Intramolecular and Interionic Structural Studies of Novel Olefin Palladium(II) and Platinum(II) Complexes Containing Poly(pyrazol-1-yl)borate and -methane Ligands. X-ray Structures of Palladium Five-Coordinate Complexes

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Complexes $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_2\text{-}YH_2)]^{(+)}$ (M = Pd, Y = C, **1**; M = Pt, Y = C, **2**; M = Pt, Y = B, **3**) and $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}YH)]^{(+)}$ (M = Pd, Y = C, **4**; M = Pd, Y = B, **5**; M = Pt, Y = C, **6**; M = Pt, Y = B, **7**) were synthesized by the reaction of the dimers $[M(\eta^1,\eta^2\text{-}C_8H_{12}\text{-}OMe)Cl]_2$ with the poly(pyrazol-1-yl)borate and -methane ligands. Complexes **1**−**7** were characterized in solution by multinuclear and multidimensional low-temperature NMR spectroscopy. The solid-state structures of olefinic five-coordinate Pd complexes **4** and **5** were investigated by X-ray single-crystal studies. The relative cation−anion position (interionic structure) was investigated in solution, for all cationic complexes at room and low temperature by ^{19}F, ^1H-HOESY NMR spectroscopy, and in the solid state for **4**. A remarkable specifity of the interionic contacts is observed in solution: the counterion is placed close to the peripheral protons of the pyrazolyl ligands probably due to the partial protection of the apical positions introduced by the nonplanar ligands and the delocalization of the positive charge on the pyrazolyl rings. In the case of complex **4** there is an excellent agreement between the solid state and solution results: the anion selectively interacts with the CH and five protons of the pz_3-CH ligand via an assembly of hydrogen bonds.

Introduction

The importance of having direct structural information about transition metal complex ion pairs in solution is demonstrated daily by the increasing number of reactions in which the noncovalent anion−cation interactions play a crucial role.[1]

In the past few years, we have shown that detailed information about the relative cation−anion position in solution (interionic structure) can be gained by detecting interionic dipolar interactions, between nuclei belonging to the cation and others belonging to its counterion, in the NOESY and HOESY NMR spectra.[2]

After having investigated "model" compounds, we have now started to study charged organometallic complexes that are active homogeneous catalysts,[3] or strictly related to them,[4] whose activity is a function of the counterion. In complexes $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)\text{-}(bipy)]^+X^-$ (where bipy = 2,2′-bipyridine), which are active catalysts for the CO/styrene copolymerization,[3] the counterion is located in solution above or below the bipy ligand shifted toward the pyridine ring trans to the Pd−C σ bond. Interestingly, but not surprisingly considering the low level of stabilization energy that determines the average favored structure, the interionic structure in solution is different than that observed in the solid state. Furthermore, the least coordinating anion is, as usual, the best for the catalytic activity of the organometallic complex.

An increased steric hindrance above and below the coordination plane should prevent the counterion from

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(4) Zuccaccia, C.; Macchioni, A.; Orabona, I.; Ruffo, F. *Organometallics* **1999**, *18*, 4367.

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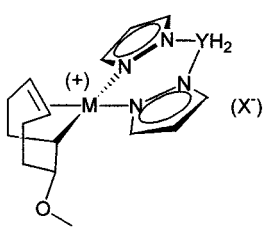
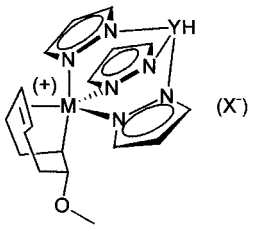
Chart 1

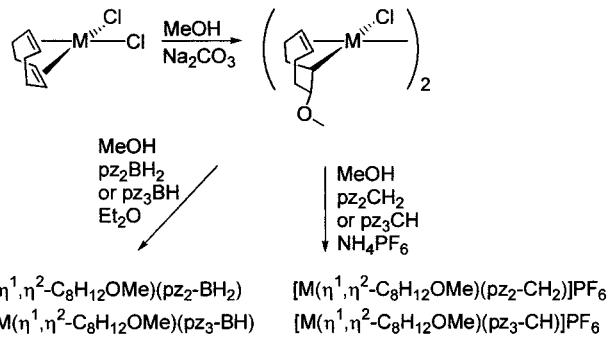


1: M = Pd; Y = C; $X^- = PF_6^-$.
2: M = Pt; Y = C; $X^- = PF_6^-$.
3: M = Pt; Y = B.



4: M = Pd; Y = C; $X^- = PF_6^-$.
5: M = Pd; Y = B.
6: M = Pt; Y = C; $X^- = PF_6^-$.
7: M = Pt; Y = B.

Scheme 1



$Pt(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_2\text{-}BH_2)$ or $M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}BH)$

$[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_2\text{-}CH_2)]PF_6$ or $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}CH)]PF_6$

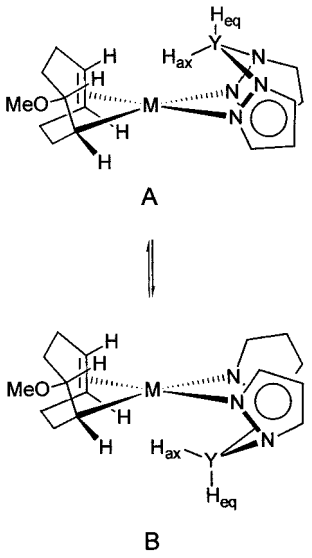
occupying the apical positions. For this reason, we decided to substitute the planar bipy ligand with ligands, namely, the bis- and tris(pyrazol-1-yl)borate and -methane ligands, that can cause steric hindrance above and below the square planar coordination plane.

In this paper we report the synthesis of four-coordinate $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_2\text{-}YH_2)]^{(+)}$ (**1**−**3**) and five-coordinate $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}YH)]^{(+)}$ (**4**−**7**) complexes (Chart 1) and their NMR characterization at room and low temperature. The interionic structures of complexes **1**, **2**, **4**, and **6** in methylene chloride deduced by ^{19}F, ^1H-HOESY NMR spectroscopy is described. Finally, the X-ray molecular structures of five-coordinate **4** and **5** complexes is also reported.

Results and Discussion

Synthesis. Organometallic complexes **1**−**7** were synthesized according to Scheme 1. The first step of the reaction[5] involves a direct exo attack[6] of MeO^- on the coordinated cyclooctadiene of $[M(C_8H_{12})Cl_2]$ with the formation of the dimers $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ as air-stable, pale yellow solids. The latter react in methanol with bis- and tris(pyrazol-1-yl)methane ligands in the presence of NH_4PF_6, forming complexes (**1**, **2**, **4**, and **6**) that precipitate from solution. The reactions of the aforementioned dimers with bis- and tris(pyrazol-1-yl)-borate ligands afford complexes **3**, **5**, and **7**, which precipitate from the methanolic solution after the addition of ethylic ether. Several attempts to synthesize the Pd complex analogous to **3** were unsuccessful. In all cases the reaction afforded Pd metal.

Scheme 2



Five-coordinate complexes **4**−**7** are stable in both the solid state and in solution and little sensitive to moisture; as usual, the Pt compounds are more stable than the Pd ones. Four-coordinate 16-electron complexes are stable in the solid state and little sensitive to moisture, while in solution they undergo decomposition processes that may be initiated by the activation of the Y−H bond. The stability decreases going from Pt to Pd and from Y = C to Y = B; as a confirmation, attempts to synthesize the four-coordinate complex where M = Pd and Y = B were unsuccessful.

Five-coordinate Pd and Pt olefin complexes are well known in the literature,[7] even if the palladium ones are much less numerous. However, to our knowledge, there are no complexes where the olefin takes part in a chelate ring while the other ligand spans three coordination sites. Furthermore, five-coordinate Pd olefin complexes containing the trispyrazolylborate or -methane ligands are not known; this makes complexes **4** and **5** quite interesting and pushed us to thoroughly investigate their structures in both solution and in the solid state (see below).

NMR Intramolecular Characterization. Complexes **1**−**7** were characterized in CD_2Cl_2 by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopies. All the complexes present some dynamic processes and were, consequently, investigated by low-temperature NMR experiments. In particular, complexes **1**−**3** undergo exchange of the two pyrazolyl rings and inversion of the six-membered chelate rings. Two isomers are present in solution (indicated with A and B in Scheme 2) and both exchange their pyrazolyl rings. Complexes **4**−**7** also undergo pyrazolyl ring exchange. At low temperature, the resonances of the aromatic protons 3′, 3″, 5′, and 5″ of the two isomers A and B shown in Scheme 2 are separated (see Chart 2 for the numbering scheme[8] of protons and carbons). Despite this, the inversion of the six-membered ring (MNNYNN) is still fast compared to the ^1H

(5) For the Pt dimer see: Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496. For the Pd dimer see: Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.

(6) Hoel, G. R.; Stockland, R. A., Jr.; Anderson, G. K.; Lapido, F. T.; Braddock-Wilking, J.; Rath, N. P.; Mareque-Rivas, J. C. *Organometallics* **1998**, *17*, 1155.

(7) Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, *133*, 67, and references therein.

(8) The numeration of compounds **1**−**3** follows the same criteria considering that the ‴-ring is no longer present and the ring trans to C1 is again labeled with ′.

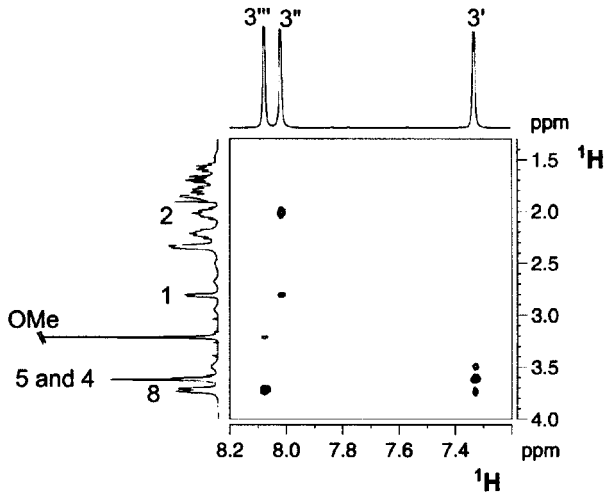
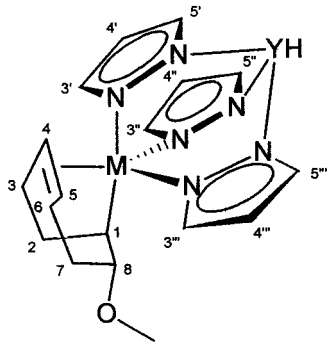


Figure 1. Section of the ^{1}H-NOESY NMR spectrum (400.13 MHz, 217 K) of compound **6** recorded in CD_2Cl_2 showing the assignment of the 3′, 3″, and 3‴ protons based on the "contacts" with the protons belonging to the cyclooctenylmethoxy moiety.

Chart 2



longitudinal relaxation time, and it is not possible to assign the resonances relative to the A and B isomers.[9]

The C8 was the starting point for the assignment of the proton and carbon resonances, as its chemical shift is known from previous studies and is well separated from other carbon resonances. H8 was easily assigned from the ^{1}H, ^{13}C HMQC spectrum. All the proton resonances of the cyclooctenyl group were then assigned following the scalar connectivity in the ^{1}H-COSY spectrum. The carbon resonances of this group were again identified from the ^{1}H, ^{13}C HMQC spectrum. The assignment of the resonances relative to the pyrazolyl-rings were carried out on the basis of intramolecular dipolar interactions detected in the ^{1}H-NOESY spectra. In particular, for compounds **1**−**3**, the 3′ proton dipolarly interacts with the olefinic protons 4 and 5, while 3″ shows a contact with proton 1. For complexes **4**−**7**, the 3′ proton shows a contact with the olefinic protons 4 and 5, 3″ interacts with 1 and 2, and 3‴ shows contacts with 8 and OMe (see Figure 1). The other protons of the pyrazolyl rings and of the YH_n groups were assigned either from the ^{1}H-COSY or -NOESY spectra. Finally, their carbons were identified by the ^{1}H, ^{13}C HMQC spectra.

It is interesting to note that the resonances of 4 and 5 olefinic protons and carbons follow well-defined trends

Table 1. Selected ^{1}H and ^{13}C NMR Chemical Shift Values (ppm) Obtained in CD_2Cl_2

complex			1	4	5	8	3′	3″	3‴
1	^{1}H	A	3.38	6.30	5.74	3.75	7.49	7.87	
		B	3.18	6.23	5.67	3.59	7.40	7.63	
	^{13}C	A	50.0	111.7	106.4	82.5	141.8	142.8	
		B	48.7	107.7	104.4	82.3	141.3	142.2	
2	^{1}H	A	2.62	5.12	5.28	3.65	7.66	7.98	
		B	2.62	5.00	5.21	3.40	7.44	7.75	
	^{13}C	A	28.4	90.5	93.6	82.8	141.4	142.5	
		B	27.6	87.1	90.6	82.6	140.8	142.5	
3	^{1}H		2.60	4.96	4.81	3.54	7.33	7.67	
	^{13}C		26.2	87.5	84.9	83.6	139.5	137.7	
4	^{1}H		3.51	5.35	4.70	3.75	7.26	8.00	7.98
	^{13}C		48.2	90.3	81.3	82.7	142.7	142.7	142.7
5	^{1}H		3.36	5.12	4.53	3.91	7.11	7.91	7.91
	^{13}C		43.9	84.9	75.5	83.1	137.6	140.0	141.2
6	^{1}H		2.81	3.61	3.64	3.72	7.33	8.02	8.08
	^{13}C		23.7	58.2	48.0	81.9	139.5	142.2	143.6
7	^{1}H		2.70	3.24	3.30	3.85	7.12	7.89	7.95
	^{13}C		20.5	52.7	42.2	82.2	135.6	139.5	141.2

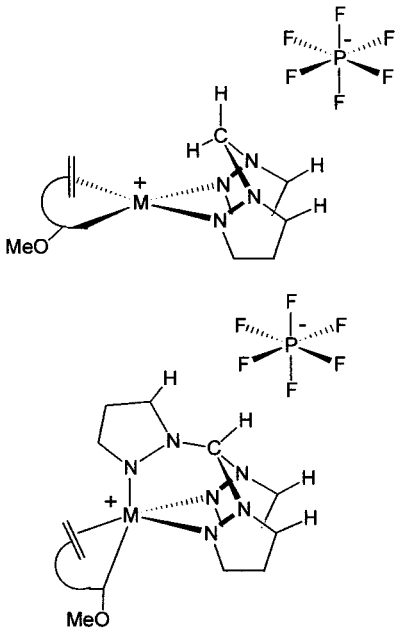
(see Table 1): they resonate at lower frequency going (a) from palladium to platinum, (b) from four- to five-coordinate complexes, and (c) from the (pyrazol-1-yl)-borate to the -methane ligands. All these trends can be explained assuming that the correlation between the low-frequency shift and the extent of π-back-donation is correct.[10] It is in fact known that the π-back-donation is smaller in Pd compounds, for four-coordinate complexes, and when the ligands are less nucleophilic. In the case of complex **1**, there is no shielding effect; on the contrary, the proton resonances have a higher frequency than those due to the protons of free olefin.

NMR Interionic Characterization. The interionic structure of **1**, **2**, **4**, and **6** cationic complexes was investigated in methylene chloride-d_2 at low temperature (188 K) by detecting the dipolar interactions between F-nuclei belonging to the anion and H-nuclei of the cation in the ^{19}F, ^{1}H-HOESY spectra. The only interionic dipolar interactions detected were those between the fluorine atoms of the counterion and the 5 and CH_n protons ($n = 2$, **1** and **2**; $n = 1$, **4** and **6**). The resulting interionic structure is depicted in Scheme 3. In Figure 2 the ^{19}F, ^{1}H-HOESY spectrum of complex **4** is reported and is clearly visible as PF_6^- interacts strongly with 5′/5‴ and CH protons, while it gives only a very weak contact with 4′/4‴ protons. No other cross-peaks are present. Figure 3 shows the ^{19}F, ^{1}H-HOESY spectrum of complex **1**; again PF_6^- interacts only with CH_2, 5′/5″, and 4′/4″ (weakly) protons. In our previous investigations on transition metal complex ion pairs, we found that there can be two conditions that allow a well-defined anion−cation relative position: (1) electron polarizability of the complex that causes an accumulation of positive charge far away from the metal; and (2) axial steric protection of the metal. The second condition is naturally reached in octahedral complexes[11,12] where the ion-pair structure is, consequently, determined by point (1). In the case of square planar complexes, the axial positions must be sterically protected in order to prevent the anion from occupying the "natural" position

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

(10) For a more detailed dicussion about the correlation between the low-frequency shift of olefinic protons and carbons and the extent of π-back-donation see: Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269.

Scheme 3



above and below the coordination plane.[4] A degree of specificity comparable to that of complexes **1** and **2** was observed only for complex [PtMe(dpa)(Me_2SO)]X, where dpa = bis(2-pyridyl)amine, which contains two pyridyl rings separated by a bridging NH group even though the apical positions are almost free of steric hindrance.[13] In such a case, the NH bridging proton has a strong electropositive character and gives robust hydrogen-bonding interaction with the counteranion X^-. While the interionic structure of five-coordinate **4** and **6** complexes can be rationalized with considerations similar to those valid for octahedral complexes, the interionic structure of complexes **1** and **2** is not easy to explain. In such cases the apical positions are only partially protected by the steric hindrance introduced by the boat conformation of the MNNYNN cycle and the anion should be able to occupy the apical position that is not hindered by CH_2. Instead, it prefers to locate in the peripheral part of the N,N ligand, which leads one to think that the accumulation of positive charge on the N,N ligands is considerably higher than the "residual" positive charge on palladium. Such accumulation could also favor the formation of F···H hydrogen bonds between the CH moiety and the counteranion.

Molecular Structures of [Pd(η^1,η^2-C_8H_{12}OMe)(pz_3-CH)][PF_6] (4) and [Pd(η^1,η^2-C_8H_{12}OMe)(pz_3-BH)] (5). X-ray structural studies of the title complexes established the five-coordination of the metal center in both species, instead of the more usual four-coordination. Structure models of **4** and **5** are reported in Figures 4 and 5, together with their crystallographic numbering, while the stereogeometries are reported in Table 2. Complex **4** consists of discrete [Pd(η^1,η^2-C_8H_{12}OMe)(pz_3-CH)]$^+$ cations and PF_6^- counterions. Both **4** and **5** exhibit equivalent stereogeometries and are the first

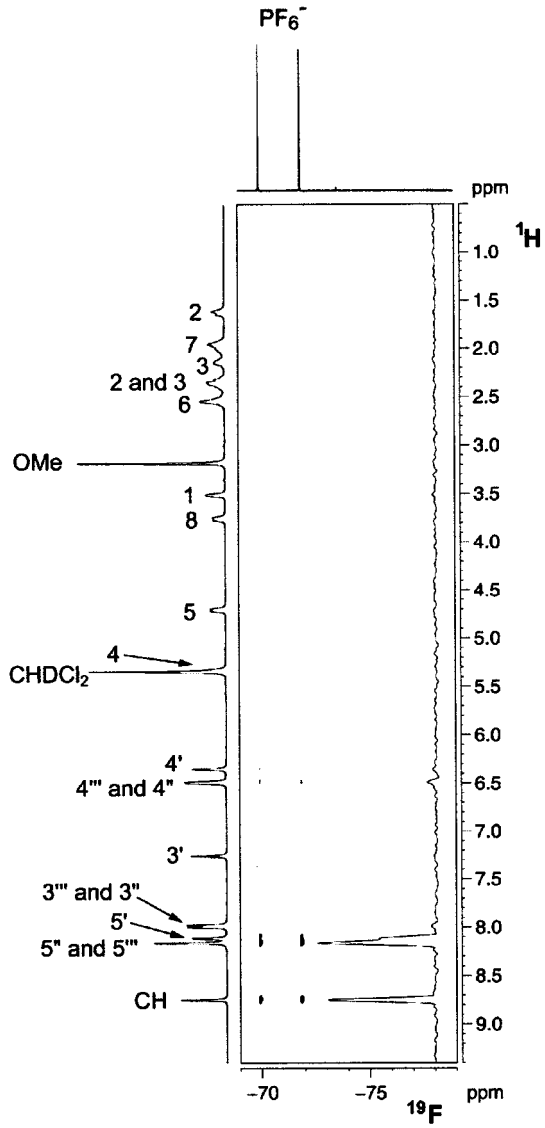


Figure 2. ^{19}F, ^1H-HOESY NMR spectrum (376.63 MHz, 188 K) of compound **4** recorded in CD_2Cl_2 showing the remarkable specificity of interaction between PF_6^- and the 5′−5‴ and 4′−4‴ protons of the cation. The 1D-trace relative to the PF_6^- column is reported on the right.

examples of five-coordinate Pd olefin complexes containing trispyrazolylmethane or trispyrazolylborate ligands as well as the first examples of cyclooctenyl five-coordinate Pd complexes. The palladium ligand bonds are as follows: the axial positions are occupied by one pyrazolyl nitrogen and the C sp^3 atom of the cyclooctenyl moiety [C(15)−Pd−N(2) 175.6(3)° and 173.9(2)°, Pd−C(15) 2.048(9), 2.042(6) Å, Pd−N(2) 2.186(6) and 2.168(5) Å in **4** and **5**, respectively]. The equatorial sites are occupied by two pyrazolyl nitrogens [Pd−N(4) 2.343(6), 2.226(6) Å and Pd−N(6) 2.254(6), 2.322(5) Å for **4** and **5**, respectively] and by the olefin double bond [Pd−C(11) 2.116(8), 2.122(7) Å, Pd−C(12) 2.128(8), 2.110(7) Å, C(11)−C(12) 1.40 (1) and 1.38(1) Å for **4** and **5**, respectively]. The Pd−C interactions can be compared with those observed in the five-coordinate Pt(II) complex [Pt(η^1,η^2-C_8H_{12}-OMe)Cl(Me_2Phen)] [2.057(9) and 2.052(7), 2.075(7) Å for the Pt−C axial and the Pt−olefin interactions respectively].[14] Only four other examples of five-coordinate Pt(II) complexes containing the cyclooctenyl ligand have been found, and their relative Pt−C bond

(11) Bellachioma, G.; Cardaci, G.; D'Onofrio, F.; Macchioni, A.; Sabatini, S.; Zuccaccia, C. *Eur. J. Inorg. Chem.* **2001**, 1605.
(12) Macchioni, A.; Zuccaccia, C.; Clot, E.; Gruet, K.; Crabtree, R. H. *Organometallics* **2001**, *20*, 2367.
(13) Romeo, R.; Nastasi, N.; Monsù Scolaro, L.; Plutino, M. R.; Albinati, A.; Macchioni, A. *Inorg. Chem.* **1998**, *37*, 5460.

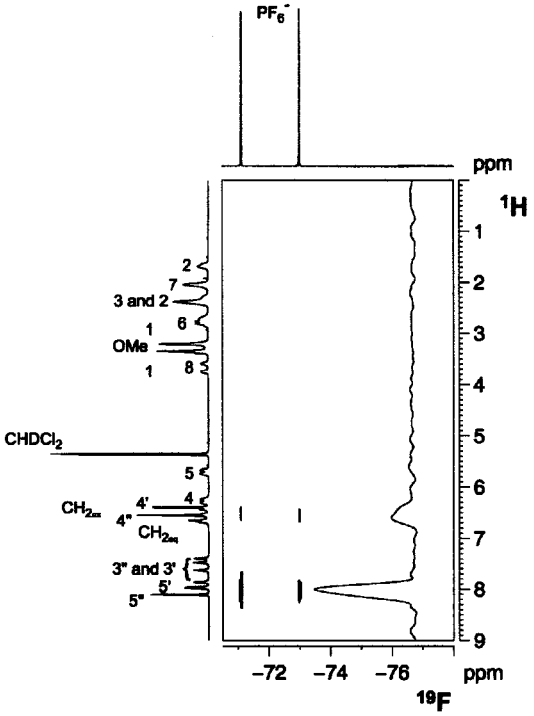


Figure 3. ^{19}F, ^{1}H-HOESY NMR spectrum (376.63 MHz, 188 K) of compound **1** recorded in CD_2Cl_2 showing the specificity of interaction between PF_6^- and the 5′−5″ and 4−4″ protons of the cation. The 1D-trace relative to the PF_6^- column is reported on the right.

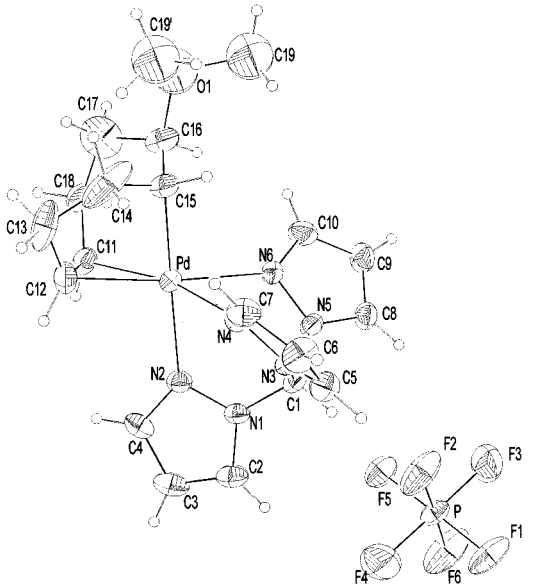


Figure 4. Molecular structure of [Pd(η^1,η^2-C_8H_{12}OMe)-(pz_3-CH][PF_6] (**4**) showing the ionic pair and the atomic numbering (thermal ellipsoids at 30% probability level); both positions C19 and C19′ for the disordered methyl group are shown.

distances, which show great variability (being influenced by the nature of the other equatorial ligands), are reported in Table 3 for comparison.

The cyclooctenyl ligand forms a five-membered and a six-membered metallacycle, the latter bearing the substituent −OMe. The complex molecules are intrinsically chiral because they contain four chiral centers at C(11), C(12), C(15), and C(16). Both crystals are racemic and contain the diastereoisomer with the following configuration: C(11) *R*, C(12) *S*, C(15) *R*, and C(16) *R* (with reference to Figures 4 and 5) and its enantiomer. The η^1,η^2-cyclooctenyl ring has the boatlike conformation usually found for this ligand and exhibits trans-orientation of the C(16)−O methoxy bond with respect

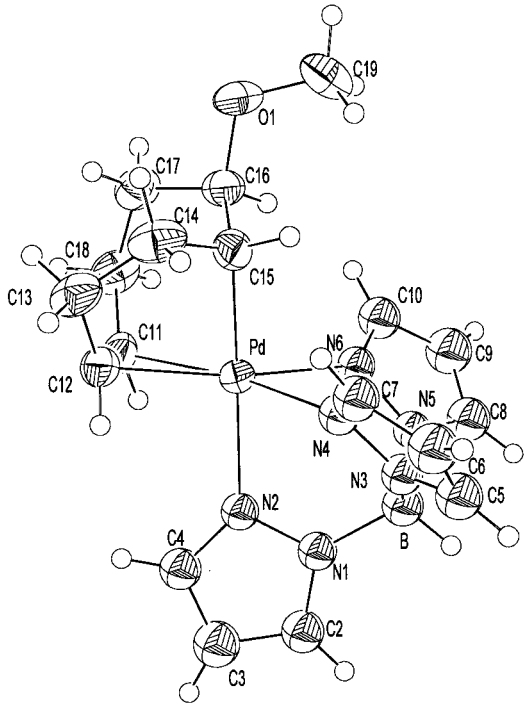


Figure 5. Molecular structure of [Pd(η^1,η^2-C_8H_{12}OMe)-(pz_3-BH)] (**5**) showing the atomic numbering (thermal ellipsoids at 50% probability level).

Table 2. Relevant Bond Distances (Å) and Angles (deg) for 4 and 5

	4	5
Pd−N(2)	2.186(6)	2.168(5)
Pd−N(4)	2.343(6)	2.226(6)
Pd−N(6)	2.254(6)	2.322(5)
Pd−C(11)	2.116(8)	2.122(7)
Pd−C(12)	2.128(8)	2.110(7)
Pd−C(15)	2.048(9)	2.042(6)
C(1)−N(1)	1.454(10)	B−N(1) 1.545(9)
C(1)−N(3)	1.465(10)	B−N(3) 1.527(10)
C(1)−N(5)	1.438(10)	B−N(5) 1.543(10)
N(1)−N(2)	1.367(9)	1.357(7)
N(3)−N(4)	1.366(9)	1.363(8)
N(5)−N(6)	1.357(8)	1.343(7)
N(2)−Pd−N(4)	83.4(2)	84.6(2)
N(2)−Pd−N(6)	83.7(2)	85.3(2)
N(4)−Pd−N(6)	77.5(2)	82.5(2)
N(2)−Pd−C(11)	95.6(3)	94.0(2)
N(2)−Pd−C(12)	98.0(3)	96.9(2)
N(2)−Pd−C(15)	175.6(3)	173.9(2)
N(4)−Pd−C(11)	156.7(3)	163.1(2)
N(4)−Pd−C(12)	118.4(3)	125.4(3)
N(4)−Pd−C(15)	92.4(3)	91.5(2)
N(6)−Pd− C(11)	125.7(3)	114.2(2)
N(6)−Pd−C(12)	164.1(3)	152.1(3)
N(6)−Pd−C(15)	96.7(3)	98.8(2)
C(11)−Pd−C(12)	38.5(3)	37.9(3)
C(11)−Pd−C(15)	87.7(4)	88.4(3)
C(12)−Pd−C(15)	82.8(4)	81.6(3)
N(1)−C(1)−N(3)	111.6(6)	N(1)−B−N(3) 109.4(6)
N(1)−C(1)−N(5)	112.2(6)	N(1)−B−N(5) 108.2(6)
N(3)−C(1)−N(5)	110.7(6)	N(3)−B−N(5) 110.7(6)

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Table 3. Metal-to-Carbon Interactions (Å) in Five-Coordinate Pt and Pd Cyclooctenyl Complexes

complex	M−C sp^3_{axial}	M−C $sp^2_{equatorial}$
$[Pt(NO_2C_6H_4)_2N_4)(\eta^1,\eta^2\text{-}C_8H_{12}PEt_3)(PEt_3)]$[24]	2.079(6)	2.095(6), 2.101(7)
$[(CO)_4Cr(\mu\text{-}PPh_2)(\mu\text{-}CO)Pt(\eta^1,\eta^2\text{-}C_8H_{12})]$[25]	2.073(7)	2.275(7), 2.272(7)
$[PtCl_2(\eta^1,\eta^2\text{-}C_8H_{12}\{CH(PPh_3)CO_2Me\})]$[26]	2.051(9)	2.15(1), 2.10(1)
$[Pt(py)_2(\eta^1,\eta^2\text{-}C_8H_{12}\{CH(PPh_3)CO_2Me\})]^+$ [26]	2.057(7)	2.140(6), 2.144(7)
$[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}CH][PF_6]$ (**4**)	2.048(9)	2.116(8), 2.128(8)
$[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}BH]$ (**5**)	2.042(6)	2.122(7), 2.110(7)

to the C(15)−Pd bond. Complex **4** shows two different orientations of the carbon atom belonging to the methoxy group (see Experimental Section).

The trispyrazolylmethane or trispyrazolylborate ligands are usually found as trihapto donors in octahedral complexes,[15] otherwise they behave like dihapto donors in square planar complexes according to the electronic requirements of the metal centers.[16] In the present complexes, the ligand trihapticity is stabilized by the attainment of the effective atomic number of the metal center. The Pd−N distances in **4** and **5** show that the axial bonds are shorter than the equatorial ones. A similar effect was observed in the platinum complex $[Pt(C_2H_4)Cl(py)(Me_2phen)]^+$.[17] It is also noteworthy that the equatorial Pd−N bonds are not equivalent [2.343(6), 2.254(6) Å in **4** and 2.322(5), 2.226(6) Å in **5**], differing from what was observed in octahedral Pd complexes containing tridentate trispyrazolyl ligands which exhibit very similar values [average 2.18_2 Å].[15]

In complex **4**, however, the major focus of the solid-state structure lies in the position of the anion with respect to the cation. The formation of an ion pair is evident with preferential interactions involving anion fluorine atoms and trispyrazolyl ligand (Figure 4). H-bonding interactions are established between the highly polarized $H-C(N)_3$ proton and fluorine lone pairs. The strongest contacts have the following geometries: C(1)−H(1)···F(2) 3.16 Å, angle 165.6°; C(1)−H(1)···F(5) 3.20 Å, angle 137.1°; C(2)−H(2)···F(5) 3.25 Å, angle 117.4°. Weaker interactions are as follows: C(8)−H(8)···F(5) 3.32 Å, angle 123.5°; C(5)−H(5)···F(2) 3.43 Å, angle 130.6°; and C(2)−H(2)···F(4) 3.52 Å, angle 161.1°. The remaining three fluorine atoms are implied in H-bonding interactions of the weaker type with three different symmetry-related cations.

A cation−cation H-bonding interaction occurs between C(5)−H(5) and the symmetry-related O(1) atom [x, $y-1$, z] with a contact 3.25 Å long and an angle of 135.6°.

The anion−cation recognition is therefore extremely specific, analogous to what is observed in solution, and quite strong due to the formation of an assembly of hydrogen bonds within the ion pair, with the strongest interactions involving the −CH group. The space-filling representation of the ion pair (Figure 6) clearly shows the cation pocket where the anion fits in a sort of docking process. Actually, the cation positive charge is mainly localized on the pyrazolyl moiety, producing a

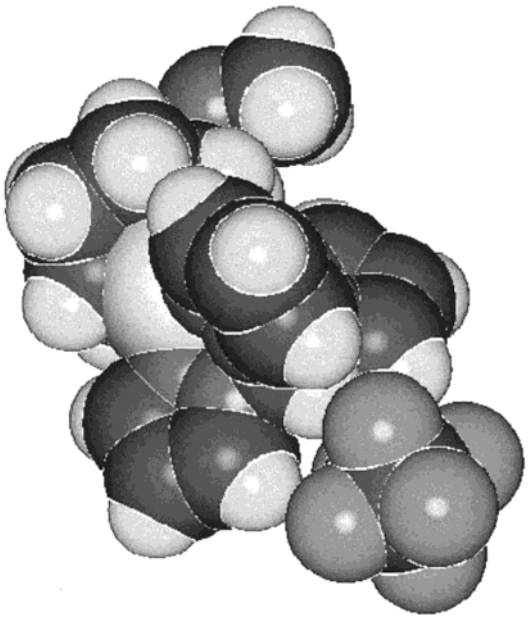

Figure 6. Space-filling diagram of complex **4** with the same orientation as in Figure 4; only C19 is shown, for clarity.

significantly polarized C−H group. The present example of cation−anion recognition will be compared with both solid-state and solution structures of analogous complexes containing different anions of comparable shape and size, capable of behaving as proton acceptors.

Catalytic Tests. Complexes **1** and **4** were tested as catalysts for the CO/styrene copolymerization carried out in methylene chloride at room temperature and at atmospheric pressure. Complex **4** is not active at all, while complex **1** affords oligomers but decomposes into Pd metal within a few minutes. The analogous complex $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]^+PF_6^-$ is a good catalyst for the CO/styrene copolymerization carried out under the same conditions. The reduction of the catalytic activity due to the substitution of the bipy ligand with the bispyrazolyl ligand can be explained by considering that the second is a weaker σ-donor compared to the first.[18] This makes complex **1** more electrophilic than complex $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]^+PF_6^-$ but also less stable.

Conclusions

We have reported the synthesis of neutral and cationic four-coordinate compounds $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_2\text{-}YH_2)]^{(+)}$ (where M = Pd and Pt; Y = B and C). Compound **1** (where M = Pd, Y = C, and having PF_6^- as counterion) catalyzes the CO/styrene oligomerization, even if its efficiency is limited by its stability.

Five-coordinate compounds $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3\text{-}YH)]^{(+)}$ (where M = Pd and Pt; Y = B and C) are

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also reported. The Pd compounds represent, to our knowledge, the first olefin five-coordinate compounds containing the trispyrazolyl ligands as well as the first examples of cyclooctenyl five-coordinate Pd complexes.

The interionic structure of all the cationic compounds was investigated in methylene chloride solution by ^{19}F, ^{1}H-HOESY NMR spectroscopy. There is a remarkable specificity in the interaction between the cation and anion that is incredibly higher than that observed in similar compounds $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]^+PF_6^-$, where the N,N ligand is planar. In fact, while in these compounds the anion interacts preferentially with the protons belonging to the bipy ligand but still "sees" the protons belonging to the cyclooctenyl ligand that are closer to the metal, in these newly reported complexes the counterion interacts exclusively with the peripheral protons of the pyrazolyl ligands. We believe that such unexpected specificity must be due not only to the partial protection of the apical position exerted by the pyrazolyl ligands but also to a considerable delocalization of the positive charge on the pz rings. All the spectroscopic evidence fully agrees with the identification of a specific ion pair in the crystalline state, stabilized by an assembly of cation−anion hydrogen bonds.

Experimental Section

One- and two-dimensional ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were measured on Bruker DPX 200 and DRX 400 spectrometers. Referencing is relative to TMS (^{1}H and ^{13}C) and CCl_3F (^{19}F). NMR samples were prepared dissolving about 20 mg of compound in 0.5 mL of CD_2Cl_2. Two-dimensional ^{1}H-NOESY and ^{19}F, ^{1}H-HOESY spectra were recorded with a mixing time of 500−800 ms. Complexes $M(C_8H_{12})Cl_2$ (M = Pd[19] and Pt[20]) and $[M(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$[5] were prepared as reported in the literature.

Preparation and Characterization of Complex 1. $pz_2\text{-}CH_2$ (79 mg, 0.53 mmol) was added to a suspension of $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ (100 mg, 0.18 mmol) in methanol (5 mL) at room temperature. The suspension became a yellow solution; NH_4PF_6 (232 mg, 1.42 mmol) was added, and the solution was put in the refrigerator at −18 °C. After 12 h, complex **1** precipitated; it was filtered off, washed with ethyl ether, and dried under vacuum. Yield: 60%. ^{1}H NMR (CD_2Cl_2, 195 K): δ 8.11 (d, $^{3}J_{HH}$ = 2.5, 5″A and 5″B), 7.98 (br, 5′A or 5′B), 7.96 (br, 5′B or 5′A), 7.87 (br, 3″A or 3″B), 7.63 (br, 3″B or 3″A), 7.49 (br, 3′A or 3′B), 7.40 (br, 3′B or 3′A), 6.66 (brd, $^{2}J_{HH}$ = 14.1, CH_{2eq}A and CH_{2eq}B),[21] 6.55 (t, $^{3}J_{HH}$ = 2.5, 4″A and 4″B), 6.54 (brd buried under 4″, CH_{2ax}A or CH_{2ax}B), 6.42 (brd, $^{2}J_{HH}$ = 14.1, CH_{2ax}B or CH_{2ax}A), 6.39 (br, 4′A and 4′B), 6.30 (br, 4A or 4B), 6.23 (br, 4B or 4A), 5.74 (br, 5A or 5B), 5.67 (br, 5B or 5A), 3.75 (br, 8A or 8B), 3.59 (br, 8B or 8A), 3.38 (br, 1A or 1B), 3.35 (s, OMeA or OMeB), 3.20 (s, OMeB or OMeA), 3.18 (br, 1B or 1A), 2.76 (br, 6A and 6B), 2.38 (br, 3A, 3B, 2A or 2B), 2.03 (br, 7A and 7B), 1.67 (br, 2B or 2A). ^{13}C{^{1}H} NMR (CD_2Cl_2, 195 K): δ 142.8 (s, 3″A or 3″B), 142.2 (s, 3″B or 3″A), 141.8 (s, 3′A or 3′B), 141.3 (s, 3′B or 3′A), 135.3 (s, 5″A or 5″B), 135.0 (s, 5″B or 5″A), 134.4 (s, 5′A or 5′B), 133.7 (s, 5′B or 5′A), 111.7 (s, 4A or 4B), 109.7 (s, 4B or 4A), 108.6 (s, 4″A and 4″B), 108.4 (s, 4′A or 4′B), 108.1 (s, 4′B or 4′A), 106.4 (s, 5A or 5B), 104.4 (s, 5B or 5A), 82.5 (s, 8A or 8B), 82.3 (s, 8B or 8A), 63.5 (s, CH_2A and CH_2B), 57.1 (s, OMeA and OMeB), 50.0 (s, 1A or 1B), 48.7 (s, 1B or 1A), 34.6 (s, 2A or 2B), 34.1 (s, 2B or 2A), 30.3 (s, 7A or 7B), 30.1 (s, 7B or 7A), 29.2 (s, 6A and 6B), 27.6 (s, 3A or 3B), 26.7 (s, 3B or 3A). ^{31}P{^{1}H} NMR (CD_2Cl_2, 200 K): δ −143.2 (sept, $^{1}J_{PF}$ = 711). ^{19}F NMR (CD_2Cl_2, 200 K): δ −72.1 (d, $^{1}J_{FP}$ = 711).

Preparation and Characterization of Complex 2. $pz_2\text{-}CH_2$ (48 mg, 0.32 mmol) was added to a suspension of $[Pt(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ (100 mg, 0.14 mmol) in methanol (3 mL) at room temperature. The suspension became a colorless solution; NH_4PF_6 (88 mg, 0.54 mmol) and ethyl ether (1 mL) were added, and the solution was put in the refrigerator at −18 °C. After 12 h, complex **2** precipitated; it was filtered off, washed with ethyl ether, and dried under vacuum. Yield: 66%. ^{1}H NMR (CD_2Cl_2, 192 K): δ 8.23 (br, 5″A or 5″B), 8.21 (br, 5″B or 5″A), 8.07 (br, 5′A and 5′B), 7.98 (br, 3″A or 3″B), 7.75 (br, 3″B or 3″A), 7.66 (br, 3′A or 3′B), 7.44 (br, 3′B or 3′A), 6.72 (brd, $^{2}J_{HH}$ = 14.7, CH_{2ax}), 6.63 (br, CH_{2ax}, 4″A and 4″B), 6.56 (brd, $^{2}J_{HH}$ = 13.8, CH_{2eq}), 6.49 (br, CH_{2eq}, 4′A and 4′B), 5.28 (br, 5A or 5B), 5.21 (br, 5B or 5A), 5.12 (br, 4A or 4B), 5.00 (br, 4B or 4A), 3.65 (br, 8A or 8B), 3.40 (br, 8B or 8A), 3.30 (br, OMeA or OMeB), 3.17 (br, OMeB or OMeA), 2.97 (br, 3A and 3B), 2.62 (br, 1A, 1B, 2A, and 2B), 2.35 (br, 6A and 6B), 2.04 (br, 6A and 6B), 1.79 (br, 7A and 7B), 1.73 (br, 7A and 7B). ^{13}C{^{1}H} NMR (CD_2Cl_2, 192 K): δ 142.5 (s, 3″A and 3″B), 141.4 (s, 3′A or 3′B), 140.8 (s, 3′B or 3′A), 136.1 (s, 5″A or 5″B), 135.6 (s, 5″B or 5″A), 134.9 (s, 5′A or 5′B), 134.1 (s, 5′B or 5′A), 109.0 (s, 4″A and 4″B), 108.6 (s, 4′A and 4′B), 93.9 (s, 5A or 5B), 90.6 (s, 5B or 5A), 90.5 (s, 4A or 4B), 87.1 (s, 4B or 4A), 82.8 (s, 8A or 8B), 82.6 (s, 8B or 8A), 63.2 (s, CH_2A and CH_2B), 56.6 (s, OMeA or OMeB), 56.5 (s, OMeB or OMeA), 33.2 (s, 7), 29.2 (s, 3), 28.9 (s, 2 and 6), 28.7 (s, 2), 28.4 (s, 1A or 1B), 27.6 (s, 1B or 1A). ^{31}P{^{1}H} NMR (CD_2Cl_2, 302 K): δ −143.1 (sept, $^{1}J_{PF}$ = 711). ^{19}F NMR (CD_2Cl_2, 192 K): δ −71.9 (d, $^{1}J_{FP}$ = 711).

Preparation and Characterization of Complex 3. $pz_2\text{-}BH_2$ (60 mg, 0.32 mmol) was added to a suspension of $[Pt(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ (100 mg, 0.14 mmol) in methanol (3 mL) at 0 °C. The suspension became a yellow solution; it was put in the refrigerator at −18 °C. After 12 h, complex **3** precipitated; it was filtered off, washed with cold methanol, and dried under vacuum. Yield: 56%. ^{1}H NMR (CD_2Cl_2, 230 K): δ 7.67 (d, $^{3}J_{HH}$ = 2.3, 3″ and 5″), 7.56 (dd, $^{3}J_{HH}$ = 2.2, $^{4}J_{HH}$ = 0.5, 5′), 7.33 (br, 3′), 6.35 (t, $^{3}J_{HH}$ = 2.3, 4″), 6.23 (t, $^{3}J_{HH}$ = 2.1, 4′), 4.96 (td, $^{3}J_{HH}$ = 8.6, $^{3}J_{HH}$ = 3.0, 4), 4.81 (br, 5), 3.54 (brd, $^{3}J_{HH}$ = 10.4, 8), 3.24 (s, OMe), 2.88 (brd, $^{2}J_{HH}$ = 17.6, 6), 2.60 (m, 1 and 6), 2.33 (m, 3), 1.96 (m, 3), 1.89 (m, 2), 1.85 (m, 2), 1.76 (m, 7). ^{13}C{^{1}H} NMR (CD_2Cl_2, 230 K): δ 139.5 (s, 3′), 137.7 (s, 3″), 137.2 (s, 5′), 136.1 (s, 5″), 105.7 (s, 4″), 105.5 (s, 4′), 87.4 (s, 4), 84.9 (s, 5), 83.6 (s, 8), 56.0 (s, OMe), 33.4 (s, 7), 29.4 (s, 2), 29.1 (s, 6), 28.6 (s, 3), 26.2 (s, 1).

Preparation and Characterization of Complex 4. $pz_3\text{-}CH$ (92 mg, 0.43 mmol) was added to a suspension of $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)Cl]_2$ (100 mg, 0.18 mmol) in methanol (5 mL) at room temperature. The suspension became a pale yellow solution; NH_4PF_6 (117 mg, 0.72 mmol) was added and after 10 min, complex **4** started to precipitate; it was filtered off, washed with ethyl ether, and dried under vacuum. Yield: 65%. ^{1}H NMR (CD_2Cl_2, 188 K): δ 8.74 (s, CH), 8.16 (br, 5″ and 5‴), 8.11 (br, 5′), 8.00 (br, 3″ or 3‴), 7.98 (br, 3‴ or 3″), 7.26 (br, 3′) 6.49 (br, 4″ and 4‴), 6.35 (br, 4′), 5.35 (br, 4), 4.70 (brd, $^{2}J_{HH}$ = 8.2, 5), 3.75 (br, 8), 3.51 (br, 1), 3.18 (s, OMe), 2.54 (br, 6), 2.34 (br, 2 and 3), 2.14 (br, 3), 1.99 (br, 7), 1.62 (br, 2). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 217 K): δ 142.7 (br, 3′, 3″, and 3‴), 133.5 (s, 5′, 5″, and 5‴), 108.1 (s, 4′, 4″, and 4‴), 90.3 (s, 4), 82.7 (s, 8), 81.3 (s, 5), 76.6 (s, CH), 57.0 (s, OMe), 48.2 (s, 1), 35.2 (s, 2), 30.5 (s, 7), 28.2 (s, 6), 27.3 (s, 3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 302 K): δ −142.6 (sept, $^{1}J_{PF}$ = 711). ^{19}F NMR (CD_2Cl_2, 188 K): δ −70.9 (d, $^{1}J_{FP}$ = 711).

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(21) CH_{2eq} and CH_{2ax} indicate the CH_2 protons of the A and B structures reported in Scheme 2 that can be considered pseudoequatorial and pseudoaxial with respect to the coordination plane. The distinction between CH_{2eq} and CH_{2ax} was made by considering that equatorial protons belonging to A and B conformational isomers (Scheme 2) are less magnetically different and should show chemical shift values that are more similar than the axial ones.

Table 4. Crystal Data and Details of Structure Refinement for Complexes 4 and 5

	4	5
empirical formula	$C_{19}H_{25}F_6N_6OPPd$	$C_{18}H_{25}BN_6OPd$
fw	604.82	458.65
temp (K)	223	293
wavelength (Å)	0.71069	0.71069
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$
unit cell dimens	$a = 23.249(5)$, $b = 10.530(5)$, $c = 20.646(5)$ Å; $\beta = 109.53°$	$a = 12.280(2)$, $b = 12.702(3)$, $c = 13.751(2)$ Å; $\beta = 113.63°$
volume (Å^3)	4764(3)	1965(1)
Z	8	4
density (Mg/m^3)	1.687	1.550
F(000)	2432	936
cryst size (mm)	0.3 × 0.3 × 0.5	0.3 × 0.2 × 0.4
θ range for data collection	2−25°	2−25°
index range	$-25 \le h \le 25$, $0 \le k \le 12$, $0 \le l \le 24$	$-14 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 16$
no. of reflns collected	4271	3598
no. of data/restraints/params	4143/10/300	3441/0/164
goodness-of-fit on F^2	1.009	1.033
final *R* indices [$I > 2\sigma(I)$]	$R = 0.0540$, $R_w^2 = 0.159$	$R = 0.040$, $R_w^2 = 0.109$
R indices (all data)	$R = 0.109$, $R_w^2 = 0.189$	$R = 0.114$, $R_w^2 = 0.133$
largest diff peak and hole (e Å^{-3})	1.58 and −0.859	1.21 and −0.68

Preparation and Characterization of Complex 5. pz_3-BH (88 mg, 0.37 mmol) was added to a suspension of [Pd(η^1,η^2-C_8H_{12}OMe)Cl]$_2$ (100 mg, 0.18 mmol) in methanol (3 mL) at room temperature. The suspension became a colorless solution; after 30 min, complex **5** started to precipitate; after 2 h it was filtered off, washed with cold methanol, and dried under vacuum. Yield: 68%. ^{1}H NMR (CD_2Cl_2, 217 K): δ 7.91 (br, 3″ and 3‴), 7.76 (br, 5″ and 5‴), 7.68 (br, 5′), 7.11 (br, 3′), 6.32 (br, 4″ and 4‴), 6.18 (br, 4′), 5.12 (td, $^3J_{HH} = 8.7$, $^3J_{HH} = 2.9$, 4), 4.51 (vbr, BH), 4.53 (d, $^3J_{HH} = 7.8$, 5), 3.91 (m, 8), 3.36 (d, $^3J_{HH} = 4.5$, 1), 3.22 (s, OMe), 2.54 (m, 6), 2.46 (m, 2), 2.38 (m, 3), 2.13 (m, 3), 1.99 (m, 7), 1.70 (dd, $^2J_{HH} = 14.1$, $^3J_{HH} = 7.8$, 2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 217 K): δ 141.2 (s, 3″ or 3‴), 140.0 (s, 3‴ or 3″), 137.6 (s, 3′), 136.0 (s, 5″ and 5‴), 135.6 (s, 5′), 105.5 (s, 4′), 105.3 (s, 4″ and 4‴), 84.9 (s, 4), 83.1 (s, 8), 75.5 (s, 5), 56.6 (s, OMe), 43.9 (s, 1), 34.8 (s, 2), 30.6 (s, 7), 28.3 (s, 6), 27.8 (s, 3).

Preparation and Characterization of Complex 6. pz_3-CH (70 mg, 0.32 mmol) was added to a suspension of [Pt(η^1,η^2-C_8H_{12}OMe)Cl]$_2$ (100 mg, 0.14 mmol) in methanol (5 mL) at room temperature. The suspension became a pale yellow solution; NH_4PF_6 (88 mg, 0.54 mmol) was added and after 10 min, complex **6** started to precipitate; it was filtered off, washed with ethyl ether, and dried under vacuum. Yield: 59%. ^{1}H NMR (CD_2Cl_2, 217 K): δ 8.96 (s, CH), 8.32 (d,$^3J_{HH} = 2.7$, 5″ and 5‴), 8.30 (d, $^3J_{HH} = 2.7$, 5′), 8.08 (d, $^3J_{HH} = 2.0$, 3‴), 8.02 (d, $^3J_{HH} = 2.0$, 3″), 7.33 (d, $^3J_{HH} = 2.0$, 3′), 6.59 (t, $^3J_{HH} = 2.3$, 4″), 6.58 (t, $^3J_{HH} = 2.3$, 4‴), 6.48 (t, $^3J_{HH} = 2.3$, 4′), 3.72 (dd, $^3J_{HH} = 8.11$, $^3J_{HH} = 3.3$, 8), 3.64 (m, 5), 3.61 (m, 4), 3.21 (s, OMe), 2.81 (brd, $^3J_{HH} = 6.45$, 1), 2.34 (brd, $^3J_{HH} = 7.05$, 6), 2.21 (m, 3), 2.04 (m, 2), 1.86 (br, 7), 1.80 (dd, $^2J_{HH} = 11.5$, $^3J_{HH} = 7.94$, 7), 1.67 (dd, $^2J_{HH} = 14.0$, $^3J_{HH} = 6.2$, 2), 1.59 (dd, $^2J_{HH} = 14.0$, $^3J_{HH} = 8.2$, 3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 217 K): δ 143.6 (s, 3‴), 142.2 (s, 3″), 139.5 (s, 3′), 134.1 (s, 5′), 133.7 (s, 5″ or 5‴), 133.4 (s, 5‴ or 5″), 108.7 (s, 4′), 108.6 (s, 4″ and 4‴), 81.9 (s, 8), 77.3 (s, CH), 58.2 (s, 4), 56.5 (s, OMe), 48.0 (s, 5), 35.3 (s, 2), 29.4 (s, 7), 28.9 (s, 3), 27.2 (s, 6), 23.7 (s, 1). ^{31}P{^{1}H} NMR (CD_2Cl_2, 217 K): δ −142.8 (sept, $^1J_{PF} = 711$). ^{19}F NMR (CD_2Cl_2, 217 K): δ −70.9 (d, $^1J_{FP} = 711$).

Preparation and Characterization of Complex 7. pz_3-BH (77 mg, 0.32 mmol) was added to a suspension of [Pt(η^1,η^2-C_8H_{12}OMe)Cl]$_2$ (100 mg, 0.14 mmol) in methanol (3 mL) at room temperature. Complex **7** immediately precipitated from solution. After 30 min, it was filtered off, washed with cold methanol, and dried under vacuum. Yield: 69%. ^{1}H NMR (CD_2Cl_2, 217 K): δ 7.95 (br, 3‴), 7.89 (br, 3″), 7.83 (d, $^3J_{HH} = 1.9$, 5‴), 7.81 (d, $^3J_{HH} = 1.9$, 5″), 7.75 (d, $^3J_{HH} = 1.9$, 5′), 7.12 (br, 3′), 6.34 (br, 4″ and 4‴), 6.22 (br, 4′), 4.52 (vbr, BH), 3.85 (brd, $^3J_{HH} = 10.0$, 8), 3.30 (m, 5), 3.24 (t, $^3J_{HH} = 8.2$, 4), 3.20 (s, OMe), 2.70 (brd, $^3J_{HH} = 6.6$, 1), 2.33 (m, 6), 2.19 (m, 3), 2.08 (m, 2), 1.83 (m, 7), 1.66 (m, 2), 1.53 (m, 3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 217 K): δ 141.2 (s, $^2J_{CPt} = 33.1$, 3‴), 139.5 (s, $^2J_{CPt} = 42.0$, 3″), 136.3 (s, 5′), 136.0 (s, 5‴), 135.9 (s, 5″), 135.6 (s, 3′), 105.9 (s, 4′), 105.8 (s, 4‴), 105. 8 (s, 4″), 82.2 (s, $^1J_{CPt} = 11.2$, 8), 56.2 (s, OMe), 52.7 (s, $^1J_{CPt} = 375.4$, 4), 42.2 (s, $^2J_{CPt} = 369.6$, 5), 35.3 (s, $^2J_{CPt} = 47.0$, 2), 29.7 (s, $^2J_{CPt} = 18.9$, 7), 29.5 (s, 3), 27.3 (s, $^2J_{CPt} = 34.2$, 6), 20.5 (s, $^1J_{CPt} = 626.4$, 1).

X-ray Crystallography. Crystals of **4** and **5** suitable for X-ray single-crystal studies were precipitated from dichloromethane/ethanol. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The data were collected using an $\omega/2\theta$ scanning technique and corrected for absorption empirically. Crystal data and details of structure refinement are reported in Table 4. Five independent data collections were performed for **4** on crystals from different crystallization batches both at room temperature and at 223 K, trying to overcome the disorder problems inherent to the cation structure. Finally, the set of data at 223 K, with the highest number of observed reflections, revealed the most ordered cation model and was therefore used for structure solving and refinement. Both structures were solved by direct methods and refined on F^2 by full matrix least squares calculations using the SHELXTL/PC package.[22] Thermal vibrations were treated anisotropically except for the OMe fragment of **4**; H atoms were geometrically positioned [C−H 0.96 Å] and refined "riding" on their corresponding carbon atoms. For **4**, the carbon atom of the OMe appendage was found affected by positional disorder over two orientations. Refinement of the relative contribution to each orientation converged to an occupancy factor ratio of 50:50 (Figure 4). That accounts for the apparent very short C−C contact for C(19) with its symmetry equivalent to $1-x$, y, $1.5-z$, where the carbon atom has a different position at C(19′). The first neighbor of each molecule is the one with the opposite orientation at the −OMe group, and the contact does not occur in the crystal lattice. Taking this disorder into account as well as the greater flexibility of the cyclooctenyl ring in **4**, it can be concluded that the packing of **4**, despite the presence of the ionic pair, seems to be looser than the packing of **5**. Refinement

(22) *SHELXTLplus Version 5.1 (Windows NT version) Structure Determination Package*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1998.

converged at a final $R = 0.054$, $R_w^2 = 0.16$, $S = 1.01$ for **4**, $R = 0.040$, $R_w^2 = 0.11$, $S = 1.03$ for **5**.

Molecular graphics were prepared using ORTEP3 for WindowsNT.[23]

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Supporting Information Available: A listing of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. Crystallographic files for both complexes **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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