Interionic Solution Structure of [PtMe(η^2-olefin)(*N*,*N*-diimine)]BF_4 Complexes by $^{19}F\{^1H\}$-HOESY NMR Spectroscopy: Effect of the Substituents on the Accessibility of the Counterion to the Metal

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Received May 26, 1999

The relative cation−anion position in [Pt(Me)(η^2-olefin)(N,N)]BF_4 complexes (where N,N = 2,6-$(R')_2C_6H_3N$=C(R″)C(R″)=N-2,6-$(R')_2C_6H_3$, R′ = H, Me, Et, and *i*-Pr, R″ = H, Me; olefin = CH_2=CHR, R = H, Me, COOMe) in methylene chloride has been investigated by detecting specific interionic dipolar interactions in the $^{19}F\{^1H\}$-HOESY NMR spectra. The counterion shows strong interionic contacts with R″ and R′ protons and weak contacts with R and olefinic protons only when R′ < Et and R″ = Me. For R′ ≥ Et the accessibilty to the metal center is completely inhibited and the counterion is located above or below the backside of the diimine ligand. The same position is also observed when R″ = H and R′ = R = Me despite the limited steric hindrance of the substituents due to specific interactions between H″ and the fluorine of BF_4^-. In the other cases (R′ < Et), the counterion also interacts with Me, R, and olefinic protons, indicating that the accessibility to the metal center is not forbidden.

Introduction

The reactivity of [M(R)(η^2-olefin)(N,N)]X (M = Ni, Pd, and Pt) complexes is known to be strongly dependent on the choice of N,N-chelating ligands. In particular, a crucial role is attributed to the capability of the N,N-ligand to introduce steric hindrance above and below the square-planar coordination plane. When a substantial hindrance is introduced, the complexes are (1) catalysts for the homogeneous polymerization of α-olefin affording high molecular weight polymers (M = Ni and Pd)[1] and (2) kinetically stable compounds (M = Pt),[2] even with electron-poor alkenes.[3] This is attributed to inhibition of associative termination processes in (1) and prevents the attack of a generic nucleophile in (2).

Due to the importance of metal alkyl diimine olefin π-complexes, which have been established[1a,c] to be the catalytic resting state of olefin polymerization catalyzed by M−diimine catalysts (M = Ni and Pd), we decided to investigate their interionic structure in solution when M = Pt. In previous studies, we have shown[4] that the dominant placement of the counterion with respect to the organometallic fragment can be achieved in solution by detecting anion−cation dipolar interactions in the ^1H-NOESY and $^{19}F\{^1H\}$-HOESY NMR spectra. These ion−counterion interactions may be used to probe the accessibility of a nucleophile to the metal and, consequently, to directly investigate the role of the substituents in blocking the axial sites of the metal center.

In this paper we report the results of our $^{19}F\{^1H\}$-HOESY NMR investigation in methylene chloride on [Pt(Me)(η^2-olefin)(N,N)]BF_4 complexes reported in Chart 1. The principal aim of this study is to determine how steric hindrance above and below the square-planar coordination plane introduced by the substituents of the *N*,*N*-diimine ligands affects the relative BF_4^-−cation position in solution.

Results and Discussion

Intramolecular Characterization. Complexes **1**−**8** were characterized in methylene chloride solution by ^1H, ^{13}C, and ^{19}F NMR spectroscopies.

To precisely localize the relative cation−anion position, accurate preliminary work must be done to assign

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(1) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

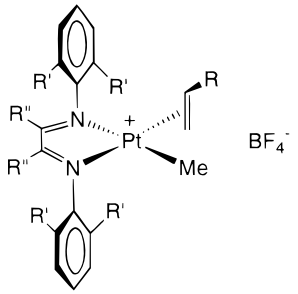
(2) (a) Fusto, M.; Giordano, F.; Orabona, I.; Ruffo, F. *Organometallics* **1997**, *16*, 5981. (b) Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1998**, *17*, 5102.

(3) Ganis, P.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Organometallics* **1998**, *17*, 2646.

(4) (a) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Terenzi, S.; *Organometallics* **1996**, *15*, 4349. (b) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Gramlich, V.; Rüegger, H.; Terenzi, S.; Venanzi, L. M. *Organometallics* **1997**, *16*, 2139. (c) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Cruciani, G.; Foresti, E.; Sabatino, P.; Zuccaccia, C. *Organometallics* **1998**, *17*, 5549. (d) Bellachioma, G.; Cardaci, G.; Gramlich, V.; Macchioni, A.; Valentini, M.; Zuccaccia, C. *Organometallics* **1998**, *17*, 5025. (e) Zuccaccia, C.; Bellachioma, G.; Cardaci, G.; Macchioni, A. *Organometallics* **1999**, *18*, 1.

10.1021/om990401r CCC: $18.00
Publication on Web 09/14/1999

Chart 1



1: R = Me; R' = H; R" = Me
2: R = Me; R' = Me; R" = Me
3: R = Me; R' = Et; R" = Me
4: R = Me; R' = *i*-Pr; R" = Me
5: R = Me; R' = Me; R" = H
6: R = H; R' = Et; R" = Me
7: R = CO_2Me; R' = Et; R" = Me
8: R = CO_2Me; R' = *i*-Pr; R" = Me

as many resonances as possible in both fragments. In the case of complexes **1**−**8**, the anion is symmetric and only two resonances were observed in the ^{19}F NMR spectra due to $^{10}BF_4^-$ and $^{11}BF_4^-$. On the other hand, the cationic fragment consists of several proton resonances, inhomogeneously distributed around platinum. Not only do all four coordination positions contain magnetically inequivalent protons but the region above and below the square-coordination plane can also be differentiated when R ≠ H. Furthermore, in the case of complex **4** (R′ = isopropyl), there is a differentiation of the methyl groups of R′ that point forward or backward with respect to the plane containing the two phenyl groups. This is due to restricted rotation around both the N−C^{ipso} and R′−C^{o} bonds.

The assignment of all the proton resonances of complex **4**, based primarly on phase-sensitive ^{1}H-NOESY NMR spectra, is discussed in detail because of the above-mentioned peculiarities. The resonances of Me, R, and olefinic protons were easily assigned and were used as starting points. Ten more resonances were present in the chemical shift region 2.46−1.18 ppm, each of them integrating for three protons. Eight of these resonances (1.45−1.18 ppm) appeared as doublets and must be due to the methyl groups of R′ (Me′) that are all chemically inequivalent. Only one Me′ gave an NOE contact with Me of R and with the olefin proton geminal to it (see Figure 1, parts a and b). This Me′ has to stay cis to the olefin (O), in front of the Me of R (down, indicated with d), and oriented forward (f) with respect to the plane containing the two phenyl groups. We will label such a methyl group as Me′(Odf) (see Scheme 1). Another Me′ gave a contact only with the CH_2═ protons, and we can call it Me′(Ouf) (where u stands for up with respect to the olefinic R group; see Figure 1a). Me′(Odf) and Me′(Ouf) interact strongly with Me′(Odb) and Me′-(Oub), respectively (where b stands for backward), which were easily assigned. The latter gave specific NOE contacts only with Me″(O). The other singlet must be due to Me″(M) (where M stands for cis to the methyl group). It was possible to distinguish between Me′(Muf), Me′(Mdf) and Me′(Mub), Me′(Mdb) by the NOE contacts between the Me group and the remaining Me′ groups (see Figure 1c). The components of the two pairs were able to be distinguished by the observation of a weak contact between the Me of R and Me′(Mdf) only (see Figure 1b). The CH′ protons were assigned by observing both the NOE contacts and the COSY peaks with "their" Me′ groups (see Figure 2). Finally, the H^m and H^p afforded a typical set of A_2B spin system resonances. From the assigned ^{1}H resonances all the ^{13}C resonances were assigned by the ^{1}H{^{13}C}-COSY NMR "standard" and long range with gradients spectra.[5]

The assignment of the resonances for the other complexes was carried out in the same way. The spatial differentiation was inevitably smaller because (1) when R = H (complex **6**), it is impossible to distinguish above from below the coordination plane; (2) when R′ = H and Me (complexes **1** and **2**), the olefin rotation is fast compared to the chemical shift NMR time scale, and again, it is impossible to distinguish between above from below the coordination plane; (3) when R′ = Me (complex **2** and **5**), the rotation around the R′−C^{o} bond is no longer restricted and the three protons are equivalent; and (4) in the case of electron-poor olefins (complexes **7** and **8**) the two N,N halves (left/right) are in exchange.[6] A ^{1}H-NOESY NMR spectrum was recorded at 217 K for complex **8** in order to slow the exchange process and, consequently, to differentiate the two halves and the positions above or below the coordination plane. The latter differentiation occurs only on the side cis to the olefin, where specific contacts were observed between H olefin and Me′ protons (see Figure 3). Due to the absence of contact between the COOMe and Me′ protons, it was impossible to distinguish between Me′(Muf) and Me′(Mdf). It is interesting to note that in the exchange process the acrylate primarily orients the CO_2-Me group toward Me, as indicated, for example, by the absence of NOE between the HC(COOMe)═CH_{2trans} and any CH′ in Figure 3. Another interesting point is the specificity of the exchange peaks between Me′(Odf) and only one of the Me′(Mf) groups, which, on the basis of the chemical shift trend observed for complex **4**, should be Me′(Mdf).

Interionic Solution Structure. The interionic structure of complexes **1**−**8** was investigated in methylene chloride, at room temperature (302 K), by recording the ^{19}F{^{1}H}-HOESY NMR spectra. Methylene chloride has a low dielectric constant (8.71 at 303 K), ensuring that the complexes are substantially intimate ion-pairs.[7] This is a fundamental requirement for detecting the NOE contacts between dipolar coupled nuclei which must be closer than 4.5−5.0 Å.[8]

All the complexes **1**−**8** show very strong interionic contacts between the fluorine atoms of the counterion and the protons of the R″ groups. There are also strong interionic contacts with the protons of some R′ groups. For complexes **4** and **8**, where all the Me′ groups are magnetically inequivalent, it can be noted that only the backside Me′ pointing toward the R″ groups (indicated with b in Scheme 1) strongly interacts with the coun-

(5) For the economy of this article, the data are reported in the Experimental Section but will not be discussed.

(6) The process of slow exchange was individuated by the detection of exchange peaks (having the same signal as the diagonal peaks) in the phase-sensitive ^{1}H-NOESY NMR spectra between all the signals relative to the two halves.

(7) Romeo, R.; Arena, G.; Monsù Scolaro, L.; Plutino, M. R. *Inorg. Chim. Acta* **1995**, *240*, 81.

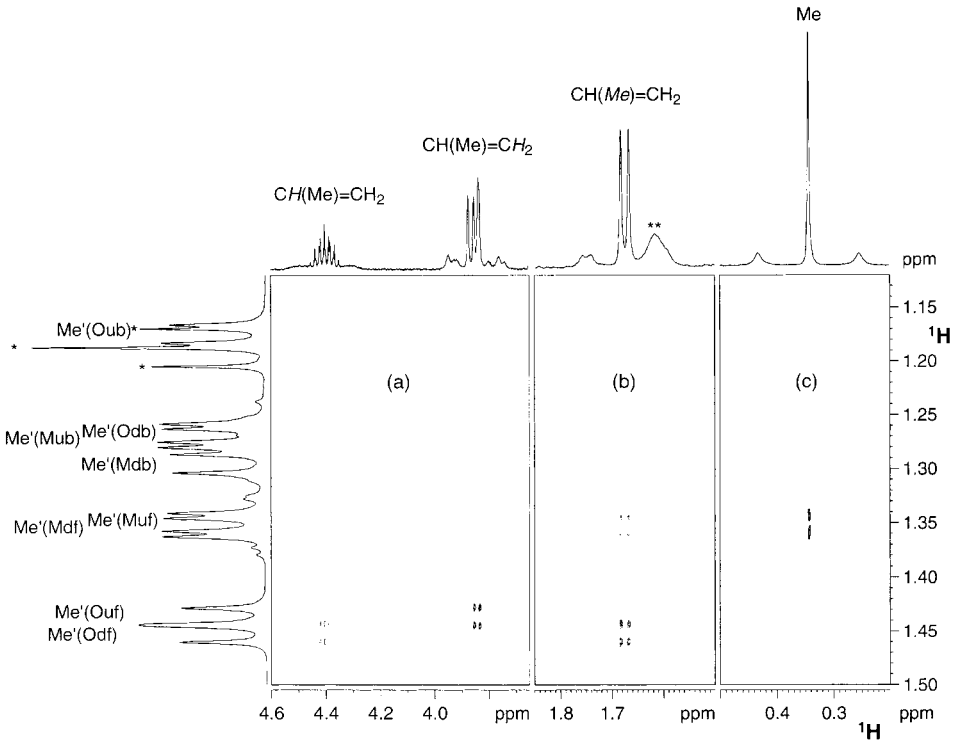
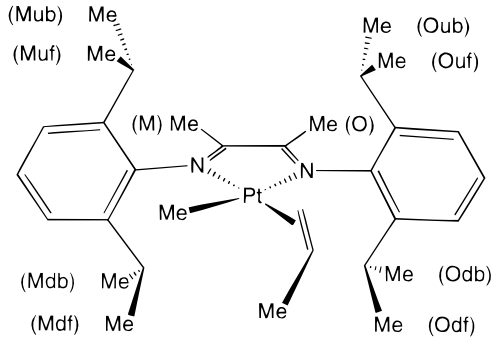


Figure 1. Three sections of the ^{1}H-NOESY NMR spectrum of complexes **4** recorded at 400.13 MHz in CD_2Cl_2 at 302 K showing the specific contacts of (a) Me′(Ouf) with CH_2= protons, (b) Me′(Odf) with Me of R group, and (c) Me with Me′(Muf) and Me′(Mdf). * indicates the $O(CH_2CH_3)_2$ resonances relative to an impurity of diethyl ether. ** denotes the resonance due to an impurity of H_2O.

Scheme 1



terion (see Figure 4).[9] As the steric hindrance above and below the coordination plane introduced by the *N*,*N*-diimine ligands decreases, weak interionic contacts with the Me, R, and olefinic protons start to appear. The ratios between the percentage of NOEs of the interionic contacts due to R″ and Pt-Me groups for complexes **1**−**3** are the following: R″/Me 14 (**1**), 41 (**2**), and 116 (**3**). The interionic contacts with the Me, R, and olefinic protons are not observed in the case of complex **4**. The substitution of the Me″ with H″ groups (complex **5**) affords higher specificity of interionic contacts between H″ and the counterion. The ratio between the percentage of NOEs H″/Me is equal to 115. In the case of complex **6**, the above indicated ratio is closer to that of complex **2** (it amounts to 51) due to decreased steric hindrance in the olefinic ligand even though R′ = Et as in complex **3**. Complexes **7** and **8** behave like **3** and **4**, respectively.

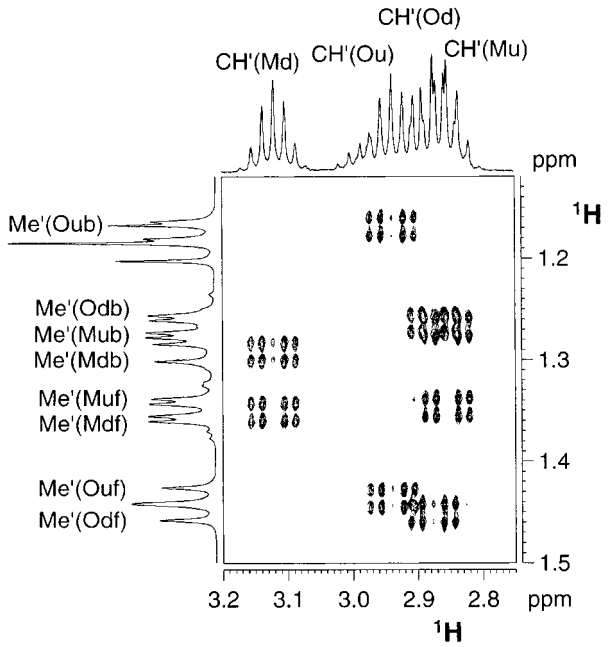


Figure 2. Section of the ^{1}H-COSY NMR spectrum of complexes **4** recorded at 400.13 MHz in CD_2Cl_2 at 302 K showing the assignment of the CH′ protons by the "cosy" peaks with their Me′ protons.

The results illustrated above indicate that the counterion BF_4^- pairs with the organometallic fragment from the side of the N,N-ligand, preferentially interacting with the R″ and R′ substituents. Its exact position is tuned by the steric hindrance of the R, R′, and R″

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

(9) In complexes **3** and **7**, the rotation around the R′−C^o is also restricted. Owing to the complexity and partial overlap of the CH_1H_2Me resonances, it is difficult to understand if specific interactions are present.

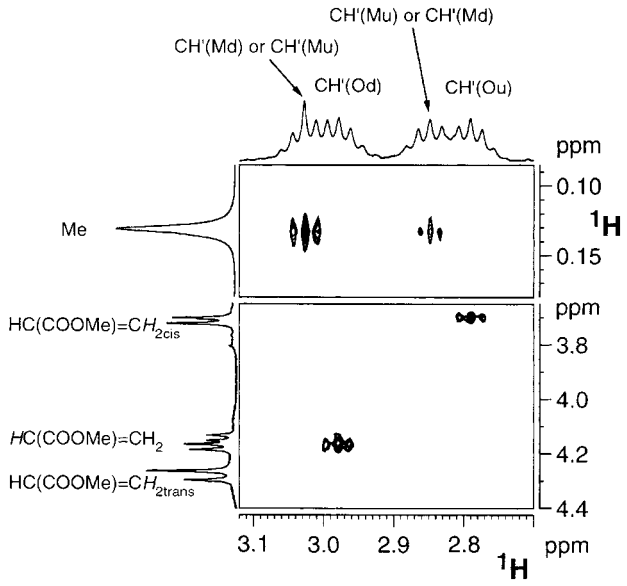


Figure 3. Two sections of the ^{1}H-NOESY NMR spectrum of complexes **8** recorded at 400.13 MHz in CD_2Cl_2 at 217 K showing the interactions of (i) Me with CH′(Md) and CH′(Mu), (ii) HC(COOMe)=CH_{2cis} with CH′(Ou), and (iii) *H*C(COOMe)=CH_2 with CH′(Od).

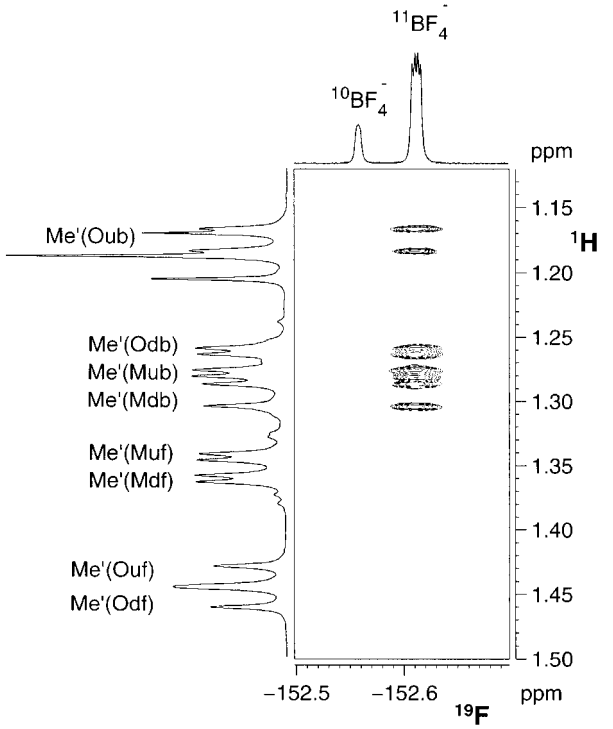


Figure 4. Section of the ^{19}F{^{1}H}-HOESY spectrum of complexes **4** recorded at 376 MHz in CD_2Cl_2 at 302 K showing the specific interionic contacts of BF_4^- with Me′ groups pointing toward R″.

substituents. With the exception of complex **5**, as the steric hindrance of the substituents decreases, the counterion populates positions closer to the platinum even if it is still substantially shifted toward the N,N-ligands. In complex **1**, the interionic interactions are also much stronger with R″ than with Me. Interestingly, in the complexes investigated here, it appears that the addition of a methyl group in R and R′ substituents has the same effect on the accessibility of the counterion to the metal. This is reasonable because both protect the metal more or less perpendicularly to the square-planar coordination plane. Complex **5** behaves similarly to complex **3** despite the substantial reduction of steric hindrance in the R′ substituent. In the latter case, the electronic contribution plays an important role: H″ contributes to localizing the counterion on that side via (a) weak H···F interaction(s). A similar case was reported[10] for the complex [PtMe(Me$_2$SO)N,N]X (where N,N = bis(2-pyridyl)amine and X^- = Cl^-, $CF_3SO_3^-$, BF_4^-, and PF_6^-), which gives very specific interactions. In that case, the amino group separating the two pyridyl rings has a strong tendency to attract the counterion, forming a hydrogen bond.

The reason the counterion prefers the "N,N" side instead of the less hindered olefin and methyl one has to be related to the positive charge distribution. In particular, there must be a delocalization of the positive charge on the N,N-ligands, as observed in previously studied octahedral complexes.[4] It was also found that in square planar complexes [Pd(η^1,η^2-C_8H_{12}OMe)N,N]X (where N,N = 2,2′-bipyridine and X^- = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^-, and B[3,5-$(CF_3)_2C_6H_3]_4^-$),[11] the counterion is located above or below the coordination plane and shifted toward the N,N-ligand but it still substantially interacts with protons that do not belong to it.

The results reported here are in general agreement with those coming from both experimental[1,12] and theoretical investigations carried out on nickel,[13] palladium,[13b,c] and platinum[13c] diimine catalysts for ethylene polymerization. By increasing the bulk of the substituents (in both R and R′), we observe a decreased accessibility of the counterion to the metal center and an increased specificity of the interionic contacts of BF_4^- with the R″ and R′(b) protons. This is a direct proof that associative processes on axial sites of the metal center are unlikely to occur, at least for R′ > Et. The only discrepancy comes from the analysis of the spectra of complex **5**. It is known[1] that replacing Me″ with H″ decreases the productivity of the Ni and Pd diimine catalysts. This could to be due to an increased steric interaction between the aryl rings and the auxiliary methyl fragments bound to the diimine ligand.[13a] On the basis of the above discussion, we should observe smaller NOE ratios (H″/Me), but instead we observe the exact opposite because H″ are suitable to form hydrogen bond(s) with BF_4^-.

Conclusions

The results from the present ^{19}F{^{1}H}-HOESY NMR investigation of the interionic solution structure of Pt complexes **1**−**8**, analogous to Ni and Pd catalysts for ethylene polymerization, have shed light on the accessibility of a nucleophile to the metal center. By increas-

(10) Romeo, R.; Nastasi, N.; Monsù Scolaro, L.; Plutino, M. R.; Albinati, A.; Macchioni, A. *Inorg. Chem.* **1998**, *37*, 5460.
(11) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061.
(12) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65−74.
(13) (a) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177. (b) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581. (c) Musaev, D. G.; Froese, R. D.; Morokuma, K. *New J. Chem.* **1997**, *21*, 1269.

ing the bulk of the substituents on the aryl moieties, the accessibility to the metal center is reduced. When such substituents are larger than or equal to Et, the counterion BF_4^- does not interact at all with Me and the olefinic protons, indicating that the axial sites of the metal center exhibit little binding to the BF_4^-. Our assumption to consider the counterion as a probe for investigating the associative process of a generic nucleophile to the metal was correct for all the complexes, except complex **5**, where H″ diimine backbone substituents afford weak H···F interactions.

Experimental Section

One- and two-dimensional ^1H, ^{13}C, and ^{19}F NMR spectra were measured on Bruker DPX 200 and DRX 400 spectrometers. Referencing is relative to TMS (^1H 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 ^1H-NOESY and $^{19}F\{^1H\}$-HOESY spectra were recorded with a mixing time of 500−800 ms.

Complexes **1**−**4**, **6**,[2a] **7** and **8**,[3] and $[PtClMe(SMe)_2]$[14] were synthesized as reported in the literature.

Characterization of Complex 1. ^1H NMR (CD_2Cl_2, 302 K): δ 7.58, 7.43, 7.14 (aromatics) 4.66 (m, *H*C(Me)═CH_2), 3.89 (m, $^3J_{HH}$ = 7.8, $^3J_{PtH}$ = 63.9 HC(Me)═C*H*$_{cis}$), 3.67 (m, $^3J_{HH}$ = 14.1, $^3J_{PtH}$ = 63.9 HC(Me)═C*H*$_{trans}$), 2.36 (s, Me″(M)), 2.11 (s, Me″(O)), 1.61 (m, $^3J_{HH}$ = 6.2, $^4J_{HPt}$ = 63.2, HC(*Me*)═CH_2), 0.32 (m, $^2J_{HPt}$ = 71.9, Me). $^{13}C\{^1H\}$ NMR: δ 185.7 (s, C(O)), 178.0 (s, C(M)), 144.7 (s, C^{ipso}(M)), 143.8 (s, C^{ipso}(O)), 130.2, 130.0, 128.4, 122.5, 121.6 (aromatics), 97.7(s, H*C*(Me)═CH_2), 69.7 (s, HC(Me)═*C*H$_2$), 20.5 (s, HC(*Me*)═CH_2), −3.1 (s, Me). $^{19}F\{^1H\}$ NMR: δ −151.7 (b, $^{10}BF_4^-$), −151.8 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

Characterization of Complex 2. **^1H NMR** (CD_2Cl_2, 302 K): δ 7.30 (aromatics) 4.43 (m, $^3J_{PtH}$ = 72 *H*C(Me)═CH_2), 3.78 (m, $^3J_{HH}$ = 8.7, $^2J_{HH}$ = 1.1, $^4J_{HH}$ = 0.7, $^3J_{PtH}$ = 64, HC(Me)═C*H*$_{2cis}$), 3.77 (m, $^3J_{HH}$ = 15.1, $^2J_{HH}$ = 1.1, $^4J_{HH}$ = 0.7, $^3J_{PtH}$ = 64, HC(Me)═C*H*$_{2trans}$), 2.37 (s, Me″(M)), 2.32 (s, Me′(Md or Mu)), 2.30 (s, Me′(Od or Ou)), 2.27 (s, Me′(Mu or Md)), 2.23 (s, Me′(Ou or Od)), 2.13 (s, Me″(O)), 1.67 (m, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 0.7, $^3J_{HPt}$ = 60, HC(*Me*)═CH_2), 0.21 (m, $^2J_{HPt}$ = 72, Me). $^{13}C\{^1H\}$ NMR: δ 186.3 (s, C(O)), 178.5 (s, C(M)), 141.8 (s, C^{ipso}(M)), 140.8 (s, C^{ipso}(O)), 129.9 (s, C^o(Md) or C^o(Mu)), 129.8 (s, C^o(Mu) or C^o(Md)), 128.9 (s, C^o(Od) or C^o(Ou)), 128.6 (s, C^o(Ou) or C^o(Od)), 129.6, 129.3, 129.1, 129.0, 128.5 (other aromatics), 99.8 (s, $^2J_{PtC}$ = 177, H*C*(Me)═CH_2), 71.8 (s, $^2J_{PtC}$ = 171, HC(Me)═*C*H$_2$), 20.7 (s, HC(*Me*)═CH_2), 20.6 (s, Me″(M)), 20.2 (s, Me″(O)), 17.88 (s, Me′(Md) or Me′(Mu)), 17.87 (s, Me′(Mu) or Me′(Md)), 17.7 (s, Me′(Od) or Me′(Ou)), 17.6 (s, Me′(Ou) or Me′(Od)), −3.61 (s, $^1J_{PtC}$ = 693, Me). $^{19}F\{^1H\}$ NMR: δ −151.82 (b, $^{10}BF_4^-$), −152.88 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

Characterization of Complex 3. ^1H NMR (CD_2Cl_2, 302 K): δ 7.39 (m, aromatics), 4.35 (m, $^3J_{PtH}$ = 72, *H*C(Me)═CH_2), 3.76 (m, $^3J_{HH}$ = 14.3, $^2J_{HH}$ = 1.1, $^4J_{HH}$ = 0.7, HC(Me)═C*H*$_{2trans}$), 3.74 (m, $^3J_{HH}$ = 8.0, $^2J_{HH}$ = 1.1, $^4J_{HH}$ = 0.7, $^3J_{PtH}$ = 64, HC(Me)═C*H*$_{2cis}$), 2.62 (m, CH_2′(AB system)), 2.38 (s, Me″(M)), 2.15 (s, Me″(O)), 1.63 (m, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 0.7, $^3J_{HPt}$ = 59, HC(*Me*)═CH_2), 1.38 (t, $^3J_{HH}$ = 7.5, Me′(Od)), 1.36 (t, $^3J_{HH}$ = 7.5, Me′(Mu) or Me′(Md)), 1.34 (t, $^3J_{HH}$ = 7.5, Me′(Md) or Me′(Mu)), 1.32 (d, $^3J_{HH}$ = 7.5, Me′(Ou)), 0.23 (s, $^2J_{HPt}$ = 71.6, Me). $^{13}C\{^1H\}$ NMR: δ 185.9 (s, C(O)), 178.3 (s, C(M)), 140.7 (s, C^{ipso}(M)), 139.5 (s, C^{ipso}(O)), 135.0 (s, C^o(Md) or C^o(Mu)), 134.9 (s, C^o(Mu) or C^o(Md)), 134.0 (s, C^o(Od)), 133.8 (s, C^o(Ou)), 129.1, 128.9, 126.9, 126.8, 126.6 (aromatics), 99.7 (s, $^2J_{PtC}$ = 90, H*C*(Me)═CH_2), 71.9 (s, $^2J_{PtC}$ = 85, HC(Me)═*C*H$_2$), 24.3 (s, CH_2′(Ou) and CH_2′(Od)), 23.88 (s, CH_2′(Md) or CH_2′(Mu)), 23.77 (s, CH_2′(Mu) or CH_2′(Md)), 20.9 (s, Me″(M)), 20.9 (s, Me″(O)), 20.6 (s, HC(*Me*)═CH_2), 13.54 (s, Me′(Od)), 13.52 (s, Me′(Ou)), 13.41 (s, Me′(Mu) or Me′(Md)), 13.37 (s, Me′(Md) or Me′(Mu)), −3.0 (s, $^1J_{PtC}$ = 700, Me). $^{19}F\{^1H\}$ NMR: δ −152.3 (b, $^{10}BF_4^-$), −152.4 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

Characterization of Complex 4. ^1H NMR (CD_2Cl_2, 302 K): δ 7.45 (m, aromatics), 4.40 (m, *H*C(Me)═CH_2), 3.85 (m, HC(Me)═C*H*$_2$), 3.12 (sept, $^3J_{HH}$ = 6.8, CH′(Md), 2.94 (sept, $^3J_{HH}$ = 6.8, CH′(Ou)), 2.87 (sept, $^3J_{HH}$ = 6.8, CH′(Od)), 2.85 (sept, $^3J_{HH}$ = 6.8, CH′(Mu)), 2.46 (s, Me″(M)), 2.25 (s, Me″(O)), 1.67 (m, $^3J_{HH}$ = 6.2, $^3J_{HPt}$ = 53, HC(*Me*)═CH_2), 1.45 (d, $^3J_{HH}$ = 6.8, Me′(Odf)), 1.44 (d, $^3J_{HH}$ = 6.8, Me′(Ouf)), 1.36 (d, $^3J_{HH}$ = 6.8, Me′(Mdf)), 1.35 (d, $^3J_{HH}$ = 6.8, Me′(Muf)), 1.30 (d, $^3J_{HH}$ = 6.8, Me′(Mdb)), 1.27 (d, $^3J_{HH}$ = 6.8, Me′(Mub)), 1.27 (d, $^3J_{HH}$ = 6.8, Me′(Odb)), 1.18 (d, $^3J_{HH}$ = 6.8, Me′(Oub)), 0.34 (s, $^2J_{HPt}$ = 71, Me). $^{13}C\{^1H\}$ NMR: δ 186.0 (s, C(O)), 178.5 (s, C(M)), 140.1 (s, C^o(Md)), 139.9 (s, C^{ipso}(M)), 139.4 (s, C^o(Od)), 139.2 (s, C^o(Ou)), 139.2 (s, C^o(Mu)), 137.6 (s, C^{ipso}(O)), 99.7 (s, H*C*(Me)═CH_2), 71.7 (s, HC(Me)═*C*H$_2$), 29.2 (s, CH′(Mu)), 29.1 (s, CH′(Md)), 29.0 (s, CH′(Ou)), 28.8 (s, CH′(Od)), 25.2 (s, Me′(Oub)), 24.8 (s, Me′(Odb)), 24.2 (s, Me′(Mdb)), 24.1 (s, Me′(Mub)), 23.6 (s, Me′(Muf)), 23.5 (s, Me′(Ouf) and Me′(Odf)), 23.0 (s, Me′(Mdf)), 22.6 (s, Me″(O)), 22.2 (s, Me″(M)), 20.6 (s, HC(*Me*)═CH_2), −2.5 (s, Me). $^{19}F\{^1H\}$ NMR: δ −152.5 (b, $^{10}BF_4^-$), −152.6 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

Synthesis of [Pt(Cl)Me{2,6-$Me_2C_6H_3N$═CHCH═N-2,6-$Me_2C_6H_3$}]. The N,N-ligand (1.2 mmol) was added to a suspension of $[PtClMe(SMe)_2]$ (1.0 mmol) in 10 mL of diethyl ether. After 48 h of stirring the orange product was collected, washed with diethyl ether, and dried under vacuum (yield: 80%). ^1H NMR ($CDCl_3$, 298 K): δ 9.37 (s, $^3J_{HPt}$ = 106, H″(M)), 8.71 (s, $^3J_{HPt}$ = 36, H″(Cl)), 7.24 (m, aromatics), 2.32 and 2.27 (s, all Me′), 1.39 (s, $^2J_{HPt}$ = 80, Me).

Synthesis of Complex 5. A solution of [Pt(Cl)Me{2,6-$Me_2C_6H_3N$═CHCH═N-2,6-$Me_2C_6H_3$}] (1.0 mmol) in 5 mL of dichloromethane was added to a suspension of $AgBF_4$ (1.0 mmol) in 10 mL of dichloromethane under a propene atmosphere. After 48 h of stirring at room temperature, AgCl was removed by filtration through Celite and the volume of the resulting solution was reduced to 5 mL under vacuum. Slow addition of diethyl ether afforded yellow-orange microcrystals of product, which was collected, washed with diethyl ether, and dried under vacuum (yield: 75%).

Characterization of Complex 5. ^1H NMR (CD_2Cl_2, 302 K): δ 9.09 (s, $^3J_{PtH}$ = 99, H″(M)), 9.04 (s, $^3J_{PtH}$ = 41, H″(O)), 7.28 (aromatics), 4.76 (m, $^3J_{PtH}$ = 69 *H*C(Me)═CH_2), 4.07 (m, $^3J_{HH}$ = 7.8, $^2J_{HH}$ = 1.1, $^4J_{HH}$ = 0.7, $^3J_{PtH}$ = 67, HC(Me)═C*H*$_{2cis}$), 3.89 (m, $^3J_{HH}$ = 14.3, $^2J_{HH}$ = 1.1, $^4J_{HH}$ = 0.7, $^3J_{PtH}$ = 65, HC(Me)═C*H*$_{2trans}$), 2.37 (s, Me′(Od)), 2.35 (s, Me′(Mu or Md)), 2.33 (s, Me′(Md or Mu)), 2.27 (s, Me′(Ou)), 1.70 (m, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 0.7, $^3J_{HPt}$ = 62, HC(*Me*)═CH_2), 0.48 (s, $^2J_{HPt}$ = 72, Me). $^{13}C\{^1H\}$ NMR: δ 176.4 (s, C(M)), 170.0 (s, C(O)), 143.7 (s, C^{ipso}(M)), 143.5 (s, C^{ipso}(O)), 130.5 (s, C^o(Md) or C^o(Mu)), 130.2 (s, C^o(Mu) or C^o(Md)), 129.2 (s, C^o(Od)), 128.9 (s, C^o(Ou)), 129.5, 129.2, 129.0, 128.9, 128.8 (other aromatics), 101.8 (s, $^2J_{PtC}$ = 172, H*C*(Me)═CH_2), 72.9 (s, $^2J_{PtC}$ = 171, HC(Me)═*C*H$_2$), 21.1 (s, HC(*Me*)═CH_2), 18.1 (s, Me′(Md) and Me′(Mu)), 18.0 (s, Me′(Od)), 17.8 (s, Me′(Ou)), −3.7 (s, $^1J_{PtC}$ = 683, Me). $^{19}F\{^1H\}$ NMR: δ −151.75 (b, $^{10}BF_4^-$), −152.80 (q, $^1J_{BF}$ = 1.4, $^{11}BF_4^-$).

Characterization of Complex 6. ^1H NMR (CD_2Cl_2, 302 K): δ 7.39 (m, aromatics), 3.74 (m, $^3J_{HPt}$ = 67.5, H_2C═CH_2), 2.66 (qd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 2.3, CH_2′(M)), 2.57 (m, CH_2′(O)), 2.42 (s, Me″(M)), 2.16 (s, Me″(O)), 1.35 (t, $^3J_{HH}$ = 7.5, Me′(O)), 1.34 (t, $^3J_{HH}$ = 7.5, Me′(M)), 0.16 (s, $^2J_{HPt}$ = 69, Me). $^{13}C\{^1H\}$ NMR: δ 186.8 (s, C(M) or C(O)), 178.2 (s, C(O) or C(M)), 140.7 (s, C^{ipso}(M)), 139.0 (s, C^{ipso}(O)), 134.9 (s, C^o(M)), 133.7 (s, C^o(O)), 129.1 (s, C^p(O) or C^p(M)), 129.0 (s, C^p(M) or C^p(O)), 126.8 (s, C^m(O)), 126.7 (s, C^m(M)), 75.2 (s, H_2C═CH_2), 24.4 (s, CH_2′(M)), 23.8 (s, CH_2′(O), 21.1 (s, Me″(M)), 20.8 (s, Me″(O)), 13.6 (s, Me′(O)), 13.5 (s, Me′(M)), −4.8 (s, Me). $^{19}F\{^1H\}$ NMR: δ −152.2 (b, $^{10}BF_4^-$), −152.2 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

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Characterization of Complex 7. ^{1}H NMR (CD_2Cl_2, 302 K): δ 7.36 (m, aromatics), 4.32 (m, $^3J_{HH}$ = 13.5, $^3J_{PtH}$ = 59, HC(COOMe)=CH_{2trans}), 4.04 (m, $^3J_{HH}$ = 13.5, $^3J_{HH}$ = 8.3, $^3J_{PtH}$ = 75, *H*C(COOMe)=CH_2), 3.67 (s, HC(COO*Me*)=CH_2), 3.61 (m, $^3J_{HH}$ = 8.3, $^3J_{PtH}$ = 71, HC(Me)=CH_{2cis}), 2.65 (m, CH_2′(AB system)), 2.51 (s, Me″(M)), 2.24 (s, Me″(O)), 1.40 (t, $^3J_{HH}$ = 7.5, Me′(Od)), 1.35 (t, $^3J_{HH}$ = 7.5, Me′(Md) or Me′(Mu)), 1.34 (t, $^3J_{HH}$ = 7.5, Me′(Mu) or Me′(Md)), 1.33 (t, $^3J_{HH}$ = 7.5, Me′(Ou)), 0.20 (s, $^2J_{HPt}$ = 69.0, Me). ^{19}F{^{1}H} NMR: δ −151.89 (b, $^{10}BF_4^-$), −151.95 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

Characterization of Complex 8. ^{1}H NMR (CD_2Cl_2, 217 K): δ 7.41 (m, aromatics), 4.28 (d, $^3J_{HH}$ = 13.6, HC(COOMe)=CH_{2trans}), 4.14 (dd,$^3J_{HH}$ = 13.6, $^3J_{HH}$ = 8.0, *H*C(COOMe)=CH_2), 3.70 (d,$^3J_{HH}$ = 8.0, HC(COOMe)=CH_{2cis}), 3.62 (s, HC(COO*Me*)=CH_2), 3.03 (sept, $^3J_{HH}$ = 6.6, CH′(Md) or CH′(Mu)), 2.98 (sept, $^3J_{HH}$ = 6.6, CH′(Od)), 2.85 (sept, $^3J_{HH}$ = 6.6, CH′(Mu) or CH′(Md)), 2.79 (sept, $^3J_{HH}$ = 6.6, CH′(Ou)), 2.54 (s, Me″(M)), 2.29 (s, Me″(O)), 1.46 (d, $^3J_{HH}$ = 6.6, Me′(Odf)), 1.38 (d, $^3J_{HH}$ = 6.6, Me′(Ouf)), 1.26 (m, Me′(Muf), Me′(Mub) or Me′(Mdb), Me′(Mdf)), 1.19 (d, $^3J_{HH}$ = 6.6, Me′(Oub)), 1.18 (d, $^3J_{HH}$ = 6.6, Me′(Mdb) or Me′(Mub)), 1.12 (d, $^3J_{HH}$ = 6.6, Me′(Odb)), 0.13 (s, $^2J_{HPt}$ = 58, Me). ^{19}F{^{1}H} NMR (CD_2Cl_2, 302 K): δ −152.0 (b, $^{10}BF_4^-$), −152.1 (q, $^1J_{BF}$ = 1.0, $^{11}BF_4^-$).

Acknowledgment. The authors wish to thank Prof. G. Cardaci for very helpful suggestions and discussions. This work was supported by grants from the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST, Rome, Italy), Programma di Rilevante Interesse Nazionale, Cofinanziamento 1998−1999.

OM990401R