Dinuclear Azolato-Bridged Complexes of the Nickel Group Metals with Haloaryl Ligands: A Reinvestigation of Their Behavior in Solution

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A reinvestigation of the NMR spectra of the complexes $(NBu_4)_2[M_2(\mu\text{-LL})_2R_4]$ (M = Pd, Ni, Pt, LL = pyrazolate (pz), 3,5-dimethylpyrazolate (dmpz), 3-methylpyrazolate (mpz), indazolate (indz), R = C_6F_5; M = Pd, LL = pz, dmpz, mpz, indz, R = 2,4,6-$C_6F_3H_2$) shows that the boat-shaped dimeric structures of their anions are quite stable in solution, and the previously proposed fast equilibria or dissociations to give species such as $[R_2M(N\text{-}N)(acetone)]^-$, $[R_2M(acetone)_2]$ + 2dmpz$^-$, or $[R_2M(N^1\text{-}N^2)(acetone)]^-$ + $[R_2M(N^2\text{-}N^1)(acetone)]^-$ in no case occur. A mixture of the two diastereoisomers (head-to-head, HH, and head-to-tail, HT) is present for the asymmetrically substituted azolates (mpz and indz), in a ratio ranging from 1:7 to 1:30 for the different complexes. Strong through-space coupling between the endo *ortho* fluorine nuclei of different MR_2 fragments is observed in the ^{19}F NMR spectra of these diastereoisomers whose boatlike structures place these atoms at short distances.

Introduction

NMR has become a most powerful technique in the elucidation of structures and dynamic processes in solution. It requires, however, some attention and care to avoid misinterpretation of the data. We revisit here a case spanning several publications,[1−4] where indications for a persistently mistaken interpretation seem to have passed inadvertently not only to the authors but also to the scrutiny of referees of several journals.

During the past years several groups, including ours, have shown the advantages of haloaryl ligands to study complexes of the nickel group metals. These haloaryl groups, particularly pentafluorophenyl, have enabled the isolation and identification of a large number of complexes,[5] among them some otherwise unstable intermediates. Moreover, the easy observation of ^{19}F NMR spectra, compared to ^1H (e.g., simpler spectra, no solvent interference) facilitates the monitoring of the reactions and their application to kinetic studies, and we have used this in the study of several reactions in order to support conclusively our mechanistic proposals.[6] Last but not least, the quite frequent phenomenon of restricted rotation around the M−aryl ring makes the C_6F_5 or $C_6Cl_2F_3$ groups very good reporters on the symmetry of the complex and on possible dynamic processes associated with the ancillary ligands.[7] Basically the main features to be observed in the ^{19}F NMR spectra are the number of inequivalent rings (shown by the number of F_{para} signals) and the chemical equivalence or inequivalence of the two F_{ortho} (and the two F_{meta}) atoms in each ring depending on whether, in a restricted-rotation case, the coordination plane is or is not a symmetry plane.

In this context a few years ago a number of papers reported on the synthesis and the dynamic behavior of several di-μ-azolate−bis[bis(haloaryl)metalate(II)] complexes, $(NBu_4)_2[M_2(\mu\text{-LL})_2R_4]$ (M = Pd, Ni, Pt; R = C_6F_5, $C_6F_3H_2$),[1−4] which are easily prepared by treatment of $(NBu_4)_2[M_2(\mu\text{-OH})_2R_4]$ with 2 equiv of HLL (LL = pyrazolate (pz), 3,5-dimethylpyrazolate (dmpz), 3-methylpyrazolate (mpz), indazolate (indz)). Analysis of the published data shows that the interpretation of the ^{19}F and ^1H NMR spectra and the proposals of equilibria and dynamic behavior offered by the authors are incorrect and need to be revised. Our reinvestigation deals with the following reported complexes: $(NBu_4)_2[Pd_2(\mu\text{-LL})_2R_4]$ (R = C_6F_5, LL = pz (**1**), dmpz (**2**), mpz (**3**), indz (**4**); R = $C_6F_3H_2$, LL = pz (**5**), dmpz (**6**), mpz (**7**), indz (**8**)),[1,2] $(NBu_4)_2[Ni_2(\mu\text{-LL})_2(C_6F_5)_4]$ (LL = pz (**9**), mpz (**10**), indz (**11**)),[4] and $(NBu_4)_2[Pt_2(\mu\text{-LL})_2(C_6F_5)_4]$ (LL = pz (**12**), dmpz (**13**), mpz (**14**), indz (**15**)).[3]

Pd Complexes.[1,2] The ^{19}F NMR spectra of the symmetric complexes **1** and **2** were reported to show equivalence of the four C_6F_5 groups and displayed only one signal for the eight F_{ortho}, which was doublet for **1** but broad for **2**. However, the

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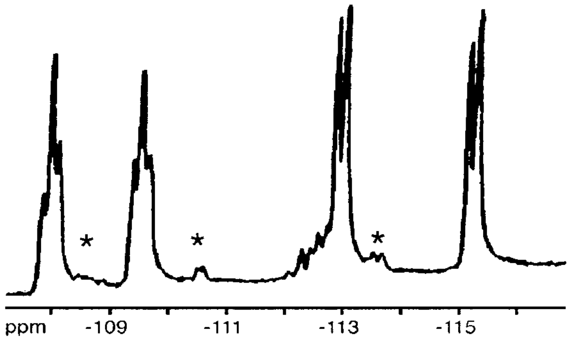
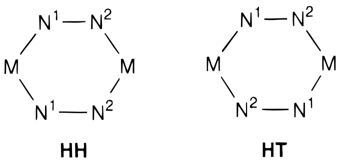


Figure 1. ^{19}F NMR spectrum of $(NBu_4)_2[Pd_2(\mu\text{-mpz})_2(C_6F_5)_4]$ (**3**) (270 MHz, $(CD_3)_2CO$, 248.15 K, F_{ortho} region) taken from ref 1. Reprinted with permission from ref 1. Copyright 1991 American Chemical Society.

Chart 1



less symmetric complexes **3** and **4** revealed the presence of four F_{ortho} signals for **3**, and two for **4**, described as broad. The F_{ortho} signals of **3** at −25 °C are shown in Figure 1 (taken from ref 1). It was interpreted that the inequivalence of the F_{ortho} arose from the existence of equimolecular amounts of the species $[R_2Pd(N^1\text{-}N^2)(N^1\text{-}N^2)PdR_2]^{2-}$ (head-to-head, HH henceforth), and $[R_2Pd(N^1\text{-}N^2)(N^2\text{-}N^1)PdR_2]^{2-}$ (head-to-tail, HT) for the complexes with asymmetrically substituted azolate rings (Chart 1). Nevertheless it was stated that the corresponding ^{1}H NMR spectra did not reveal these two isomers, not even at −70 °C. This was interpreted to prove the existence of the fast interconversion shown in eq 1, however not being able to produce equivalence in the ^{19}F NMR. Finally the unexpected triplet aspect of two of the four F_{ortho} signals of **3** was noted, and this was given the following interpretation: "The triplet signals may be attributed to the C_6F_5 rings adjacent to the methyl groups on the assumption that the frequency separation of the *o*-fluorine resonances of these rings is equal in magnitude to $J_{o,m}$".[1]

$$[R_2Pd(N^1\text{-}N^2)(N^1\text{-}N^2)PdR_2]^{2-} \rightleftharpoons [R_2Pd(N^1\text{-}N^2)(N^2\text{-}N^1)PdR_2]^{2-} \quad (1)$$

The ^{1}H NMR results and interpretation given for complexes **5**−**8**, with $C_6F_3H_2$ instead of C_6F_5, were completely similar. However, these complexes allow for easier observation of the F_{para} signals, which for C_6F_5 appear overlapped with the F_{meta} multiplets), and only one F_{para} signal was reported, regardless of the number of F_{ortho} signals.

The hints that this interpretation needs revision are as follows: (i) It is extremely unlikely that HH and HT isomers are equally stable and give rise to 1:1 equilibria (complex **3**); furthermore, for complex **4** (only two F_{ortho} signals observed) one should assume just the opposite, that one isomer is extremely more stable and is the only one observed. (ii) It is extremely unlikely that a movement very fast on the ^{1}H NMR time scale at −70 °C appears extremely slow on the ^{19}F NMR time scale at +25 °C. (iii) In all the discussion it is assumed that the two F_{ortho} on each ring are equivalent, thus the inequivalences observed are taken as inequivalences between rings. This has several consequences: (a) There is no easy explanation for the broadening observed in **2** or in **4**; (b) one should expect the same number of F_{ortho} and F_{para} signals (in a 2:1 ratio), which is not the case. (iv) If one assumes that the two F_{ortho} atoms in one ring can become "slightly" inequivalent (as it is perhaps suggested in the explanation for the triplet in complex **3**), the same effect should be expected for all the C_6F_5 groups. (v) An obvious reason for inequivalence, the boat shape of the molecule which determines exo and endo sites for all ligands disposed perpendicularly to the Pd coordination plane, is not discussed nor considered. (vi) Finally, some meaningful signals which appear clearly in the spectrum (highlighted with a star in Figure 1) have been neglected.

Ni Complexes.[4] For Ni, complex **9** gave two 1:1 signals in the *ortho* fluorine region, and the authors proposed complete dissociation of the product in solution to give $[Ni(C_6F_5)_2(pz)(acetone)]^-$, having two inequivalent C_6F_5 groups. However, the pz ligand gives only two resonances (2:1) in the ^{1}H NMR spectrum, which is inconsistent with the presence of monodentate pz. To solve this dilemma a fast (on the ^{1}H NMR time scale) pz exchange was proposed, but the ^{1}H and the ^{19}F spectra of **9** remained unchanged between −70 and +25 °C, making this hypothesis very unlikely. Similarly, from the ^{19}F NMR spectra of complexes **10** and **11** dissociation was proposed. Thus the ^{19}F NMR spectra of **10** or **11** in acetone consisted (*ortho* fluorine region only) of three signals (intensities 1:1:2, respectively), which were assigned to an equimolecular mixture $[(C_6F_5)_2Ni(N^1\text{-}N^2)(acetone)]^- + [(C_6F_5)_2Ni(N^2\text{-}N^1)(acetone)]^-$ (N^1-N^2 stands for the asymmetrically substituted mpz or indz ligand). Again the ^{1}H NMR spectrum did not reveal monodentate mpz or indz and it was necessary to invoke a very fast exchange which, however, did not affect the ^{19}F spectra. Moreover, this interpretation of the spectra requires exactly equimolecular mixtures of isomers for two different N^1-N^2 ligands, which is extremely improbable. Again the boat structure of the complexes was not taken into account.

Pt Complexes.[3] The results reported were very similar to those just described for the analogous Ni complexes, although no indication was given on the multiplicity or broad shape of the F_{ortho} signals, only its number. In order to explain their spectra the authors suggested successively (i) a dimeric $[R_2Pt(\mu\text{-}\{N\text{-}N\})_2PtR_2]^{2-}$ structure for **12** in $CDCl_3$; (ii) complete splitting of **12** in acetone to give $[R_2Pt(N\text{-}N)(acetone)]^-$; (iii) complete dissociation of **13** in acetone, this time to $[R_2Pt(acetone)_2] + 2dmpz^-$; (iv) a 1:1 mixture $[(C_6F_5)_2Pt(N^1\text{-}N^2)(acetone)]^- + [(C_6F_5)_2Pt(N^2\text{-}N^1)(acetone)]^-$ for **14** in acetone. In each case the absence of monodentate or free azolate in the ^{1}H NMR spectra was in contradiction with the proposal. Moreover, a different justification was needed for each complex although all the complexes are very similar.

Altogether, this family of closely related complexes should show, quite unexpectedly, a bewildering diversity of behavior in solution, and should present very improbable situations, such as uncommon 1:1 isomeric mixtures or dynamic phenomena very fast for ^{1}H but very slow for ^{19}F (even for close ^{19}F signals). The most obvious conclusion is that the facts are misinterpreted. Therefore we decided to reinvestigate the NMR spectra of these complexes.

Results and Discussion

$Pd(C_6F_5)_2$ Complexes. The complexes $(NBu_4)_2[Pd_2(\mu\text{-LL})_2(C_6F_5)_4]$ (**1**−**4**) were prepared and their ^{1}H and ^{19}F NMR spectra recorded in $(CD_3)_2CO$ at room temperature. The ^{1}H NMR spectra show the characteristic resonances of bridging azolate groups and indicate that, for the asymmetrically substituted

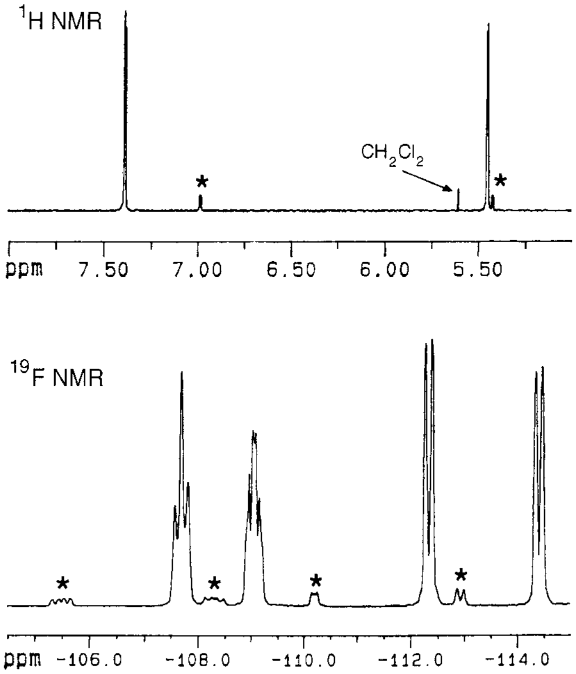


Figure 2. ^{1}H (300.13 MHz, $(CD_3)_2CO$, 293 K, H_{pz} region) and ^{19}F NMR (282.35 MHz, $(CD_3)_2CO$, 220 K, F_{ortho} region) spectra of $(NBu_4)_2[Pd_2(\mu\text{-mpz})_2(C_6F_5)_4]$ (**3**). The HH isomer (*) is the minor one.

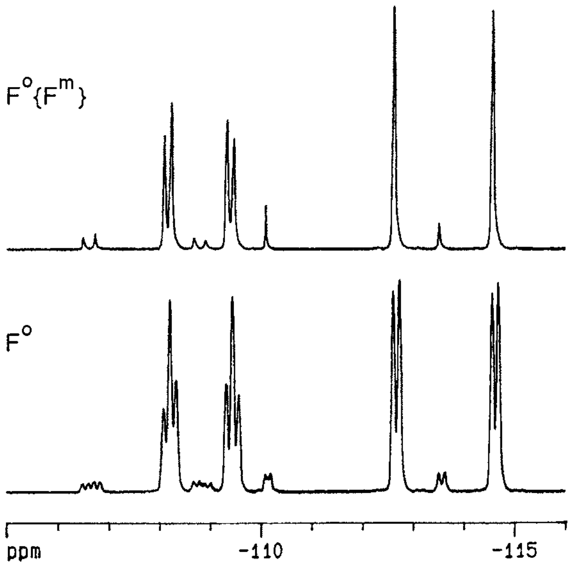


Figure 3. ^{19}F and $^{19}F\{^{19}F\}$NMR (F_{meta} region irradiated) spectra of $(NBu_4)_2[Pd_2(\mu\text{-indz})_2(C_6F_5)_4]$ (**4**) (282.35 MHz, $(CD_3)_2CO$, 220 K, F_{ortho} region).

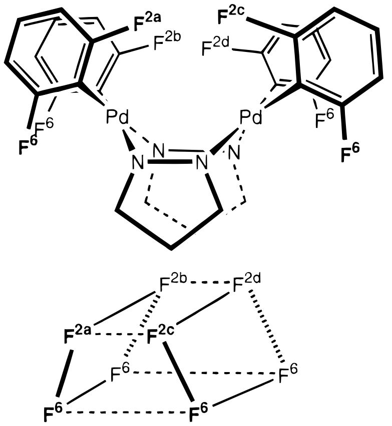


Figure 4. Boatlike structure for a dinuclear pyrazolato-bridged complex and schematic representation of the F_{ortho} atoms.

azolates (mpz and indz), the two diastereoisomers HT and HH are present in a molar ratio close to 10:1 (Figure 2).

The room temperature ^{19}F NMR spectra exhibit in almost all cases one or several broad bands in the F_{ortho} region suggesting the occurrence of some fluxional process. In order to study the spectra of **1**−**4** in the slow-exchange limit they were recorded at 220 K (**1**, **3**, **4**) or 190 K (**2**). The palladium complexes with symmetric azolates (**1**, **2**) display in their ^{19}F NMR spectra two signals in the F_{ortho} region and three signals in the $F_{para} + F_{meta}$ (1 + 2) region. This is consistent with the static ^{19}F NMR spectrum expected for a di-μ-azolate complex with a boat conformation, because the four C_6F_5 groups are equivalent but the coordination plane is not a mirror plane, making the two halves of each C_6F_5 inequivalent.

The palladium complexes **3** and **4** have a lower symmetry (C_2 for the HT; C_s for the HH), and four F_{ortho} signals are expected and obtained for each diastereoisomer (Figure 2). Again the spectrum clearly shows the presence of the HT and HH isomers in a 10:1 molar ratio, which can also be recognized easily in the original Figure 1.[8] Only the two upfield signals for both isomers are the expected pseudodoublets usually observed in C_6F_5 derivatives. The appearance of the downfield signals for both diastereoisomers as complex pseudotriplets (for the major isomer) or pseudodoublets of doublets (for the minor one) reveal that these F_{ortho} atoms are subjected to an extra coupling. The selective decoupling of the F_{meta} resonances facilitates the recognition of these large couplings. Figure 3 shows this experiment carried out on complex **4** where the proximity of its F_{meta} resonances facilitates this selective irradiation. Some signals remain as doublets due to this large extra F−F coupling between some F_{ortho} nuclei. This coupling must have a large through-space component[9] (the remaining scalar couplings have to be very small), and, since it has never been detected in other complexes with *cis*-PdR_2 moieties, it has to be attributed to a coupling interaction between F_{ortho} nuclei of different PdR_2 moieties. In other words, the curvature of the azolate bridges brings some endo F_{ortho} nuclei of different PdR_2 moieties close enough to produce a large through-space coupling. This is shown in Figure 4 along with a schematic representation of the F_{ortho} atoms, which is used in the discussion.

The assignments of the F_{ortho} signals to the HT or the HH isomer for complexes **3** and **4**, and of the different signals to the different F_{ortho} nuclei in each isomer, required some additional experiments, which are discussed for **3** (for **4** the results were identical). First of all (see labels in the COSY spectrum in Figure 5), a $^{19}F-^{19}F$ EXSY experiment at 260 K revealed only chemical exchange between the signals A and K, and also between the signals X and M. Thus it is reasonable to assign these pairs of signals to pairs of F_{ortho} in the same C_6F_5 ring, which are undergoing slow exchange via C_6F_5 rotation, boat inversion, or a combination of both. This slow-exchange process is responsible for the broadening of ^{19}F signals at room temperature but should not affect the mpz or indz

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(8) An additional multiplet at ca. −112.5 ppm in Figure 1, which is absent in our spectrum in Figure 2, is due to an impurity quite difficult to remove.

(9) Through-space F−F coupling constants have been observed in many organic derivatives whose structures place these atoms at short distances. See, for instance: Ernst, L.; Ibrom, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1881−1882 and references therein.

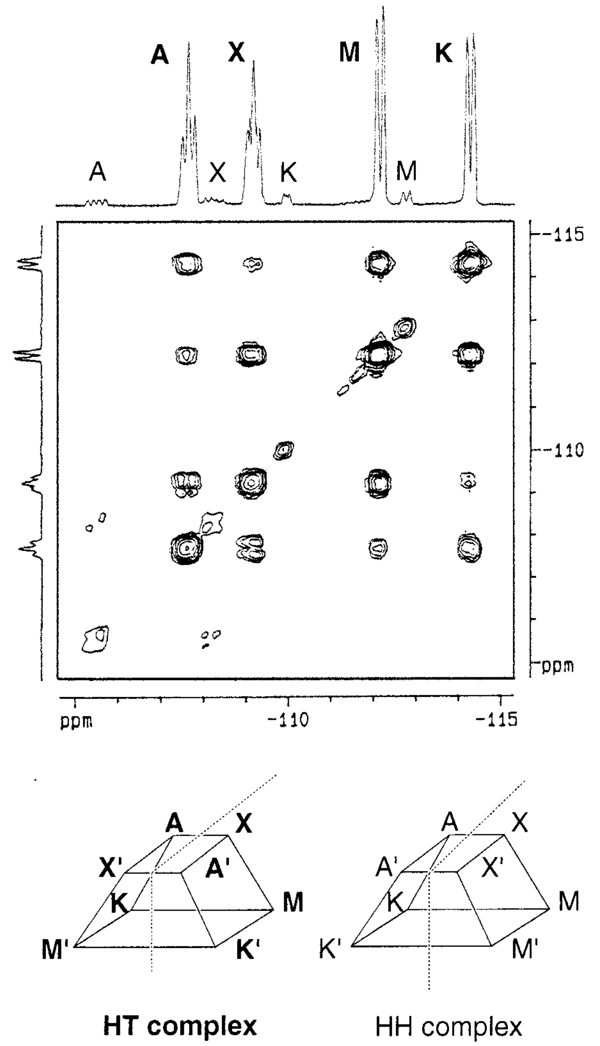

Figure 5. ^{19}F COSY (282.35 MHz, $(CD_3)_2CO$, 240 K, F_{ortho} region) of $(NBu_4)_2[Pd_2(\mu\text{-}mpz)_2(C_6F_5)_4]$ (**3**), assignment of the different F_{ortho} signals and spin systems (considering only the F_{ortho}) for the HT and HH diastereoisomers. The dashed line separates the two PdR_2 fragments (A and K (X and M) are F_{ortho} of the same R group).

signals. Moreover, there is no chemical exchange between HH and HT isomers detectable by EXSY at 260 K. The A and X signals, showing the extra coupling, have to be assigned to endo F_{ortho} atoms. With this in mind and considering their different symmetry, the spin systems for the HT and HH isomers are labeled as shown in Figure 5.

The COSY spectrum in Figure 5 reveals some smaller couplings not obvious in the normal spectra because of the broad and complicated pattern of the signals. Only the major isomer shows coupling between all its signals, and particularly between K and M (or M′). This should involve a scalar coupling through six bonds in the HT isomer and through nine bonds in the HH isomer. Hence it seems reasonable to assign the major isomer as the HT complex.[10]

Finally, it is worth noting that, given the complexity of the spin patterns in these systems, the apparent coupling constants that can be measured approximately in the irradiated spectra are $J_{AX} + J_{AX'}$ for both isomers. The main contribution is due to J_{AX}, which is basically a through-space F−F coupling between F_{ortho} nuclei that belong to different PdR_2 fragments,[9] since the scalar contribution $^9J_{AX}$ can probably be neglected. However, its value cannot be measured as we do not know $J_{AX'}$.

Other Complexes. The ^1H and ^{19}F NMR spectra of the rest of the Pd complexes $(NBu_4)_2[Pd_2(\mu\text{-}LL)_2(C_6F_3H_2)_4]$ (**5**−**8**), the nickel complexes (**9**−**11**), and platinum complexes (**12**−**15**) are very similar to those of the palladium analogues (**1**−**4**) and can be interpreted on the same basis just discussed. All the chemical shift and coupling constant assignments made for the discussed complexes are given in the Experimental Section.

It can be noted that for the Ni complexes with asymmetrically substituted azolates $J_{AX} + J_{AX'}$ for both HT and HH complexes are larger than for the palladium or platinum analogues probably as a result of the smaller size of Ni, which forces closer proximity of the endo F_{ortho} atoms.

For the complexes with asymmetrically substituted azolates the different HT:HH ratios (20:1 for Ni, 30:1 for Pt, 10:1 for Pd with C_6F_5, and 7:1 for Pd with $C_6F_3H_2$) reveal in all cases a higher stability for the HT complexes.

Conclusions

The reinvestigation of the complexes $(NBu_4)_2[M_2(\mu\text{-}LL)_2R_4]$ (LL = azolate; M = Pd, Ni, Pt; R = polyhaloaryl) shows that the boat-shaped dimeric structures of their anions are quite stable in solution, and the previously proposed equilibria or dissociations to give species such as $[R_2M(N\text{-}N)(acetone)]^-$, $[R_2M(acetone)_2] + 2dmpz^-$, or $[R_2M(N^1\text{-}N^2)(acetone)]^- + [R_2M(N^2\text{-}N^1)(acetone)]^-$ in no case occur. A mixture of the two diastereoisomers (head-to-head, HH, and head-to-tail, HT) is present for the asymmetrically substituted azolates (mpz and indz), in a ratio ranging from 1:7 to 1:30 for the different complexes.

Experimental Section

The complexes $(NBu_4)_2[M_2(\mu\text{-}LL)_2R_4]$ (**1**−**15**) were prepared as previously reported.[1−4] ^1H and ^{19}F NMR spectra were recorded with a Bruker ARX-300 spectrometer (300.13 and 282.35 MHz, respectively) equipped with a VT-100 variable-temperature unit (±0.2 K). The temperature was measured by standard methods using MeOH. Chemical shifts are relative to TMS (^1H) or $CFCl_3$ at 293 K (^{19}F), with downfield values reported as positive. All the ^1H NMR spectra ($(CD_3)_2CO$, δ, 293 K) of complexes **1**−**15** show the characteristic resonances due to the hydrogens of the NBu_4^+ groups at ca. 3.4 (m, 16H, NCH_2), 1.8 (m, 16H, NCH_2CH_2), 1.4 (m, 16H, CH_2CH_3), and 0.95 (t, 24H, CH_3).

$(NBu_4)_2[Pd_2(\mu\text{-}pz)_2(C_6F_5)_4]$ (1). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 7.04 (d, $J_{34} = J_{45} = 2.1$ Hz, 4H, $H^3 + H^5$), 5.68 (t, 2H, H^4). ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): −109.33 (m, 4F, F^2), −114.03 (m, 4F, F^6), −165.16 (m, $J_{34} = J_{45} = 20.2$ Hz, 4F, F^4), −165.57 (br, 4F, F^3), −165.88 (br, 4F, F^5).

$(NBu_4)_2[Pd_2(\mu\text{-}dmpz)_2(C_6F_5)_4]$ (2). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 5.16 (s, 2H, H^4), 2.13 (s, 12H, $Me^3 + Me^5$). ^{19}F NMR ($(CD_3)_2CO$, δ, 190 K): −104.15 (m, 4F, F^2), −109.49 (m, 4F, F^6), −165.79 (m, $J_{34} = J_{45} = 20.7$ Hz, 4F, F^4), −166.39 (br, 4F, F^3), −166.98 (br, 4F, F^5).

$(NBu_4)_2[Pd_2(\mu\text{-}mpz)_2(C_6F_5)_4]$ (3). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 7.39 (d, $J_{45} = 1.8$ Hz, H^5), 5.45 (d, H^4), 1.85 (s, Me^3); HH 6.99 (d, $J_{45} = 1.7$ Hz, H^5), 5.42 (d, H^4), 2.17 (s, Me^3). HT:HH ratio determined = 10:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −107.72 (m, $F^2(R)$), −109.11 (m, $F^2(R')$), −112.35 (m, $F^6(R')$), −114.45 (m, $F^6(R)$), −165.70 to −166.20 ($F^4(R') + F^3(R') + F^4(R)$), −166.25 to −166.85 ($F^3(R) + F^5(R)$), −167.02 (m, $F^5(R')$); HH −105.53 (m, $F^2(R)$), −108.37 (m, $F^2(R')$), −110.20 (m, $F^6(R)$), −112.95 (m, $F^6(R')$), −165.54 (m, F^4).

$(NBu_4)_2[Pd_2(\mu\text{-}indz)_2(C_6F_5)_4]$ (4). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 8.13 (d, $J_{37} = 1.0$ Hz, H^3), 7.44 (dm, $J_{67} = 8.6$ Hz, H^7), 7.33 (dm,

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[10] Inter-aryl (including fairly large through-space) F−F couplings between F_{ortho} nuclei belonging to different R groups in PdR_2 fragments have been reported recently: (a) Albéniz, A. C.; Casado, A. L.; Espinet, P. *Organometallics* **1997**, *16*, 5416−5423. (b) Alonso, M. A.; Casares, J. A.; Espinet, P.; Martínez-Ilarduya, J. M.; Pérez-Briso, C. *Eur. J. Inorg. Chem.* **1998**, 1745−1753.

$J_{45} = 8.0$ Hz, H^4), 6.73 (ddd, $J_{46} = 1.1$ Hz, $J_{56} = 6.6$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.56 (ddd, $J_{45} = 8.0$ Hz, $J_{56} = 6.6$ Hz, $J_{57} = 0.9$ Hz, H^5); HH 7.93 (dm, $J_{67} = 8.6$ Hz, H^7), 7.77 (d, $J_{37} = 1.0$ Hz, H^3), 7.29 (dm, $J_{45} = 8.2$ Hz, H^4), 6.84 (ddd, $J_{46} = 1.0$ Hz, $J_{56} = 6.6$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.58 (H^5). HT:HH ratio determined = 10:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −108.20 (m, $F^2(R)$), −109.40 (m, $F^2(R')$), −112.67 (m, $F^6(R')$), −114.62 (m, $F^6(R)$), −164.85 to −165.20 ($F^4(R) + F^4(R')$), −165.56 (m, $F^3(R')$), −165.68 to −166.08 ($F^3(R) + F^5(R)$), −166.29 (m, $F^5(R')$); HH −106.64 (m, $F^2(R)$), −108.83 (m, $F^2(R')$), −110.15 (m, $F^6(R)$), −113.57 (m, $F^6(R')$), −164.47 (m, F^4).

$(NBu_4)_2[Pd_2(\mu\text{-pz})_2(C_6F_3H_2)_4]$ (5). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 7.07 (d, $J_{34} = J_{45} = 1.8$ Hz, 4H, $H^3(pz) + H^5(pz)$), 6.11 (d, $J_{H3F4} = J_{H5F4} = 10.1$ Hz, 8H, $H^3(R) + H^5(R)$), 5.57 (t, 2H, $H^4(pz)$). ^{19}F NMR ($(CD_3)_2CO$, δ, 190 K): −77.11 (s, br, 4F, F^2), −82.42 (s, br, 4F, F^6), −122.63 (m, 4F, F^4).

$(NBu_4)_2[Pd_2(\mu\text{-dmpz})_2(C_6F_3H_2)_4]$ (6). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 6.01 (d, $J_{H3F4} = J_{H5F4} = 10.4$ Hz, 8H, $H^3(R) + H^5(R)$), 5.06 (s, 2H, $H^4(dmpz)$), 2.16 (s, 12H, $Me^3 + Me^5$). ^{19}F NMR ($(CD_3)_2CO$, δ, 190 K): −70.81 (s, 4F, F^2), −76.92 (s, 4F, F^6), −123.81 (m, 4F, F^4).

$(NBu_4)_2[Pd_2(\mu\text{-mpz})_2(C_6F_3H_2)_4]$ (7). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 7.42 (d, $J_{45} = 1.7$ Hz, $H^5(mpz)$), 5.36 (d, $H^4(mpz)$), 1.87 (s, Me^3); HH 7.04 (d, $J_{45} = 1.6$ Hz, $H^5(mpz)$), 5.32 (d, $H^4(mpz)$), 2.18 (s, Me^3); HH + HT 6.35−5.85 (br, $H^3(R) + H^3(R') + H^5(R) + H^5(R')$). HT:HH ratio determined = 7:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −75.68 (m, $F^2(R)$), −76.13 (m, $F^2(R')$), −80.83 (m, $F^6(R)$), −82.86 (m, $F^6(R')$), −123.65 (m, $J_{24} = J_{46} = 5.2$ Hz, $J_{F4H3} = J_{F4H5} = 10.2$ Hz, $F^4(R)$), −123.96 (m, $J_{24} = J_{46} = 5.2$ Hz, $J_{F4H3} = J_{F4H5} = 10.2$ Hz, $F^4(R')$); HH −72.80 (m, $F^2(R)$), −75.86 (m, $F^2(R')$), −78.27 (m, $F^6(R)$), −81.39 (m, $F^6(R')$), −123.46 (m, $F^4(R')$).

$(NBu_4)_2[Pd_2(\mu\text{-indz})_2(C_6F_3H_2)_4]$ (8). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 8.13 (d, $J_{37} = 1.0$ Hz, H^3), 7.61 (dm, $J_{67} = 8.6$ Hz, H^7), 7.26 (dm, $J_{45} = 8.0$ Hz, H^4), 6.64 (ddd, $J_{46} = 1.2$ Hz, $J_{56} = 6.6$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.49 (ddd, $J_{45} = 8.0$ Hz, $J_{56} = 6.6$ Hz, $J_{57} = 1.0$ Hz, H^5); HH 8.06 (dm, $J_{67} = 8.6$ Hz, H^7), 7.80 (d, $J_{37} = 1.0$ Hz, H^3), 7.23 (dm, H^4), 6.75 (ddd, $J_{46} = 1.0$ Hz, $J_{56} = 6.5$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.52 (H^5); HH + HT 6.55−5.85 (br, $H^3(R) + H^3(R') + H^5(R) + H^5(R')$). HT:HH ratio determined = 7:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −76.45 (m, $F^2(R)$), −77.02 (m, $F^2(R')$), −81.24 (m, $F^6(R)$), −83.10 (m, $F^6(R')$), −122.79 (m, $J_{24} = J_{46} = 5.2$ Hz, $J_{F4H3} = J_{F4H5} = 10.3$ Hz, $F^4(R)$), −122.87 (m, $J_{24} = J_{46} = 5.2$ Hz, $J_{F4H3} = J_{F4H5} = 10.3$ Hz, $F^4(R')$); HH −74.58 (m, $F^2(R)$), −76.68 (m, $F^2(R')$), −78.56 (m, $F^6(R)$), −82.14 (m, $F^6(R')$), −122.24 (m, $F^4(R')$), −123.07 (m, $F^4(R)$).

$(NBu_4)_2[Ni_2(\mu\text{-pz})_2(C_6F_5)_4]$ (9). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 6.99 (d, $J_{34} = J_{45} = 2.0$ Hz, 4H, $H^3 + H^5$), 5.49 (t, 2H, H^4). ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): −110.16 (m, 4F, F^2), −115.82 (m, 4F, F^6), −166.03 (m, $J_{34} = J_{45} = 20.0$ Hz, 4F, F^4), −166.20 to −166.80 (m, 8F, $F^3 + F^5$).

$(NBu_4)_2[Ni_2(\mu\text{-mpz})_2(C_6F_5)_4]$ (10). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 7.40 (d, $J_{45} = 1.9$ Hz, H^5), 5.25 (d, H^4), 1.98 (s, Me^3); HH 6.97 (d, $J_{45} = 1.9$ Hz, H^5), 5.24 (d, H^4), 2.32 (s, Me^3). HT:HH ratio determined = 20:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −108.26 (m, $F^2(R)$), −109.88 (m, $F^2(R')$), −114.39 (m, $F^6(R')$), −115.09 (m, $F^6(R)$), −166.50 to −167.15 ($F^3(R') + F^4(R) + F^4(R')$), −167.15 to −167.75 ($F^3(R) + F^5(R)$), −168.20 (m, $F^5(R')$); HH −105.43 (m, $F^2(R)$), −109.28 (m, $F^2(R')$), −112.31 (m, $F^6(R)$), −114.15 (m, $F^6(R')$), −166.39 (m, F^4).

$(NBu_4)_2[Ni_2(\mu\text{-indz})_2(C_6F_5)_4]$ (11). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 8.20 (s, H^3), 7.73 (dm, $J_{67} = 8.6$ Hz, H^7), 7.18 (dm, $J_{45} = 8.0$ Hz, H^4), 6.67 (ddd, $J_{46} = 1.0$ Hz, $J_{56} = 6.6$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.46 (ddd, $J_{45} = 8.0$ Hz, $J_{56} = 6.6$ Hz, $J_{57} = 1.0$ Hz, H^5); HH 8.22 (H^7), 7.81 (s, H^3), 7.15 (H^4), 6.77 (m, H^6), 6.49 (H^5). HT:HH ratio determined = 20:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −108.46 (m, $F^2(R)$), −110.29 (m, $F^2(R')$), −114.84 (m, $F^6(R')$), −115.23 (m, $F^6(R)$), −165.86 ($F^4(R) + F^4(R')$), −166.15 to −166.70 ($F^3(R') + F^5(R)$), −166.87 (m, $F^3(R)$), −167.36 (m, $F^5(R')$); HH −106.46 (m, $F^2(R)$), −109.67 (m, $F^2(R')$), −112.06 (m, $F^6(R)$), −165.32 (m, F^4).

$(NBu_4)_2[Pt_2(\mu\text{-pz})_2(C_6F_5)_4]$ (12). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 7.15 (d, $J_{34} = J_{45} = 2.0$ Hz, 4H, $H^3 + H^5$), 5.74 (t, 2H, H^4). ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): −112.63 (m, $J_{FPt} = 473$ Hz, 4F, F^2), −117.52 (m, $J_{FPt} = 482$ Hz, 4F, F^6), −166.5 to −167.20 (8F, $F^3 + F^4$), −167.38 (m, 4F, F^5).

$(NBu_4)_2[Pt_2(\mu\text{-dmpz})_2(C_6F_5)_4]$ (13). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): 5.28 (s, 2H, H^4), 2.11 (s, 12H, $Me^3 + Me^5$). ^{19}F NMR ($(CD_3)_2CO$, δ, 190 K): −108.48 (m, br, $J_{FPt} = 380$ Hz, 4F, F^2), −113.42 (m, br, $J_{FPt} = 463$ Hz, 4F, F^6), −167.30 to −168.15 (8F, $F^3 + F^4$), −168.41 (m, br, 4F, F^5).

$(NBu_4)_2[Pt_2(\mu\text{-mpz})_2(C_6F_5)_4]$ (14). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 7.49 (d, $J_{45} = 1.7$ Hz, H^5), 5.55 (d, H^4), 1.80 (s, Me^3); HH 7.08 (d, $J_{45} = 1.7$ Hz, H^5), 2.15 (s, Me^3). HT:HH ratio determined = 30:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −110.94 (m, $J_{FPt} = 509$ Hz, $F^2(R)$), −114.11 (m, $J_{FPt} = 403$ Hz, $F^2(R')$), −117.03 (m, $J_{FPt} = 554$ Hz, $F^6(R')$), −117.87 (m, $J_{FPt} = 456$ Hz, $F^6(R)$), −167.07 (m, $F^3(R')$), −167.45 to −168.70 ($F^3(R) + F^4(R) + F^4(R') + F^5(R) + F^5(R')$); HH −109.20 (m, $F^2(R)$), −111.35 (m, $F^2(R')$), −113.75 (m, $F^6(R)$), −116.75 (m, $F^6(R')$).

$(NBu_4)_2[Pt_2(\mu\text{-indz})_2(C_6F_5)_4]$ (15). ^1H NMR ($(CD_3)_2CO$, δ, 293 K): HT 8.25 (d, $J_{37} = 0.8$ Hz, H^3), 7.39 (dm, $J_{67} = 8.6$ Hz, H^7), 7.36 (dm, $J_{45} = 8.0$ Hz, H^4), 6.74 (ddd, $J_{46} = 1.0$ Hz, $J_{56} = 6.6$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.57 (ddd, $J_{45} = 8.0$ Hz, $J_{56} = 6.6$ Hz, $J_{57} = 1.0$ Hz, H^5); HH 7.97 (dm, $J_{67} = 8.6$ Hz, H^7), 7.86 (d, $J_{37} = 1.0$ Hz, H^3), 7.30 (dm, $J_{45} = 8.2$ Hz, H^4), 6.86 (ddd, $J_{46} = 1.0$ Hz, $J_{56} = 6.6$ Hz, $J_{67} = 8.6$ Hz, H^6), 6.60 (H^5). HT:HH ratio determined = 30:1. ^{19}F NMR ($(CD_3)_2CO$, δ, 220 K): HT −111.44 (m, $J_{FPt} = 499$ Hz, $F^2(R)$), −114.02 (m, $J_{FPt} = 409$ Hz, $F^2(R')$), −117.11 (m, $J_{FPt} = 542$ Hz, $F^6(R')$), −117.87 (m, $J_{FPt} = 428$ Hz, $F^6(R)$), −166.45 to −168.00 ($F^3(R') + F^3(R) + F^4(R) + F^4(R') + F^5(R) + F^5(R')$); HH −110.21 (m, $F^2(R)$), −111.91 (m, $F^2(R')$), −113.67 (m, $F^6(R)$), −116.40 (m, $F^6(R')$), −166.31 (m, F^4).

$J_{AX} + J_{AX'}$ Values (±2) in Hertz Corresponding to the $(NBu_4)_2[M_2(\mu\text{-mpz})_2R_4]$ Complexes: **3** (HT, 37; HH, 63), **7** (HT, 29; HH, 46), **10** (HT, 53; HH, 79), **14** (HT, 30; HH, 70). The values for the indz analogues are very similar.

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