PH}|$ =

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6.4, PMe_3), 0.34 (q, $^2J_{BH}$ = 3.8, BMe). ^{13}C NMR (methylene chloride-d_2, 298 K): δ 258.5 (br, *C*OMe), 205.2 (br, CO), 168.1 (q, $^1J_{BC}$ = 49.1, C-*ipso*), 149.3 (s, C3), 146.1 (s, C3′), 137.1 (s, C5), 135.7 (s, C5′), 135.3 (s, *o*C), 126.9 (s, *m*C), 122.9 (s, *p*C), 109.1 (s, C4), 108.3 (s, C4′), 61.6 (s, CH_2), 50.7 (s, CO*Me*), 15.6 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 29.4, PMe_3), 13.9 (q, $^1J_{BC}$ = 42.2, BMe). ^{31}P NMR (methylene chloride-d_2, 298 K): δ −3.6 (s). Characterization of **1c**: yield = 35%. Anal. calcd (found) for $C_{38}H_{53}BN_4O_2P_2Ru$: H, 6.87 (6.97); C, 59.14 (59.35); N, 7.26 (7.31). IR (CH_2Cl_2): ν_{CO} = 1950.0 cm^{-1}; ν_{COMe} = 1601.4 cm^{-1}. ^1H NMR (methylene chloride-d_2, 298 K): δ 8.32 (d, $^3J_{HH}$ = 2.3, H3), 7.71 (d, $^3J_{HH}$ = 2.3, H3′), 7.49 (m, *o*H), 7.03 (d, $^3J_{HH}$ = 2.6, H5′), 7.03 (t, $^3J_{HH}$ = 7.2, *m*H), 6.94 (d, $^3J_{HH}$ = 2.6, H5), 6.84 (t, $^3J_{HH}$ = 7.1, *p*H), 6.39 (m, H4 and H4′), 4.49 (s, CH_2), 2.49 (s, COMe), 1.31 (m, CH_2(3)), 1.03 (m, CH_2(1) and CH_2(2)), 0.99 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 6.5, PMe_3), 0.85 (t, $^3J_{HH}$ = 7.3, Me(4)).

Synthesis of *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]BPh$_3$(*n*-Hex) (1d). *cis*,*trans*-RuI(Me)(CO)$_2$(PMe$_3$)$_2$ (141 mg, 0.31 mmol) and pz$_2$(CH$_2$) (62.5 mg, 0.42 mmol) were dissolved in 10 mL of CH_3NO_2. After a few hours, the carbonyl stretching bands of the starting material disappeared, and K[BPh$_3$(*n*-Hex)] (115 mg, 0.31 mmol) was added to the solution. The solution was filtered, the solvent was removed, and the residual was dissolved in MeOH. After the addition of H_2O, the final product precipitated; it was washed with cold Et_2O and dried. Yield = 37%. Anal. calcd (found) for $C_{40}H_{58}BN_4O_2P_2Ru$: H, 7.30 (7.24); C, 60.00 (59.78); N, 7.00 (7.12). IR (CH_2Cl_2, 298 K): ν_{CO} = 1950.0 cm^{-1}; ν_{COMe} = 1602.6 cm^{-1}. ^1H NMR (methylene chloride-d_2, 298 K): δ 8.33 (d, $^3J_{HH}$ = 2.3, H3), 7.71 (d, $^3J_{HH}$ = 1.5, H3′), 7.48 (m, *o*H), 7.02 (t, $^3J_{HH}$ = 7.2, *m*H), 7.01 (d, $^3J_{HH}$ = 2.3, H5′), 6.93 (d, $^3J_{HH}$ = 2.2, H5), 6.83 (t, $^3J_{HH}$=7.2, *p*H), 6.39 (m, H4 and H4′), 4.52 (s, CH_2), 2.49 (s, COMe), 1.28 (m, CH_2(2), CH_2(4), CH_2(5)), 1.04 (m, CH_2(1) and CH_2(3)), 1.00 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 6.5, PMe_3), 0.88 (t, $^3J_{HH}$ = 6.6, Me(6)).

Synthesis of *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]B(3,5-(CF$_3$)$_2$(C$_6$H$_3$))$_4$ (1e). *cis*,*trans*-RuI(Me)(CO)$_2$(PMe$_3$)$_2$ (150 mg, 0.33 mmol) and pz$_2$(CH$_2$) (63 mg, 0.42 mmol) were dissolved in 10 mL of MeOH and stirred until the two carbonyl stretching bands of the starting material disappeared from the IR spectrum. Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (432 mg, 0.48 mmol) was added, and after the addition of H_2O, the final product precipitated. Yield = 70%. Anal. calcd (found) for $C_{48}H_{42}N_4BF_{24}O_2P_2Ru$: H, 3.09 (3.21); C, 43.16 (43.38); N, 4.19 (4.17). IR (CH_2Cl_2): ν_{CO} = 1953.9 cm^{-1}; ν_{COMe} = 1606.9 cm^{-1}. ^1H NMR (methylene chloride-d_2, 298 K): δ 8.61 (d, $^3J_{HH}$ = 2.4, H3), 7.96 (d, $^3J_{HH}$ = 2.2, H3′), 7.91 (d, $^3J_{HH}$ = 2.8, H5), 7.88 (d, $^3J_{HH}$ = 2.7, H5′), 7.78 (m, *o*H), 7.62 (s, *p*H), 6.67 (dd, $^3J_{HH}$ = 2.4, H4), 6.64 (dd, $^3J_{HH}$ = 2.4, H4′), 5.97 (s, CH_2), 2.58 (s, COMe), 1.11 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 6.4, PMe_3). ^{19}F NMR (methylene chloride-d_2, 298 K): δ −63.2 (s).

Synthesis of *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]PF$_6$ (1f). *cis*,*trans*-RuI(Me)(CO)$_2$(PMe$_3$)$_2$ (100 mg, 0.22 mmol) was dissolved in 5 mL of methylene chloride. Solid $TlPF_6$ (78 mg, 0.22 mmol) was added to the solution, and TlI precipitated immediately. The solid was filtered off, and pz$_2$(CH$_2$) (53 mg, 0.30 mmol) was added to the solution. After 30 min, *n*-hexane was added until incipient precipitation of complex **1f** occurred. The solid was washed with cold *n*-hexane and dried under vacuum. Yield = 69%. Anal. calcd (found) for $C_{16}H_{30}N_4F_6O_2P_3Ru$: H, 4.89 (4.94); C, 31.08 (31.53); N, 9.06 (9.17). IR (CH_2Cl_2): ν_{CO} = 1953.9 cm^{-1}; ν_{COMe} = 1606.9 cm^{-1}. ^1H NMR (methylene chloride-d_2, 298 K): δ 8.49 (d, $^3J_{HH}$ = 1.6, H3), 8.20 (d, $^3J_{HH}$ = 2.2, H3′), 8.18 (d, $^3J_{HH}$ = 2.8, H5), 7.88 (d, $^3J_{HH}$ = 2.7, H5′), 6.59 (m, H4 and H4′), 6.21 (s, CH_2), 2.55 (s, COMe), 1.09 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 6.6, PMe_3). ^{19}F NMR (methylene chloride-d_2, 298 K): δ −72.46 (d, $^1J_{FP}$ = 711).

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Supporting Information Available: NOE percentages as a function of mixing time (τ_m) relative to *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]BPh$_4$ (**1a**) (2×10^{-1} M) measured in methylene chloride-d_2 at 302 K (Table 1S); NOE percentages as a function of mixing time (τ_m) relative to *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]BPh$_3$Me (**1b**) (4×10^{-2} M) measured in methylene chloride-d_2 at 302 K (Table 2S); dipolar cross relaxation rate constants as a function of temperature for *trans*-[Ru(COMe){(pz$_2$)CH$_2$}(CO)(PMe$_3$)$_2$]BPh$_3$Me (**1a**) (2×10^{-1} M) measured in methylene chloride-d_2 with a mixing time of 0.4 s (Table 3S); trend of % NOE as a function of τ for the irradiation of H5 proton of the cation (T = 302 K) for complex **1a** (Figure 1S); theoric trend of σ_{IS} as a function of rotational correlation time τ_c for three pairs of protons 2.5, 3.0, and 3.5 Å apart (Figure 2S); plot of the best nonlinear least-squares fit of intramolecular (Figure 3S) and interionic (Figure 4S) σ_{IS} as a function of temperature for complex **1a** (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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