Cationic Bis- and Tris(η^2-(pyrazol-1-yl)methane) Acetyl Complexes of Iron(II) and Ruthenium(II): Synthesis, Characterization, Reactivity, and Interionic Solution Structure by NOESY NMR Spectroscopy

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The complexes *trans,cis*-M(PMe$_3$)$_2$(CO)$_2$(Me)I (M = Fe and Ru, **1a**,**b**) react with bis- and tris(pyrazol-1-yl)methane, in the presence of NaBPh$_4$, affording *trans*-[M(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BPh$_4$ (**2a**,**b**) and *trans*-[M(PMe$_3$)$_2$(CO)(COMe)(η^2-pz$_3$-CH)]BPh$_4$ (**3a**,**b**), respectively (pz = pyrazolyl ring). The reactions of **1b** with 5,5′-Me$_2$-pz$_2$-CH$_2$ and 3,5′-Me$_2$-pz$_2$-CH$_2$ produce *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(5,5′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (**4**) and *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(3,5′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (**5**), respectively. A mixture of *trans,cis*-[Ru(PMe$_3$)$_2$(CO)$_2$(η^1-3,3′-Me$_2$-pz$_2$-CH$_2$)(Me)]BPh$_4$ (**6**) and *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(3,3′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (**7**) is obtained from reaction of **1b** and 3,3′-Me$_2$-pz$_2$-CH$_2$. The reactions of **2**−**7** with nucleophiles either give back the starting complex (Nu = I$^-$) or analogous complexes (Nu = Br$^-$ and Cl$^-$) or produce decomposition products of the complexes (Nu = I$_2$, Br$_2$, Cl$_2$, and OMe$^-$). The solid state structures of **2b** and **3b** were obtained using single-crystal X-ray diffraction. For all complexes, **2**−**7** as well as complex **8** (analogue to **2a**, having a BF$_4^-$ counterion instead of BPh$_4^-$), the ion-pair structures and the localization of the counterion in solution with respect to the organometallic moiety were investigated by the detection of interionic contacts in the ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY NMR spectra.

Introduction

The previously described methyl complexes *trans,cis*-M(PMe$_3$)$_2$(CO)$_2$(Me)I (M = Fe[1] and Ru,[2] **1a**,**b**, respectively), prepared by oxidatively adding MeI to M(PMe$_3$)$_2$(CO)$_3$, are a useful class of compounds for the investigation of the stereochemistry and energetics of the insertion reaction. It has been shown that the ionic dissociation of the M−I bond, which occurs very readily, plays an important role in the mechanism of this reaction.[3,4]

From the synthetic point of view, as an ionic dissociation of iodide and migration of the methyl group, with formation of the M−COMe fragment, generate two vacant sites, in principle, it should be possible to coordinate any bidentate ligand (or two monodentate ligands). However, in practice, only ligands exerting a moderate steric hindrance promote the insertion process.

In the last few years, complexes containing nitrogen-coordinating ligands have become more and more important in homogeneous catalysis.[5] An increasing number of transition metal complexes containing poly(pyrazol-1-yl)borato ligands have been synthesized.[6,7] Instead, the isosteric poly(pyrazol-1-yl)methane ligands have been studied relatively little.[8]

Here, we report the results of our studies on the reactivity of complexes **1a**,**b** with several bis- and tris(pyrazol-1-yl)methane ligands, which has allowed us to synthesize complexes **1**−**8**, shown in Chart 1, and to develop a methodology, based on the nuclear Overhauser effect (NOE), for investigating the ion-pair solution structures of organometallic complexes.[9] This last point may be relevant in connection with the well-documented importance of charged organometallic complexes in homogeneous catalysis,[10] in particular, of the role of the counterion in activating or preventing these catalytic processes, and the lack of techniques for "directly" investigating the relative position of the counterion with respect to the organometallic fragment in solution.

Results and Discussion

Synthesis and Reactivity. (a) Bis(pyrazol-1-yl) Complexes. The reaction of **1a**,**b** with pz$_2$-CH$_2$ (pz =

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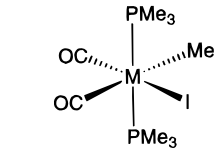
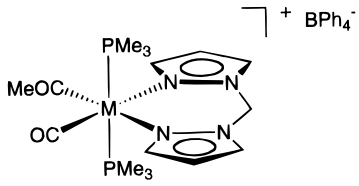
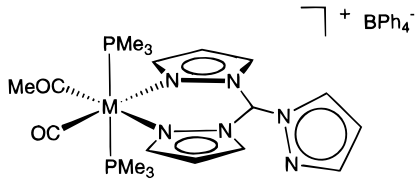
Chart 1



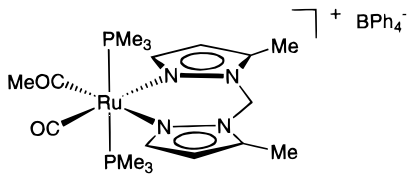
1a-b (M = Fe, Ru)



2a-b (M = Fe, Ru)



3a-b (M = Fe, Ru)



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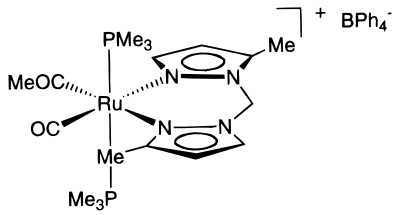

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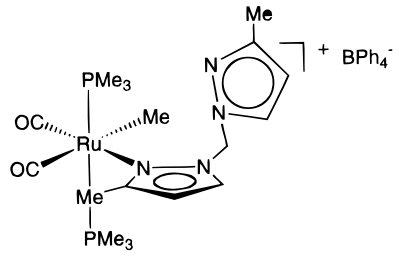

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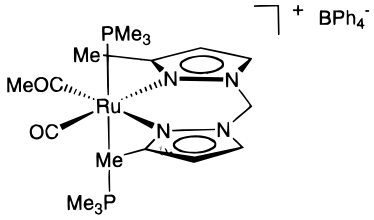

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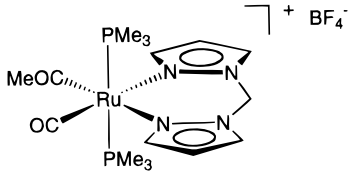

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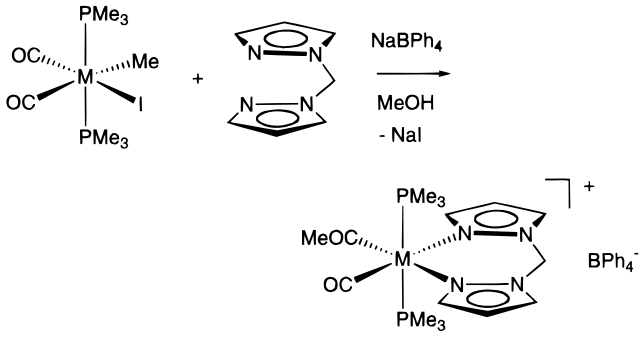
Scheme 1



pyrazol-1-yl-ring) in the presence of $NaBPh_4$ affords the acetyl complexes **2a**,**b** according to Scheme 1. Both compounds are stable in the solid state, and **2b** is even air- and moisture-stable for several days in solution, while **2a** decomposes in about 1 h at room temperature. The reactions reported in Scheme 1 are completely reversible. The addition of NBu_4X (X = I, Br, and Cl) to a solution of **2a**,**b** in CH_2Cl_2 gives back the starting complex or the analogous compound having a Br and Cl instead of I, the free ligand, and NBu_4BPh_4. Attempts to decarbonilate **2a**,**b** either by bubbling nitrogen through the solution, even when the temperature was increased up to 80 °C, or by reacting with Me_2NO were unsuccessful. Reactions of **2a**,**b** with X_2 (X = Cl, Br, and I) and $CuCl_2$ caused the elimination of the pz_2-CH_2 ligand and successive decomposition of the resulting unsaturated species. Finally, nucleophiles such as MeO^- prefer to substitute one pz ring rather than attack CO or COMe.

(b) Me_2-bis(pyrazol-1-yl) Complexes. The reaction of **1b** with 3,5′-Me_2-pz_2-CH_2 affords only complex **5**, where 3-Me is *cis* to CO. The formation of the product **5** can be explained by assuming that the rate of formation of the other possible isomer is slowed down by the steric hindrance between COMe and the 3-Me-pz ring.

The reactions of 3,3′-Me_2-pz_2-CH_2 or 5,5′-Me_2-pz_2-CH_2 with **1b** in the presence of $NaBPh_4$ do not afford any precipitate. In order to facilitate the reaction, the iodide must be removed by reacting **1b** with AgOTf (OTf = CF_3SO_3). After this operation, 5,5′-Me_2-pz_2-CH_2 coordinates forming complex **4**, while 3,3′-Me_2-pz_2-CH_2 affords a mixture of complexes **6** (η^1) and **7** (η^2). When this mixture is left in solution at 298 K, an equilibrium between **6** and **7** is established (1:2). The ^{1}H-NOESY NMR spectrum of the mixture shows an exchange cross

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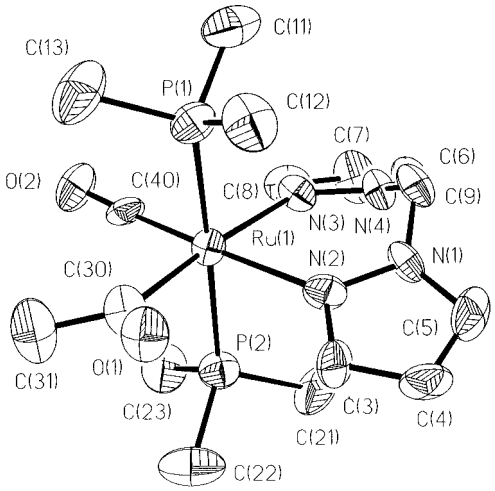


Figure 1. ORTEP view of the cationic fragment of **2b**.

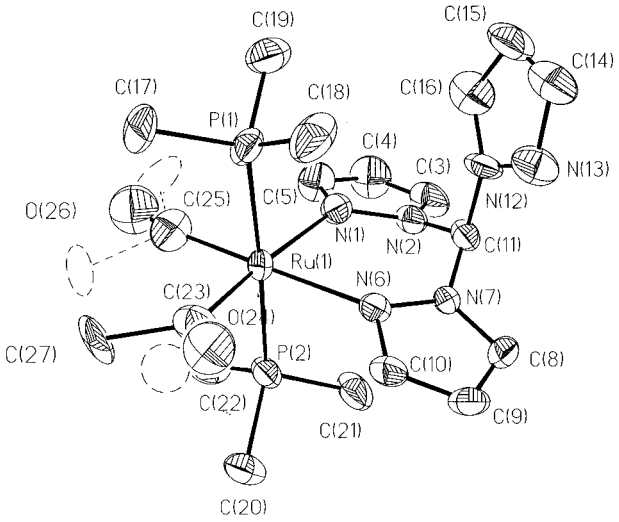


Figure 2. ORTEP view of the cationic fragment of **3b**. Disorder of CO and COMe is indicated by dashed lines.

peak between the protons of the Me group of **6** and those of COMe of **7**, indicating that the coordination of the second arm, with the consequent migration of Me on the *cis* CO, is slow relative to the $\Delta\delta$ of the Me of **6** and COMe of **7** (2.73 ppm, 1.37×10^3 Hz). The ligand 5,5′-Me_2-pz_2-CH_2 exerts the same steric hindrance and has similar electronic properties to pz_2-CH_2. Its weaker tendency to coordinate to **1b** can be attributed to the difficulty of BPh_4^- to approach the organic part of **4** consisting of the Me groups in 5-positions (see below).[9a] On the other hand, the presence of the η^1 complex **6** at the equilibrium is clearly due to the steric repulsion between one of the 3,3′-Me groups and the *cis* COMe. This also confirms that the selective formation of **5** is due to steric rather than mechanistic factors.

(c) η^2-Tris(pyrazol-1-yl) complexes. **1a**,**b** and pz_3-CH react in the presence of $NaBPh_4$ giving complexes **3a**,**b**, where one of the pz rings remains uncoordinated. It was not possible to eliminate PMe_3 or CO, even by increasing the temperature to 70 °C, to allow the coordination of the third pz ring. Decarbonylation as well reaction with X_2 were also tried for these compounds, with the same results as those for **2a**,**b**, i.e., the elimination of pz_3-CH and decomposition. Furthermore, the pz ring *trans* to COMe is the weakest ligand in the molecule, as clearly demonstrated by its exchange with the free pz ring and by the long Ru−N distance (see the NMR and solid state studies, respectively).

Characterization and Structure. (a) Solid State. X-ray crystallographic studies of **2b** and **3b** were carried out. ORTEP plots of **2b** and **3b** are shown in Figure 1 and 2, respectively. Table 1 gives the experimental parameters for both of the complexes, and Tables 2 and 3 list selected bond lengths and angles for **2b** and **3b**. The geometry at ruthenium in these complexes is approximately octahedral. The two Ru−N separations are significantly longer than those found in similar complexes.[8b] Furthermore, Ru−N(3) (2.257(14) Å) in **2b** is slightly longer than Ru−N(2) (2.218(15) Å), as expected from the higher *trans*-effect of COMe relative to CO. The six rings containing Ru and the four nitrogens are essentially in an envelope-like conformation: the angles between the least squares planes through the four nitrogens and the N−C−N planes are 54.4° for **2b** and 44.8° for **3b**. The angles between the N−Ru−N planes and the NNNN least-squares planes are 9.2° (boat-like conformation) and 8.9° (chair-like conformation) for **2b** and **3b**, respectively. This difference is probably due to steric repulsions between the uncoordined pz ring and the PMe_3 groups in **3b**. Other bond distances and angles fall in the expected ranges for compounds of this type. The methyl group of COMe points away from its *cis* pz ring. The conterion BPh_4^- is positioned in front of the pz_2-CH_2 ligand in **2b** and in front of the octahedral face containing the pz ring *cis* to COMe, PMe_3[2] (the second PMe_3 group), and COMe

Table 1. Experimental Data for X-ray Diffraction Study of 2b and 3b

	compound **2b**	compound **3b**
chem formula	$C_{41}H_{50}BCl_2N_4O_2P_2Ru$	$C_{46}H_{49}BN_6O_2P_2Ru$
mol wt	875.6	891.7
T, °C	20	20
space group	$P2_1/n$	$P\bar{1}$
a, Å	11.327(14)	12.60(4)
b, Å	24.57(3)	13.67(3)
c, Å	15.92(2)	13.67(3)
α, deg	90	85.3(2)
β, deg	94.03(10)	87.5(3)
γ, deg	90	75.2(2)
Z	4	2
V, Å^3	4421(9)	2269(11)
ρ(calcd), g cm^{-3}	1.316	1.305
λ, Å	0.710 73 Mo Kα	0.710 73 Mo Kα
μ, mm^{-1}	0.585	0.459
R	0.0521	0.0674
R_w	0.0586	0.0915

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2b

Ru−P(1)	2.342(5)	N(3)−N(4)	1.379(22)
Ru−P(2)	2.388(5)	N(1)−C(9)	1.412(21)
Ru−N(3)	2.257(14)	N(4)−C(9)	1.423(20)
Ru−N(2)	2.218(15)	C(40)−O(2)	1.149(20)
Ru−C(40)	1.809(16)	C(30)−O(1)	1.196(21)
Ru−C(30)	2.055(18)	P(1)−C(11)	1.778(18)
N(1)−N(2)	1.377(21)		

P(1)−Ru−P(2)	175.2(2)	P(2)−Ru−C(30)	88.9(5)
P(1)−Ru−N(3)	96.4(3)	N(3)−Ru−C(30)	175.3(6)
P(2)−Ru−N(3)	88.1(3)	C(40)−Ru−C(30)	92.2(7)
P(1)−Ru−C(40)	89.1(5)	N(2)−Ru−C(30)	91.8(6)
P(2)−Ru−C(40)	92.6(5)	Ru−N(3)−N(4)	123.3(9)
N(3)−Ru−C(40)	91.6(6)	Ru−N(2)−N(1)	123.9(10)
P(1)−Ru−N(2)	92.2(3)	N(2)−N(1)−C(9)	121.8(13)
P(2)−Ru−N(2)	86.5(3)	N(3)−N(4)−C(9)	119.2(13)
N(3)−Ru−N(2)	84.3(5)	N(1)−C(9)−N(4)	112.8(12)
C(40)−Ru−N(2)	175.9(6)	Ru−C(40)−O(2)	177.7(14)
P(1)−Ru−C(30)	86.5(5)	Ru−C(30)−O(1)	122.5(13)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 3b

Ru−P(1)	2.364(8)	N(6)−N(7)	1.386(10)
Ru−P(2)	2.388(8)	N(12)−N(13)	1.308(17)
Ru−N(1)	2.229(10)	N(2)−C(11)	1.426(14)
Ru−N(6)	2.214(10)	N(7)−C(9)	1.404(13)
Ru−C(23)	1.889(13)	N(12)−C(11)	1.461(14)
Ru−C(30)	1.906(15)	C(23)−O(24)	1.252(24)
N(1)−N(2)	1.365(11)	C(25)−O(26)	1.181(21)
P(1)−Ru−P(2)	177.2(2)	P(2)−Ru−C(25)	90.8(5)
P(1)−Ru−N(1)	93.8(3)	N(1)−Ru−C(25)	92.9(5)
P(2)−Ru−N(1)	87.4(3)	N(6)−Ru−C(25)	176.4(5)
P(1)−Ru−N(6)	95.4(3)	C(23)−Ru−C(25)	90.9(6)
P(2)−Ru−N(6)	92.6(5)	Ru−N(1)−N(2)	125.6(6)
N(1)−Ru−N(6)	84.1(3)	Ru−N(6)−N(7)	124.4(6)
P(1)−Ru−C(23)	88.6(4)	N(2)−C(11)−N(7)	115.0(8)
P(2)−Ru−C(23)	90.4(4)	N(1)−N(2)−C(11)	123.6(7)
N(1)−Ru−C(23)	175.7(4)	N(6)−N(7)−C(11)	123.5(6)
N(6)−Ru−C(23)	92.2(4)	Ru−C(25)−O(26)	169.0(22)
P(1)−Ru−C(25)	86.6(5)	Ru−C(23)−O(24)	129.6(14)

in **3b**. Interionic distances can be evaluated by adding together the size of the hydrogen to carbon atoms using standard values. The more important contacts are as follows. **2b**: *o*-H−CH_2, 2.56 Å; *m*-H−CH_2, 2.71 Å; *m*-H−PMe_3, 3.50 Å. **3b**: *o*-H−PMe_3^2, 2.79 Å; *o*-H−H-5 or H-5′, 4.05 Å; *m*-H−H-5 or H-5′, 3.59 Å, *p*-H−PMe_3^2, 3.53 Å.

(b) Solutions. Characterization of complexes **2**−**8** in this phase was carried out by IR and ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectroscopies. Preliminary results of the ^{1}H-NOESY studies, especially for **2b**, have appeared elsewhere.[9a] Complexes **2a** and **3a** are not stable in solution at room temperature in all of the solvents tested, even under a nitrogen atmosphere. The complexes decompose giving small amounts of paramagnetic species, making their NMR characterization difficult. The spectra were recorded at 263 K. All of the ^{1}H resonances, except those due to PMe_3^1 and PMe_3^2 in **3a**, appear as singlets. As in the case of **2b**,[9a] the spectrum of **2a** shows a resonance assigned to the CH_2 protons at an unusually low value (4.06 ppm), which can be explained considering the shielding effect exerted on CH_2 protons by the aromatic protons of BPh_4^-. The two phosphines in **3a** are magnetically inequivalent due to the presence of different substituents on the CH fragment. The ^{31}P{^{1}H} NMR spectrum is typical of an AB system having $^2J_{PP}$ = 137 Hz. This value falls in the expected range for complexes with a high electron density on the metal.[11]

The ^{1}H NMR spectrum of **3b** shows broad pz resonances, indicating that an exchange process is active. This was confirmed by the phase-sensitive ^{1}H-NOESY spectrum, which shows only one coordinated pz ring in equilibrium with the free pz ring (see Figure 3). An interligand COMe−H-3 contact allows a complete assignment of all of the pz resonances. This allows the assignment of the exchanging pz ring to be that in the *trans* position to COMe, in agreement with the extent of the *trans*-effect (see Scheme 2).[12]

It is reasonable that the ligand dissociating is *trans* to the group having the strongest *trans*-effect (COMe). This type of dynamic behavior was already observed for tris(pyrazol-1-yl)borato complexes of Rh(I),[13,14] where it

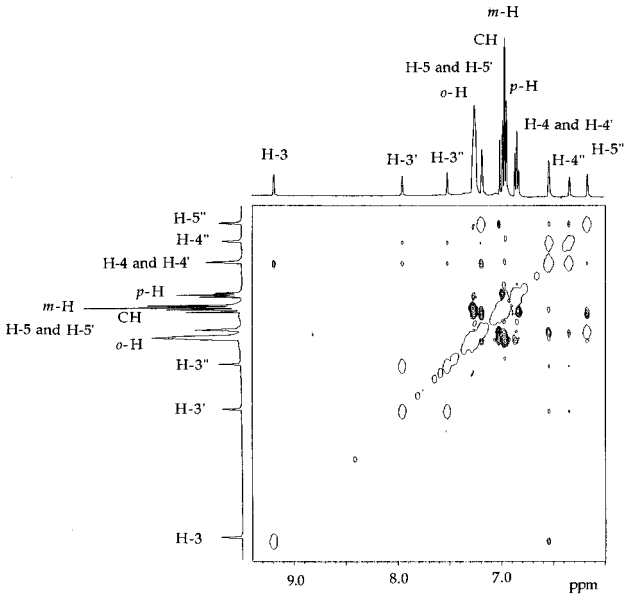
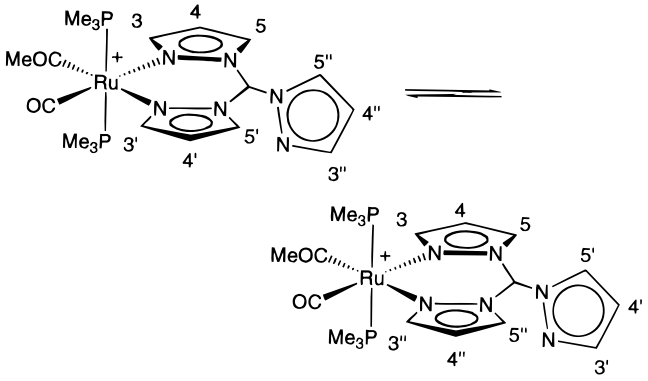


Figure 3. Section of the ^{1}H-NOESY spectrum of **3b** recorded at 400 MHz in CD_2Cl_2, showing the selective exchange between the pz ring trans to COMe and the uncoordinated pz ring. The exchange peaks are reported without contour levels.

Scheme 2



is usually so fast that it cannot be frozen out even at the lowest possible temperature (ca. −100 °C).

As found in **3a**, the two phosphines in **3b** are magnetically inequivalent. The ^{1}H NMR spectrum in the PMe_3 region shows two doublets at 0.86 and 0.82 ppm due to PMe_3^1 and PMe_3^2. The former is close to the uncoordinated pz ring, while the latter is close to the CH group. The assignment was made based on the ^{1}H-NOESY spectrum, which shows intramolecular contacts between PMe_3^1 and H-3, H-3′, H-3″, H-4″, and H-5″ and between PMe_3^2 and H-4, H-4′, CH, H-5, and H-5′.

Interionic Contacts. The phase-sensitive ^{1}H-NOESY spectra of all of the ruthenium complexes were recorded with the principal aim of understanding the type of ion-pair present in solution and the relative positions of the counterion and the organometallic moiety. The following interionic contacts were detected. For complex **2b**, H-5 and H-5′ show contacts with the *o*-H of BPh_4^-. The CH_2 protons show contacts with the *o*-H and weak contacts with the *m*-H. Finally, the

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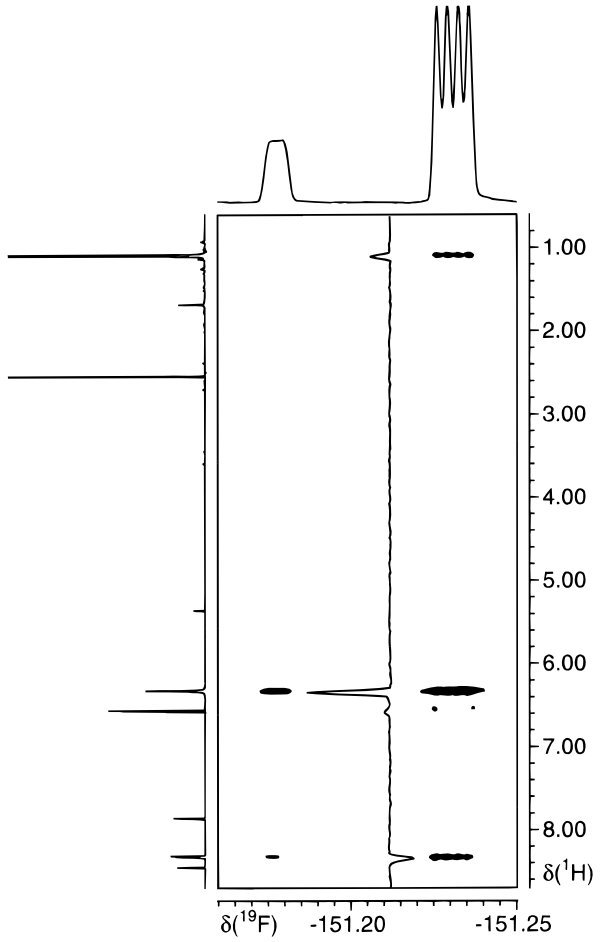

Figure 4. Countor plot of the $^{19}F\{^1H\}$-HOESY spectrum of complex **8** recorded at 376 MHz in CD_2Cl_2. The ^{19}F projection shows two sets of resonances due to $^{10}BF_4^-$ (−151.18 ppm) and $^{11}BF_4^-$ (−151.23 ppm). The phase of the cross peaks is visualized with the trace shown in the middle of the spectrum. Conventional ^1H and ^{19}F NMR spectra are plotted to the left and on the top, respectively.

protons of the PMe_3 groups interact with all of the protons of BPh_4^-. For complex **3b**, PMe_3[2] shows contacts with *o*-H and *p*-H (weak) and H-5 and/or H-5′ with *o*-H. For complex **4**, the 5-Me and 5′-Me groups show strong contacts with *o*-H and *m*-H. For complex **5**, the PMe_3 groups show contacts with *o*-H, *m*-H, and *p*-H (weak); the CH_2 protons show contacts with *o*-H; the 5-Me group shows contacts with *o*-H and *m*-H; and CH_2 as well as PMe_3 protons show contacts with *o*-H, *m*-H, and *p*-H (weak). In complexes **6** and **7**, the CH_2 protons show contacts with *o*-H and *m*-H (weak) and the PMe_3 groups interact with *o*-H(weak), *m*-H (weak), and *p*-H. In complex **8**, the fluorine atoms of BF_4^- show contacts with the CH_2, H-5, and PMe_3 protons (Figure 4). As can be seen from Figure 4, the phase of the cross peak due to H-5 and BF_4^- is different from that of the other cross peaks. This can be explained by assuming an indirect NOE between H-5 and BF_4^- mediated by the CH_2 protons. Studies to ascertain this hypothesis are in progress.

None of the spectra showed contacts between the COMe protons and the NMR-active atoms of the counterion. This observation and the detection of selective interaction between the counterion and only one PMe_3 group in **3b** and in other complexes where the two phosphines are inequivalent (unpublished results from this laboratory) make us sure that the counterion has a well-defined averaged position and does not interact with all the groups of the organometallic fragment.

The fact that interionic contacts were detected in all complexes indicates that under the experimental conditions used (ca. 0.04 M in CD_2Cl_2 at 298 K), complexes **2**−**8** are present as intimate or solvent-shared ion-pairs.[15]

The observed interionic contacts in complexes **2b** and **3b** are indeed those predicted from the X-ray crystal structures, assuming that the interactions between protons that are closer than 3.5−4 Å are detectable: the BPh_4^- anion places itself close to the organic part of the cation in order to maximize the lyophilic interaction.[9a] This anion is localized close to the pz ring and phosphine groups even when the steric hindrance in the external position is increased by adding one (**5**) or two (**6**) Me groups in the 5-position or using a completely different "inorganic" counterion, such as BF_4^- (**8**). We must conclude that the electrostatic interactions play an important role and that the positive charge is not localized on the ruthenium but it is partially delocalized in the pz rings.

Conclusions

The simultaneous ionization of the M−I bond and methyl migration on the *cis* carbonyl ligand allowed the preparation of several new cationic acetyl complexes of Fe(II) and Ru(II) containing the bis- and tris(pyrazolyl)-methane ligands. The complexes were spectroscopically characterized and their reactivity tested.

The interionic structure was clarified by NOESY spectroscopy, which detected the interactions between the protons of the cationic organometallic fragment and the NMR-active nuclei of the counterion. This has allowed the localization of the counterions relative to the organometallic moieties. Generally speaking, the possibility of localizing the counterion with respect to the charged organometallic fragment offers a unique tool to shed light on the role of the non- or weak-coordinating ion in activating or preventing important processes in homogeneous catalysis. Work is in progress to understand the effects of the experimental parameters (temperature, concentration, solvents, etc.) on the interionic contacts and to quantify the nuclear Overhauser effect in order to have information about averaged distances between the interacting nuclei.

Experimental Section

General Data. Complexes **1a** and **1b** were prepared according to the literature methods.[1,2] Reactions were carried out in a dried apparatus under a dry inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified prior to use by conventional methods.[16] The ligands pz_2-CH_2 and pz_3-CH were synthesized according to the literature methods.[17] Pyrazole and 3-methylpyrazole were purchased from Fluka and utilized without further purification.

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IR spectra were taken on a 1725 X FTIR Perkin-Elmer spectrophotometer. One- and two-dimensional ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on Bruker AC 200, DPX 300, DPX 400, AMX 500, and DMX 500 and Varian UNITY 400WB spectrometers. All chemical shifts are reported in ppm and coupling constants in Hertz. Referencing is relative to TMS and external 85% H_3PO_4. NMR samples were prepared by dissolving about 20 mg of compound in 0.5 mL of CD_2Cl_2 and bubbling for 5 min with dried nitrogen. Two-dimensional ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY spectra, with a mixing time of 500−800 ms, were measured as previously described.[18]

X-ray Crystallography. Crystals of **2b** and **3b** suitable for X-ray single-crystal analysis were obtained from CH_2Cl_2/ether/*n*-hexane. Diffraction intensities were collected at room temperature by the scan method on a graphite-monochromatized Syntex P21 diffractometer and reduced to F_o^2 values. Both structures were solved by Patterson methods and refined by full-matrix least-squares calculations. For all computations, the SHELXTL package of crystallographic programs were used. Thermal vibrations were treated anisotropically for all non-H atoms. All H atoms were positioned geometrically (C−H = 0.96 Å) and refined with adequate constraints. Final difference-Fourier maps showed residual peaks lower than 1.3 e Å^{-3} in the proximity of the Ru atom for both compounds. Poor crystal quality (and disorder in the case of **3b**) did not allow collection of data sets of high quality; the standard deviations of the bond distances are therefore rather large. The disorder of CO and COMe in **3b** was evident from the Fourier synthesis. Preliminary refinements indicated a 50% occupation probability of CO and COMe at each side: the positional occupancy parameters were finally kept fixed at 0.5.

Preparation of 3,3′-Me$_2$-pz$_2$-CH$_2$, 5,5′-Me$_2$-pz$_2$-CH$_2$, and 3,5′-Me$_2$-pz$_2$-CH$_2$. The ligands were synthesized according to the literature by the reaction of 3-methylpyrazole with CH_2Cl_2 in the presence of an aqueous solution of NaOH and NBu_4HSO_4.[17] The procedure for the separation and purification of the mixture of the three ligands obtained was modified. In fact, column chromatography using $CHCl_3$/*n*-hexane (9:1) suggested in ref 17 did not afford complete separation and purification of the ligands. Upon fractional sublimation of the mixture of the ligands and successive HPLC (inverse column C_{18} PAK 500, CH_3CN/H_2O 19:81, 0.6 mL/min), it was possible to obtain the ligands pure within 0.5−1% (yield 40%).

Preparation of *trans*-[Fe(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BPh$_4$ (2a). Compound **1a** (200 mg, 0.49 mmol) was dissolved in 5 mL of CH_3OH, and $NaBPh_4$ (large excess) was added. A solution of pz$_2$-CH (116 mg, 0.78 mmol) was slowly added. Immediately, a yellow solid precipitated. The solution was stirred for 30 min. The solid was filtered, washed with cold CH_3OH, dried, and crystallized from CH_2Cl_2/*n*-hexane (297 mg, yield 81%). Anal. Calcd (found) for $C_{40}H_{49}BFeO_2N_4P_2$: H, 6.57 (6.8); C, 64.4 (64.9); N, 7.5 (7.2). ^{1}H NMR (CD_2Cl_2, 263 K): δ 8.01 (s, H-3), 7.85 (s, H-3′), 7.47 (m, *o*-H), 7.01 (s, *m*-H), 6.81 (s, *p*-H), 6.71 (s, H-5), 6.63 (s, H-5′), 6.29 (s, H-4 and H-4′), 4.06 (s, CH_2), 2.48 (s, COMe), 0.87 (Harris t,[19] PMe_3). ^{13}C-{^{1}H} NMR: 277.9 (t, $^2J_{CP}$ = 22.0, *C*OMe), 220.6 (t, $^2J_{CP}$ = 30.5, CO), 164.2 (q, $^1J_{BC}$ = 49.3, C-*ipso*), 149.5 (s, C-3), 145.5 (s, C-3′), 137.1 (s, C-5), 136.3 (s, *o*-C), 135.6 (s, C-5′), 126.7 (s, *m*-C), 122.8 (s, *p*-C), 108.8 (s, C-4), 107.9 (s, C-4′), 60.1 (s, CH_2), 50.0 (s, CO*Me*), 14.6 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 25.3, PMe_3). ^{31}P-{^{1}H} NMR: 14.0 (s). IR: ν_{CO} 1929 cm^{-1}; ν_{COMe} 1597 cm^{-1}.

Preparation of *trans*-[Fe(PMe$_3$)$_2$(CO)(COMe)(η^2-pz$_3$-CH)]BPh$_4$ (3a). The procedure was the same as that of **2a**. Yield 77%. Anal. Calcd (found) for $C_{43}H_{51}BFeO_2N_6P_2$: H, 6.28 (6.2); C, 63.57 (63.4); N, 10.34 (10.0). ^{1}H NMR (CD_2Cl_2, 263 K): 8.90 (s, H-3), 8.20 (s, H-3′), 7.58 (s, H-3″), 7.24 (m, *o*-H), 7.04 (s, CH and H-5), 6.99 (s, *m*-H), 6.86 (s, *p*-H), 6.53 (s, H-5′ and H-5″), 6.37 (s, H-4, H-4′ and H-4″), 2.47 (s, COMe), 0.83 (d, $^2J_{PH}$ = 5.7, PMe_3^1), 0.74 (d, $^2J_{PH}$ = 7.1, PMe_3^2). ^{13}C{^{1}H} NMR: 277.9 (t, $^2J_{CP}$ = 25.8, *C*OMe), 221.2 (t, $^2J_{CP}$ = 31.5, CO), 164.1 (q, $^1J_{BC}$ = 49.5, C-*ipso*), 153.2 (s, C-3), 148.4 (s, C-3′), 143.2 (s, C-3″), 141.4 (s, C-5), 139.3 (s, C-5′), 136.4 (s, *o*-C), 130.1 (s, C-5″), 126.4 (s, *m*-C), 122.7 (s, *p*-C), 110.2 (s, C-4), 109.5 (s, C-4′), 107.7 (s, C-4″), 80.6 (s, CH), 49.4 (s, CO*Me*), 14.6 (d, $^1J_{CP}$ = 23.7, PMe_3^1), 14.2 (d, $^1J_{CP}$ = 25.6, PMe_3^2). ^{31}P-{^{1}H} NMR: 13.3 (d, $^2J_{PP}$ = 137, PMe_3^1), 9.4 (d, $^2J_{PP}$ = 137, PMe_3^2). IR: ν_{CO} 1927 cm^{-1}; ν_{COMe} 1597 cm^{-1}.

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BPh$_4$ (2b). The procedure was the same as that of **2a**. Yield 86%. Anal. Calcd (found) for $C_{40}H_{49}BRuO_2N_4P_2$: H, 6.20 (6.1); C, 60.7 (61.3); N, 7.08 (6.8). ^{1}H NMR (CD_2Cl_2): 8.30 (d, $^3J_{HH}$ = 2.2, H-3), 7.68 (d, $^3J_{HH}$ = 2.1, H-3′), 7.43 (m, *o*-H), 7.02 (td, $^3J_{HH}$ = 7.2, *m*-H), 6.90 (d, $^3J_{HH}$ = 3.1, H-5′), 6.84 (t, $^3J_{HH}$ = 7.5, *p*-H), 6.83 (d, $^3J_{HH}$ = 3.2, H-5), 6.33 (dd, H-4 and H-4′), 4.57 (s, CH_2), 2.45 (s, COMe), 0.96 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 6.6, PMe_3). ^{13}C{^{1}H} NMR: 257.8 (br, *C*OMe), 204.7 (t, $^2J_{CP}$ = 14.1, CO), 164.2 (q, $^1J_{BC}$ = 49.4, C-*ipso*), 149.0 (s, C-3), 145.7 (s, C-3′), 136.9 (s, C-5′), 136.3 (s, *o*-C), 135.3 (s, C-5), 126.4 (s, *m*-C), 122.6 (s, *p*-C), 108.7 (s, C-4′), 107.8 (s, C-4), 61.6 (s, CH_2), 50.2 (s, CO*Me*), 15.2 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 29.3, PMe_3). ^{31}P{^{1}H} NMR: −1.60 (s). IR: ν_{CO} 1950 cm^{-1}; ν_{COMe} 1601 cm^{-1}.

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(η^2-pz$_3$-CH)]BPh$_4$ (3b). The procedure was the same as that of **2a**. Yield 80%. Anal. Calcd (found) for $C_{43}H_{51}BRuO_2N_6P_2$: H, 5.95 (5.9); C, 60.2 (60.0); N, 9.8 (9.8). ^{1}H NMR (CD_2Cl_2): 9.19 (d, $^3J_{HH}$ = 2.0, H-3), 7.95 (d, $^3J_{HH}$ = 1.6, H-3′), 7.52 (d, $^3J_{HH}$ = 1.6, H-3″), 7.25 (m, *o*-H), 7.18 (m, H-5 and H-5′), 7.01 (s, CH), 6.97 (t, $^3J_{HH}$ = 7.6, *m*-H), 6.86 (t, $^3J_{HH}$ = 7.2, *p*-H), 6.54 (m, H-4 and H-4′), 6.34 (dd, $^3J_{HH}$ = 2.0, H-4″), 6.17 (dd, 2.4, H-5″), 2.44 (s, COMe), 0.86 (d, $^2J_{PH}$ = 8.8, PMe_3^1), 0.82 (d, $^2J_{PH}$ = 8.0, PMe_3^2). ^{13}C{^{1}H} NMR: 257.6 (br, *C*OMe), 204.1 (t, $^2J_{CP}$ = 14.8, CO), 164.3 (q, $^1J_{BC}$ = 49.4, C-*ipso*), 152.2 (s, C-3), 148.0 (s, C-3′), 142.1 (s, C-5′), 141.1 (s, C-3″), 138.7 (s, C-5), 135.8 (s, *o*-C), 128.6 (s, C-5″), 125.6 (s, *m*-C), 122.0 (s, *p*-C), 109.1 (s, C-4 and C-4′), 108.4 (s, C-4″), 80.2 (s, CH), 49.2 (s, CO*Me*), 14.6 (d, $^1J_{CP}$ = 25.0, PMe_3^1), 14.0 (d, $^1J_{CP}$ = 29.3, PMe_3^2). ^{31}P{^{1}H} NMR: −1.83 (AB system, $^2J_{PP}$ = 270). IR: ν_{CO} 1947 cm^{-1}; ν_{COMe} 1600 cm^{-1}.

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(5,5′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (4). Compound **1b** (200 mg, 0.37 mmol) was dissolved in 5 mL of CH_3OH, and $NaBPh_4$ (large excess) was added. A solution of AgOTf (85 mg, 0.33 mmol) was slowly added. Immediately AgI precipitated. The solution was filtered, and 60 mg of 5,5′-Me$_2$-pz$_2$-CH$_2$ (0.34 mmol), previously dissolved in 3 mL of CH_3OH, was added. A white solid precipitates. The solution was stirred for 30 min. The solid was filtered, washed with cold CH_3OH, dried, and crystallized from CH_2Cl_2/*n*-hexane (yield 50%). ^{1}H NMR (CD_2Cl_2, 298 K): 8.35 (d, $^3J_{HH}$ = 2.25, H-3), 7.73 (d, $^3J_{HH}$ = 2.1, H-3′), 7.30 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 7.27, *m*-H), 6.88 (t, $^3J_{HH}$ = 7.14, *p*-H), 6.35 (d, $^3J_{HH}$ = 2.23, H-4), 6.32 (d, $^3J_{HH}$ = 1.96, H-4′), 5.53 (s, CH_2), 2.52 (s, COMe), 2.36 (s, Me-5), 2.34 (s, Me-5′), 1.05 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 6.6, PMe_3). ^{13}C{^{1}H} NMR: 257.3 (t, $^2J_{PC}$ = 10.2, *C*OMe), 204.1 (t, $^3J_{PC}$ = 14.3, CO), 163.7 (q, $^1J_{CB}$ = 49.3, C-*ipso*), 148.1 (s, C-3), 144.9 (s, C-3′), 143.9 (s, C-5), 142.7 (s, C-5′), 135.6 (s, *m*-C), 125.3 (s, *o*-C), 121.4 (s, *p*-C), 108.6 (s, C-4), 108.0 (s, C-4′), 55.9 (s, CH_2), 49.6 (s, CO*Me*), 14.3 (Harris t, $|^1J_{PC} + {}^3J_{PC}|$ = 29.4, PMe_3), 11.2 (s, Me-5), 10.8 (s, Me-5′). ^{31}P{^{1}H} NMR: −4.27. IR: ν_{CO} 1951 cm^{-1}; ν_{COMe} 1603 cm^{-1}.

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(3,5′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (5). The procedure was the same as that of **2a**. Yield 83%. ^{1}H NMR: δ 8.06 (d, $^3J_{HH}$ = 2.3, H-3), 7.33 (m, *o*-H), 7.02 (t, $^3J_{HH}$ = 7, *m*-H), 6.96 (d, $^3J_{HH}$ = 2.6, H-5′), 6.87 (t, $^3J_{HH}$ = 7.1, *p*-H), 6.27 (d, $^3J_{HH}$ = 2.3, H-4), 6.18 (d, $^3J_{HH}$ = 2.6, H-4′), 5.2 (s, CH_2), 2.52 (s, Me-3′), 2.49 (s, COMe), 2.23 (s, Me-5), 1.06 (Harris t, $|^2J_{PH} + {}^4J_{PH}|$ = 4.6, PMe_3). ^{13}C{^{1}H} NMR: 256.1 (s, *C*OMe), 206.4 (s, CO), 164.7 (q, $^1J_{BC}$ = 49.3, C-*ipso*), 158.1 (s, C-3), 149.1 (s, C-3′), 145.02 (s, C-5), 136.6 (s, *m*-C), 136.1 (s, C-5′), 126.5 (s, *o*-C), 122.7 (s, *p*-C), 110.2 (s, C-4), 108.7

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(s, C-4′), 59.9 (s, CH_2), 48.9 (s, CO*Me*), 16.3 (s, Me-3′), 16.0 (Harris t, $|^1J_{PC} + {}^3J_{PC}| = 29.4$, PMe_3), 12.2 (s, Me-5). $^{31}P\{^1H\}$ NMR: −1.83 (s). IR: ν_{CO} 1951 cm^{-1}; ν_{COMe} 1605 cm^{-1}.

Preparation of *trans,cis*-[Ru(PMe$_3$)$_2$(CO)$_2$(η^1-3,3′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (6). The procedure was the same as that of **4**. Yield 58%. ^1H NMR (CD_2Cl_2, 298 K): 7.44 (m, *o*-H), 7.04 (t, $^3J_{HH} = 7.4$, *m*-H), 6.89 (t, $^3J_{HH} = 7.2$, *p*-H), 6.06 (d, H-4 or H-5), 5.93 (s, H-4 or H-5), 3.51 (s, CH_2), 1.31 (Harris t, $|^2J_{PH} + {}^4J_{PH}| = 7.3$, PMe_3), −0.26 (t, $^3J_{PH} = 8$, Me). $^{13}C\{^1H\}$ NMR: 164.7 (q, $^1J_{BC} = 49.3$, C-*ipso*), 150.9 (s, C-3), 136.6 (s, *m*-C), 131.4 (s, C-5), 126.8 (s, *o*-C), 123.0 (s, *p*-C), 107.4 (s, C-4), 65.2 (s, CH_2), 15.5 (Harris t, $|^1J_{PC} + {}^1J_{PC}| = 31.6$, PMe_3), −2.3 (s, Me). $^{31}P\{^1H\}$ NMR: −8.19 (s). IR: ν_{CO} 1952 cm^{-1}; ν_{COMe} 1606 cm^{-1}.

Preparation of *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(3,3′-Me$_2$-pz$_2$-CH$_2$)]BPh$_4$ (7). ^1H NMR (CD_2Cl_2, 298 K): 7.44 (m, *o*-H), 7.04 (t, $^3J_{HH} = 7.4$, *m*-H), 6.89 (t, $^3J_{HH} = 7.2$, *p*-H), 6.80 (s, H-5), 6.74 (s, H-5′), 6.10 (d, $^3J_{HH} = 2.6$, H-4), 6.09 (d, $^3J_{HH} = 2.6$, H-4′), 4.5 (s, CH_2), 2.47 (s, COMe), 2.46 (s, Me-3), 2.07 (s, Me-3′), 1.09 (Harris t, $|^2J_{PH} + {}^4J_{PH}| = 6.5$, PMe_3). $^{13}C\{^1H\}$ NMR: 164.7 (q, $^1J_{BC} = 49.3$, C-*ipso*), 159.2 (s, C-3), 157.2 (s, C-3′), 137.0 (s, C-5), 136.6 (s, *m*-C), 126.8 (s, *o*-C), 123.0 (s, *p*-C), 110.6 (s, C-4), 109.9 (s, C-4′), 62.3 (s, CH_2), 48.8 (s, CO*Me*), 19.0 (s, Me-3), 16.9 (Harris t, $|^1J_{PC} + {}^1J_{PC}| = 30$, PMe_3), 16.1 (s, Me-3′). $^{31}P\{^1H\}$ NMR: −7.07 (s). IR: ν_{CO} 2038, 1975 cm^{-1}.

***trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BF$_4$ (8).** Compound **1b** (100 mg, 0.22 mmol) and pz_2-CH_2 (36 mg, 0.24 mmol) were dissolved in 5 and 3 mL of CH_3OH, respectively. A solution of $AgBF_4$ (39 mg, 0.20 mmol) was slowly added. Immediately, AgI precipitated. The solution was filtered and dried. The residue was dissolved in CH_2Cl_2 and crystallized from CH_2Cl_2/*n*-hexane. Yield 60%. ^1H NMR (CD_2Cl_2, 298 K): 8.45 (d, $^3J_{HH} = 1.6$, H-3), 8.33 (dd, H-5), 8.31 (d, $^3J_{HH} = 2.6$, H-3′), 7.86 (d, $^3J_{HH} = 2.1$, H-5′), 6.57 (m, H-4 and H-4′), 6.33 (s, CH), 2.54 (s, COMe), 1.09 (Harris t, $|^2J_{PH} + {}^4J_{PH}| = 6.6$, PMe_3). ^{19}F NMR: −151.23. IR: ν_{CO} 1955 cm^{-1}; ν_{COMe} 1605 cm^{-1}.

Reaction of 2a,b and 3a,b with X = Me$_2$NO, I$^-$, Br$^-$, Cl$^-$, CuCl$_2$, and MeO$^-$. The complexes (20 mg) were dissolved in ca. 3 mL of CH_2Cl_2 at room temperature and an equimolar quantity of X. The reactions were followed by IR spectroscopy. The final products were characterized with NMR spectroscopy.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients (Tables S1 and S2), anisotropic displacement coefficients (Tables S3 and S4), H-atom coordinates and isotropic displacement coefficients (Tables S5 and S6), bond lengths (Tables S7 and S8), and bond angles (Tables S9 and S10) for **2b** and **3b** (14 pages). Ordering information is given on any current masthead page.

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