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Role of Cation−Anion Interactions in Ionic Complexes Containing $[Pd\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OH_2)]^+$ and $[\{Pd(C_6H_3(CH_2NMe_2)_2\text{-}2,6)\}_2(\mu\text{-}Cl)]^+$ Cations

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The reaction of $[PdCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ ([PdCl(NCN)]) with either the sodium or silver salts of the borate anions $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ and $[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]^-$ under various reaction conditions resulted in the exclusive formation of the respective dinuclear $[\{Pd(NCN)\}_2(\mu\text{-}Cl)][B\{C_6H_4(SiMe_2R)\text{-}4\}_4]$ salts **4a** (R = Me) and **4b** ($R = CH_2CH_2C_6F_{13}$). When using BF_4^-, both dinuclear $[\{Pd(NCN)\}_2(\mu\text{-}Cl)]BF_4$ (**4c**) and mononuclear $[Pd(NCN)(OH_2)]BF_4$ (**5c**) could be obtained. The molecular structure of **5c** showed the presence of hydrogen-bridging interactions between coordinated H_2O molecules and the fluorine atoms of BF_4^-. Attempts to isolate complexes of the type $[Pd(NCN)(OH_2)][B\{C_6H_4(SiMe_2R)\text{-}4\}_4]$ were unsuccessful. This has been ascribed to a difference in stabilization of the respective mono- and dinuclear cations by the borate anions BF_4^- and $[B\{C_6H_4(SiMe_2R)\text{-}4\}_4]^-$, respectively. The conclusions are supported by DFT calculations.

Introduction

Cationic palladium complexes of the monoanionic, terdentate 2,6-bis(dimethylaminomethyl)phenyl pincer ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (abbreviated as NCN) are active catalysts in various C−C bond formation reactions, such as the aldol-condensation[1] and the Michael reaction.[2] To recover the catalysts after reaction, various methods have been employed to immobilize the NCN−Pd unit on a support. The majority of these efforts have focused on attaching the ligand covalently to a soluble carrier, e.g., carbosilane dendrimers,[2c,3] fullerenes,[2c,4] and cartwheel molecules.[2b,c] So far no attention has been paid to the use of the counterions as a site for the introduction of a suitable functionality for catalyst recovery.

The immobilization of transition-metal catalysts in perfluorinated solvents using highly fluorous anions is interesting, as this facilitates catalyst recovery using phase separation while allowing catalysis under homogeneous conditions and because it does not affect the catalytically active center. Recently we reported the introduction of perfluoroalkyl-substituted tetraphenylborate anions for the fluorous phase immobilization of cationic rhodium complexes.[5] Herein, the reaction of various tetraphenylborate salts with [PdCl(NCN)] is described. This, surprisingly, resulted in the formation of chloride-bridged dinuclear complexes, whereas a chloride-free, mononuclear $[Pd(NCN)(OH_2)]^+$ cation was isolated when commonly employed BF_4^- was used.[6]

Results and Discussion

Synthesis. Reaction of [PdCl(NCN)] (**1**) with 1 equiv of $Na[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$ (**2a**), $Na[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]$ (**2b**), $Ag[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$ (**3a**), or $Ag[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]$ (**3b**) in an acetone/

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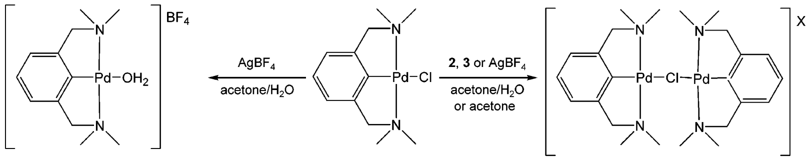
10.1021/om0303698 CCC: $27.50

Scheme 1. Preparation of μ-Cl Bridged Dinuclear NCN-Palladium Complexes



5c **1**

4a: X = $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$

4b: X = $[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]^-$

4c: X = BF_4^- (in dry acetone only)

H_2O mixture gave rise to the formation of the dinuclear complexes $[(Pd(NCN))_2(\mu\text{-}Cl)][B\{C_6H_4(SiMe_2R)\text{-}4\}_4]$ (**4a**, R = Me; **4b**, R = $CH_2CH_2C_6F_{13}$) (Scheme 1). ^1H NMR and elemental analysis confirmed that these complexes have an NCN-ligand to borate anion ratio of 2:1. Changing the solvent to CH_2Cl_2 or the molar ratio of **1** and the borate salts during the synthesis did not affect the nature of the product formed. Starting with an excess of **1** (2:1 molar ratio) or an excess of sodium borate (up to 1:4 molar ratio) yielded dinuclear **4** as the only product isolated, the complexes $[Pd(NCN)(OH_2)][B\{C_6H_4(SiMe_2R)\text{-}4\}_4]$ (**5a**, R = Me; **5b**, R = $CH_2CH_2C_6F_{13}$) proving to be inaccessible. Also addition of excess of the silver borate **3b** did not afford **5b**. When $AgBF_4$ (2 equiv) was added to acetone solutions of dinuclear **4b**, rapid formation of **5c** was observed, underlining the preference for this species. Also a 1 equiv reaction afforded only **5c** along with some unreacted **4b** but no indication for the tetraarylborate aqua complex **5b**.

The preference for the formation of μ-Cl-bridged complexes was not expected on the basis of previous reactions in which BF_4^- was used as borate anion. Under similar conditions, reaction of **1** with $AgBF_4$ resulted in the formation of a mononuclear complex with the composition $[Pd(NCN)(OH_2)]BF_4$ (**5c**).[6] The dinuclear complex $[(Pd(NCN))_2(\mu\text{-}Cl)]BF_4$ (**4c**) could be isolated only when thoroughly dried acetone was used.[7]

The reaction of **1** with **2a** was also performed in the presence of acetonitrile (Pd:MeCN = 1:3), as the formation of dicationic $[Pd_2\{C_6(CH_2NMe_2)_4\text{-}2,3,4,5\}(MeCN)_2][BPh_4]_2$ has been reported under similar conditions.[8] However, the decomposition of the borate anion was observed and no ionic palladium species containing a tetraarylborate anion could be identified.[9] The results obtained suggest that in the case of the large tetraarylborate anions formation of the chloride-bridged dinuclear palladium complex is preferred over that of the chloride-free mononuclear aqua complex. This signifies that a difference exists in the cation–anion interactions in the presence of the BF_4^- anion in comparison with those for the $[B\{C_6H_4(SiMe_2R)\text{-}4\}_4]^-$ anions (R = Me or $CH_2CH_2C_6F_{13}$). As dinuclear palladium species such as **4**, with a single halogen bridge without supporting bridging ligands, are relatively rare,[10] the nature of these interactions was investigated more thoroughly. In these studies only $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ was considered, as this anion was synthetically more accessible than $[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]^-$ and because the solid state structure of dinuclear **4a** allowed a direct comparison with those obtained for known complexes **5c**[6] and **4c**.[7]

Molecular Structures of $[\{Pd(NCN)\}_2(\mu\text{-}Cl)][B\{C_6H_4(SiMe_3)\text{-}4\}_4]$ (4a) and $[Pd(NCN)(OH_2)]BF_4$ (5c). The molecular structures of **4a** and **5c** were determined by single-crystal X-ray diffraction studies. Off-white crystals of **4a**, suitable for X-ray crystal structure determination, were obtained by slow diffusion of pentane into a concentrated solution of **4a** in methanol. The molecular structure is represented in Figure 1, and relevant bond angles and distances are collected in Table 1.

In the chloride-bridged dinuclear cation, both palladium centers have a slightly distorted square-planar geometry, with a maximum deviation from their least squares NCN–Pd–Cl planes of only 0.016(1) Å for Pd(1) and 0.010(1) Å for Pd(2, major), respectively. The boron has a slightly distorted tetrahedral coordination sphere. These observations, together with the majority of the values of bond angles and distances, correspond with structural features of the earlier determined structures for the dinuclear cation in $[\{Pd(NCN)\}_2(\mu\text{-}Cl)]BF_4$ (**4c**)[7] (Pd–N = 2.10 Å, Pd–C = 1.92 Å, N–Pd–N = 163°) and the borate anion in $[(18\text{-crown-}6)Na(THF)_2][B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ (B–C = 1.64–1.72 Å, C–B–C = 103–113°).[5b] However, significant deviations in the Pd–Cl–Pd angle (121° in **4a** vs 134° in **4c**), the Pd···Pd distance (4.2902(11) Å in **4a** vs 4.5438(15) Å in **4c**), and the angle between the planes of the NCN ligands (77° in **4a** vs 88° in **4c**) were observed. It is most likely that the steric bulk of $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ in **4a** enforces a different crystal packing in comparison with **4c**,[11] which causes the reduction of the Pd–Cl–Pd angle and the significant shorting of the Pd···Pd distance in **4a**. Another noteworthy aspect in the structure of **4a** is the

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(9) The reaction mixture was analyzed using ^1H and $^{11}B\{^1H\}$ NMR. The former shows the disappearance of all resonances corresponding with the aromatic protons of the anion, the latter that of the characteristic resonance belonging to tetraphenylboron ($^{11}B\{^1H\}$ NMR (acetone-d_6, 96.3 MHz): δ −1.1 (s)).

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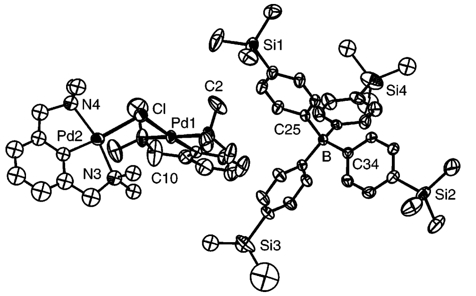

Figure 1. ORTEP drawing of dinuclear **4a** with ellipsoids at the 50% probability level. Hydrogen atoms and the mirror disorder component are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 4a

bond lengths		bond angles	
Pd(1)−Cl	2.4527(17)	Pd(1)−Cl−Pd(2)	121.11(5)
Pd(1)−N(1)	2.102(5)	N(1)−Pd(1)−N(2)	162.97(19)
Pd(1)−N(2)	2.091(5)	C(9)−Pd(1)−Cl	176.86(13)
Pd(1)−C(9)	1.906(5)		
Pd(2)−Cl	2.4738(17)	N(3)−Pd(2)−N(4)	164.5(3)
Pd(2)−N(3)	2.062(8)	C(21)−Pd(2)−Cl	174.6(2)
Pd(2)−N(4)	2.138(10)		
Pd(2)−C(21)	1.912(8)		
B−C(25)	1.653(7)	C(25)−B−C(34)	110.1(3)
B−C(34)	1.644(7)	C(25)−B−C(43)	110.4(4)
B−C(43)	1.641(6)	C(25)−B−C(52)	107.8(3)
B−C(52)	1.660(6)	C(34)−B−C(52)	111.7(4)

puckering of the five-membered rings in the NCN−Pd−Cl entities. Whereas these units have C_2-symmetry in **4c**, resulting in positioning of the axial N-methyl groups at different sides of the coordination plane, in **4a** these units have C_{2v}-symmetry and the axial N-methyl groups are positioned on the same side of this plane. The latter structural feature is possibly also the result of having to accommodate the bulky anion in the crystal lattice. No $\pi\cdots\pi$ interactions or agostic interactions between cations and anions were observed in the solid state, and investigation of **4a** in solution using $^1H-^1H$ NOESY NMR in CD_2Cl_2[12] also showed no indications for such specific cation−anion contacts.

White crystals of **5c**, suitable for single-crystal X-ray diffraction analysis, were obtained by slow diffusion of hexane into a concentrated solution of $[Pd(NCN)(OH_2)]BF_4$ in dichloromethane. The molecular structure in the crystal is represented in Figure 2, and relevant bond angles and distances are collected in Table 2.

In **5c**, the palladium and the boron centers have slightly distorted square-planar and tetrahedral coordination spheres, respectively. The NCN−Pd unit has C_2-symmetry, and the bond angles (e.g., N−Pd−N = 162.7°) and distances (e.g., Pd−N = 2.11 Å and Pd−C = 1.91 Å) correspond well with known structures for comparable NCN−Pd complexes.[13] In the crystal lattice each BF_4^- anion is connected to two water ligands, and each water molecule to two BF_4^- anions, through hydrogen bonds (Figure 3). As a result, an intermolecular hydrogen-bonding network, with infinite chains of cations and anions, exists. Within this network, two distinct lengths of F···H distances are observed (1.92(4) and 2.04(4) Å), with each water ligand and each BF_4^- anion participating in one of the shorter and one of the longer hydrogen bridges. Furthermore, the hydrogen atoms that have the shortest O−H distance, 0.76(4) Å, are connected to the fluorine atoms with the longest B−F bond distances (1.401(4) Å) and vice versa (O−H = 0.84(4) Å and B−F = 1.386(4) Å).

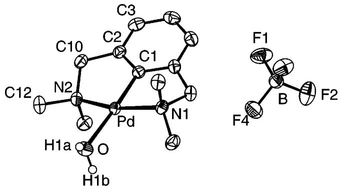

Figure 2. ORTEP drawing of mononuclear **5c** with ellipsoids at the 50% probability level. Hydrogen atoms of the NCN ligand are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 5c

bond lengths		bond angles	
Pd−O	2.192(2)	N(1)−Pd−N(2)	162.70(8)
Pd−N(1)	2.107(2)	N(1)−Pd−C(1)	81.64(9)
Pd−N(2)	2.108(2)	N(2)−Pd−C(1)	81.18(10)
Pd−C(1)	1.909(2)	C(1)−Pd−O	176.84(9)
B−F(1)	1.368(3)	F(1)−B−F(2)	110.7(2)
B−F(2)	1.386(3)	F(2)−B−F(3)	108.9(3)
B−F(3)	1.401(4)	F(2)−B−F(4)	107.2(2)
B−F(4)	1.386(4)	F(3)−B−F(4)	108.5(2)
F3−H(1a)	1.92(4)	O−H(1a)−F3	176(4)
F4−H(1b)	2.04(4)	O−H(1b)−F4	173(5)
O−H(1a)	0.76(4)		
O−H(1b)	0.84(4)		

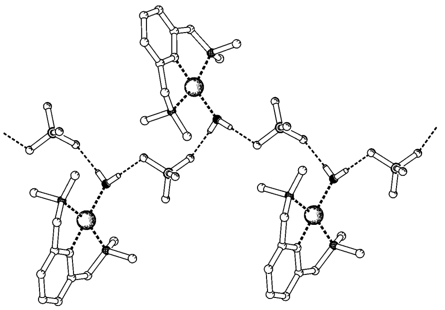

Figure 3. Crystal packing of **5c**, showing the hydrogen-bridging interactions of the BF_4^- anions and the water ligands.

Although hydrogen bonding of water to weakly coordinating anions is frequently observed in organometallic complexes,[14] direct crystallographic evidence for hydrogen-bonding interactions in palladium aqua complexes is rare. Previous examples have been encountered in $[Pd(AsPh_3)(C_6F_5)(OH_2)_2][CF_3SO_3]$,[15] $[Pd\{C_6H_3(CH_2P$-

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(14) The tendency of H_2O to act as a hydrogen-bond donor is the result of its coordination to a metal, which makes H_2O more acidic. Previous studies on $[NCN-Pt-(OH_2)][OTf]$ reported a pK_a value for the coordinated water of 10.8, whereas the value is 15.7 for noncoordinated water: Schmülling, M.; Grove, D. M.; van Koten, G.; van Eldik, R.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 1384.

^{t}Bu$_2$)-2,6}(OH$_2$)]BF$_4$,[16] and [Pd(5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane)(OH$_2$)]BF$_4$,[17] where F⋯H distances of 1.85−2.05 Å were reported. A more closely related example of F⋯H hydrogen bonding is found in the structure of [Pd{C$_6$H$_4$(CH$_2$NMe$_2$)-2}(PPh$_3$)(OH$_2$)]PF$_6$,[13a] where a F⋯H distance of 2.087 Å was observed, although the authors did not discuss the possibility of hydrogen bonding. The F⋯H distances observed in **5c** correspond with these previously reported examples.

Role of Hydrogen-Bonding Interactions in the Formation of Cationic NCN−Pd-aqua Complexes. Complex **4c** is formed when [PdX(NCN)] (X = Cl$^-$, Br$^-$, I$^-$, or CN$^-$) is reacted with [Pd(NCN)(OH$_2$)]BF$_4$ in CH$_2$Cl$_2$[18] or by the reaction of [PdCl(NCN)] with AgBF$_4$ in dry acetone (vide supra). However, when the latter reaction is carried out in the presence of water, [Pd(NCN)(OH$_2$)]BF$_4$ is formed. Thus, with the BF$_4^-$ anion both the mononuclear aqua complex and the dinuclear chloride-bridged complexes are accessible.[7b] Therefore, the observation that reaction of **1** with the tetraarylborate salts **2a** or **3a** instead of AgBF$_4$ results in the selective formation of chloride-bridged **4a** was surprising. From the crystallographic studies on **4a**, **4c**, and **5c** it is clear that BF$_4^-$ can easily form hydrogen bonds with the Pd-aqua species, whereas [B{C$_6$H$_4$(SiMe$_3$)-4}$_4$]$^-$ does not show this tendency. In fact, the large and weakly coordinating [B{C$_6$H$_4$(SiMe$_3$)-4}$_4$]$^-$ anion has little possibility for effective hydrogen bonding. Other cationic palladium(II) aqua complexes that have been spectroscopically characterized invariably contain hydrogen-bond acceptors in the form of small anions such as BF$_4^-$,[13b,19] PF$_6^-$,[13a] ClO$_4^-$,[13c−f] SO$_3$CF$_3^-$,[13f,20] and phenoxide,[21] or water[15] and ether functionalities,[17] in close proximity to the water ligand. These observations suggest that inter-ionic interactions, in the form of hydrogen bonding, could be essential for the formation of mononuclear palladium aqua species. However, given the weakness of such interactions (vide infra), it remains hard to understand why dinuclear complexes are preferred when the large tetraarylborate anions are used.

To make a more detailed evaluation of the effects of BF$_4^-$ and [B{C$_6$H$_4$(SiMe$_3$)-4}$_4$]$^-$ on the relative thermodynamic stability of **4a**, **4c**, [Pd(NCN)(OH$_2$)][B{C$_6$H$_4$(SiMe$_3$)-4}$_4$] (**5a**), and **5c**, these complexes were studied using density functional theory (DFT) calculations. The structures were preoptimized using semiempirical (PM3) molecular modeling as implemented in the Spartan 5.1.1 (SGI) software package. For **4a**, **4c**, and **5c** the crystallographic data were used as a starting point for these calculations. Geometry optimizations were finalized using the Gaussian 98[22] and Gamess-UK SGI[23] software. For these calculations, the LANL2DZ[24] basis set was chosen, as it offered a good compromise between accuracy and computational power available. Solvation of the ions was disregarded, because its assessment was beyond the capability of the methods employed. Within the limits of the basis set employed, the optimized geometries of dinuclear **4a** and **4c** and mononuclear **5c** were good representations of the structures obtained from the crystallographic studies on these complexes (Figure 4).[25] As **5a** was experimentally inaccessible, its geometry could not be compared with an experimentally determined molecular structure. Calculated molecular models of **5c** consistently showed the BF$_4^-$ anion in a F$_3$BF⋯H−O−Pd orientation (F⋯H = 1.60 Å, B−F⋯H = 113°, O−H⋯F = 171°, Scheme 2), which is characteristic for hydrogen bonding and similar to that encountered in the crystal structure of [Pd(NCN)(OH$_2$)]BF$_4$. This propensity of BF$_4^-$ for interacting with

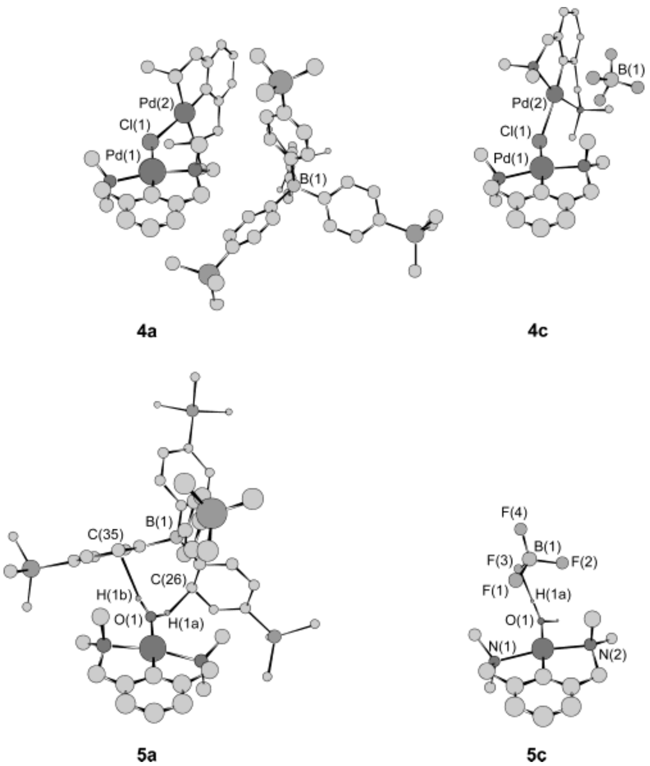

Figure 4. Calculated structures for **4a**, **4c**, **5a**, and **5c**. Hydrogen atoms, except for H$_2$O, are omitted for clarity.

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(17) Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1995**, *34*, 5656.

(18) [{Pd(NCN)}$_2$(μ-X)]BF$_4$ (X = Cl$^-$, Br$^-$, I$^-$, or CN$^-$) are reported in ref 7b.

(19) See Figure 3 for the hydrogen-bonding interactions in the molecular structure of **5c**.

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(25) For comparison, a collection of bond lengths and angles is listed in Table 4.

Scheme 2. Hydrogen-Bonding Interactions in the DFT-Optimized Structures of 5a and 5c

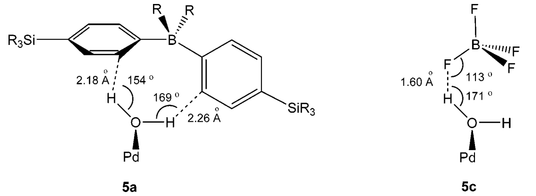

Table 3. Electronic Energy Values for the Components Participating in the Reactions of [PdCl(NCN)] with $AgBF_4$ or Ag[B{$C_6H_4(SiMe_3)$-4}$_4$]

no.	component	E_e (hartree)[a]
	H_2O	−76.41432
	BF_3	−324.55458
	$F_2BF\cdots HOH$	−400.97410
1	[PdCl(NCN)]	−719.88593
	$[Pd(NCN)]^+$	−704.67694
	$[Pd(NCN)(OH_2)]^+$	−781.12747
	$[\{Pd(NCN)\}_2(\mu\text{-}Cl)]^+$	−1424.62039
	Cl^-	−14.99863
	BF_4^-	−424.56708
	$[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$	−1443.59058
5c	$[Pd(NCN)(OH_2)]BF_4$	−1205.83881
5a	$[Pd(NCN)(OH_2)][B\{C_6H_4(SiMe_3)\text{-}4\}_4]$	−2224.82984
4c	$[\{Pd(NCN)\}_2(\mu\text{-}Cl)]BF_4$	−1849.29933
4a	$[\{Pd(NCN)\}_2(\mu\text{-}Cl)][B\{C_6H_4(SiMe_3)\text{-}4\}_4]$	−2868.28808

[a] 1 hartree = 627.52 kcal/mol.

hydrogen-bond donors[26] was also reported recently in a theoretical study on $H_3O^+\cdots BF_4^-$ ion pairs.[27] In the structure of **5a** the hydrogen atoms of the water ligand are also in close contact with the anion, the close contact distances with the phenyl ring carbons of the tetraarylborate anion being 2.18 and 2.26 Å (Scheme 2).

Subsequently, the cation−anion interactions in **4a**, **4c**, **5a**, and **5c** were assessed by stepwise assembly of these complexes starting from the $[Pd(NCN)]^+$ cation (Scheme 3). To arrive at the energies associated with each step represented in Scheme 3, the electronic energy difference between the product and the components from which the product was composed was calculated; see Table 3.

From Scheme 3, the differences in energy as a consequence of the cation−anion interactions in the mononuclear and dinuclear complexes can be clearly established. A large drop in energy (ΔE_e of −132 kcal/mol) is associated with the formation of [PdCl(NCN)] from $[Pd(NCN)]^+$ and Cl^-. Subsequent interaction of neutral [PdCl(NCN)] with another $[Pd(NCN)]^+$ cation yields just an additional −36 kcal/mol, and when $[Pd(NCN)]^+$ is combined with H_2O to form $[Pd(NCN)(OH_2)]^+$, ΔE_e is only −23 kcal/mol. Apparently, H_2O is a much weaker Lewis base than [PdCl(NCN)]. As a result, the formation of a dinuclear $[\{Pd(NCN)\}_2(\mu\text{-}Cl]^+$ cation is more favorable than that of two mononuclear $[Pd(NCN)(OH_2)]^+$ cations when no charge-compensating anion is present.

Upon introduction of the charge-compensating anions, a major difference between the small BF_4^- and the more bulky $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ could be discerned. In the case of the dinuclear $[\{Pd(NCN)\}_2(\mu\text{-}Cl)]^+$ cation the energy gained from ion-pairing with BF_4^- (formation of **4c**) is higher ($\Delta\Delta E_e$ = 22 kcal/mol) than for $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ (formation of **4a**). As no direct cation−anion interactions are observed in the molecular models of **4a** and **4c**, which is supported by the crystallographic studies on both complexes,[28] this difference in the interaction with the anions must be electrostatic in nature. As BF_4^- is smaller and has a higher charge density than the silyl-substituted tetraarylborate anion, stronger electrostatic interactions with the cation can be easily envisioned. For the combinations of $[Pd(NCN)(OH_2)]^+$ with either BF_4^- or $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ a similar trend was observed ($\Delta\Delta E_e$ = 20 kcal/mol). Furthermore, the calculations indicate that the effect of hydrogen bonding on the ΔE_e of ion-pairing is marginal. In **5c**, which displayed extensive hydrogen-bond formation in both the crystallographic and DFT studies, the ΔE_e of ion-pairing is −90 kcal/mol. Calculations performed on H···F bonding between BF_3 and H_2O indicate that the energy associated with the formation of this bond is only −3 kcal/mol, which is supported by experimental determination of hydrogen−fluorine bonds as well.[29] Within the accuracy of the computational methods, the contribution of the hydrogen bonds is not significant and the energy related with the cation−anion interactions is determined by the electrostatic contribution.

The results of the calculations can be summarized by the simplified model shown in Scheme 4, which allows a comparison of relative stability of mononuclear and dinuclear complexes.

As the formation of the dinuclear cation is energetically more favorable than that of the mononuclear cation, strong cation−anion interactions are required for the aqua complex to be stable. When these are absent, as in the presence of $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$, the stability of the chloride-bridged dinuclear species is much higher (Scheme 4). This corresponds with the experimentally observed preference for the formation of the dinuclear complex **4a** when using the tetraarylborate anion. When employing BF_4^-, the inter-ionic interactions are stronger, which enhances the stability of **5c** to such an extent that its formation is almost equally favorable to **4c** (Scheme 4), in correspondence with the experimental accessibility of both complexes. For $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ (**5a**) the aqua complex is clearly less favorable than for BF_4^- (**5c**) by as much as 19 kcal/mol.

As Scheme 4 shows that even in the presence of BF_4^- a modest preference for the dinuclear species remains, the experimentally observed preference for the aqua complex suggests the existence of an additional stabilizing contribution not taken into account in our calculations. Most likely, the high formation enthalpy of AgCl (or NaCl) provides an explanation for preference of the formation of the mononuclear compound. In the preparation of **5c**, 1 equiv of AgCl is formed per Pd against 1 equiv per two Pd centers for **4c**. As a result of the enthalpy associated with the formation of AgCl, the equilibrium between the dinuclear and mononuclear species will shift toward the latter, irrespective of the

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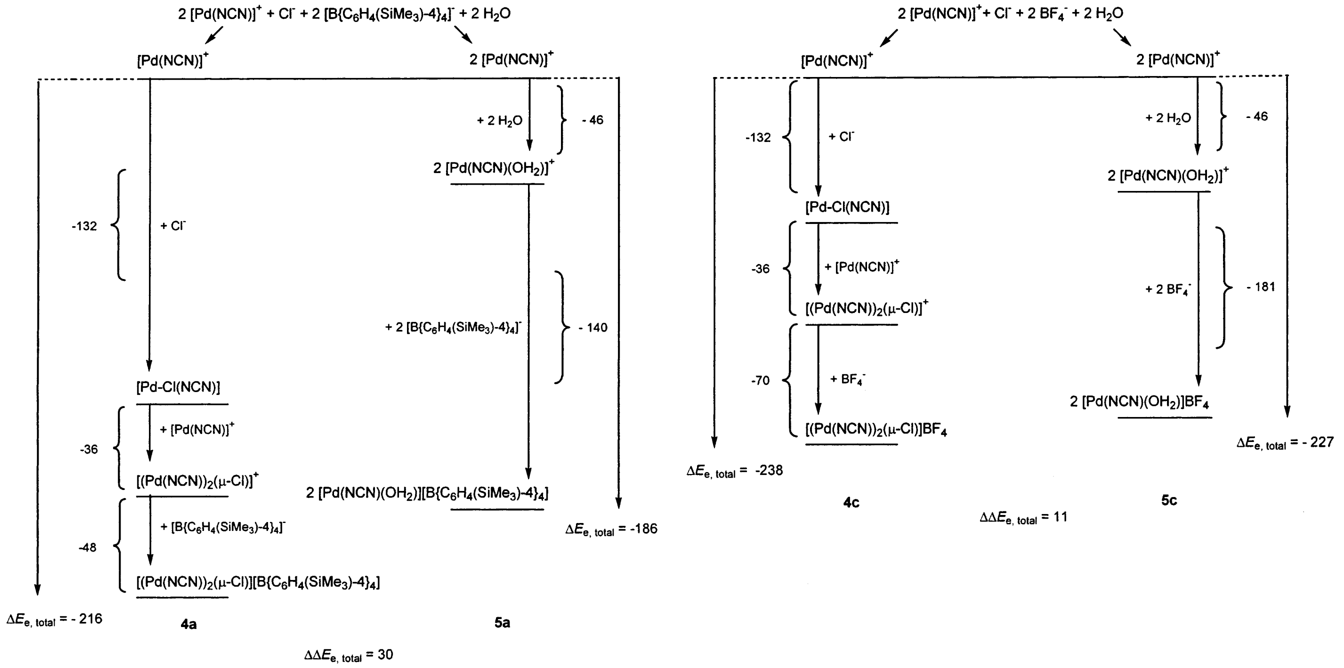
[26] For reviews see: (a) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331. (b) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[27] Farcasiu, D.; Hâncu, D. *J. Phys. Chem. A* **1999**, *103*, 754.

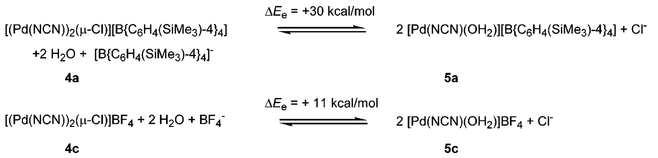
[28] For **4a** vide supra; for **4c** see ref 7b.

[29] Hydrogen bonds of the type $OH_2\cdots F$ are generally weak in character, with binding energies of ca. 2.4 kcal/mol: Desiraju, G. R.; Steiner, T. In *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.

Scheme 3. Energy of Formation (kcal/mol) for 4a, 4c, 5a, and 5c as Assembled from Separate Components (from DFT calculations, see text)



Scheme 4



anion. The small difference in E_e between the mononuclear and dinuclear complexes with the BF_4^- anion implies that **5c** will be the energetically most favorable, whereas for the $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ anion **4a** remains the most favorable configuration. The presence of an excess of water instead of stoichiometric amounts might be an additional factor that shifts the equilibrium toward mononuclear species.

As pointed out by one of the referees of this paper, although the calculations give an acceptable thermodynamic explanation of the observations, kinetic factors such as difference in the rates of attack of the different borates might be important as well. Unfortunately, quantitative kinetic studies are severly hindered by the fact that the reaction mixtures are inhomogeneous due to salt formation. One aspect that may well play a crucial kinetic role is the H−F interaction to afford a $[BF_4\cdots H_2O]^-$ fragment that makes water a better nucleophile. In an associative mechanism where (NCN)-PdCl has to be replaced from the $[(NCN)Pd{-}Cl{-}Pd(NCN)]^+$ fragment, the increased negative charge and Lewis basicity of water might be important. A general kinetic resistance of the dinuclear species toward chloride abstraction, irrespective of the type of borate, is certainly not the problem, as was shown by the fast reaction with $AgBF_4$.

Conclusions

Whereas, previously, hardly any attention was given to the nature of the weakly coordinating anion in the formation of cationic $[Pd(NCN)(OH_2)]^+$ complexes, in this study it has been shown that the interactions between the cation and the anion play a determining role in the formation of these complexes. A small anion that can participate in strong electrostatic interactions with the cationic aqua species appears to be a prerequisite for the formation of stable $[Pd(NCN)(OH_2)]^+$ complexes. Hydrogen-bonding interactions were also observed when BF_4^- was used; however their enthalpic contribution to the stability of palladium aqua species appears to be marginal. When the possibility for strong stabilizing interactions between the anion and $[Pd(NCN)(OH_2)]^+$ cation is lacking, as is the case with the very weakly coordinating silyl-substituted tetraphenylborate anions, formation of a bridged dinuclear palladium species is preferred.

With respect to the relative stabilities of other known cationic Pd-aqua and corresponding chloride-bridged complexes it can be said that there is very little reference material. However, the few known aqua complexes are invariably stabilized by small anions that form H-bridges to the water ligand. Strong electrostatic interactions no doubt add to the stability of these complexes. Brookhart's $[(N\wedge N)PdMe(OEt_2)][BAr_f]$ ($N\wedge N$ = diimine ligand) complexes containing a fluorinated tetraarylborate anion[30] need Et_2O as Lewis base to fill up the empty coordination site on the Pd center. [(dppp)-Pd((C(O)Me)(CO)][TFPB][31] and [(N^N)Pd(Me)(MeCN)]-[TFPB] (N^N = 2,2′-bipyridine or 1,10-phenanthroline)[32] also contain strongly coordinating ligands to keep them mononuclear. The only somewhat comparable halide-bridged complex, [{Pd[*C*,*N*-C(NXy)C_6H_4-NH_2](CNXy)}$_2$-

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[30] (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) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (d) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059.

[31] Schultz, C. S.; Ledford, J.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6351.

[32] Brookhart, M.; Rix, F. C.; DeSimone, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

(μ-I)]OTf, is an isocyanide complex based on a triflate anion,[10i] demonstrating that dinuclear complexes can be obtained also in the presence of a small anion when a strongly coordination Lewis base is absent. It thus appears that mononuclear and monocationic aqua complexes of the type $[L_3Pd^{II}(OH_2)]^+$ can be stable only when the water interacts efficiently with the anion. For complexes containing tetraarylborate anions, where these interactions are lacking, water becomes too weak a base and more strongly donating ligands are needed to stabilize these compounds in mononuclear form.

Experimental Section

General Procedures. All operations were carried out under a dry, oxygen-free, nitrogen atmosphere, using standard Schlenk techniques. Acetone was distilled from $CaCl_2$, CH_2Cl_2 was distilled from CaH_2, and hexane was distilled from sodium benzophenone ketyl. $Na[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$,[5a] $Na[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]$,[5a] and [PdCl(NCN)] (**1**)[6] were prepared according to reported procedures. $AgBF_4$ was dried in vacuo at 100 °C for 16 h before use. All other chemicals were used as received. NMR spectra were recorded on a Varian Inova 300 spectrometer and referenced externally against TMS. Acetone-d_6 and CD_2Cl_2 were dried over molecular sieves (3 Å). Infrared spectra were recorded on a Mattson Galaxy FT-IR 5000 spectrometer. Elemental analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr.

Silver Tetrakis[4-(trimethylsilyl)phenyl]borate (3a). A solution of 0.23 g (1.40 mmol) of $AgNO_3$ in 10 mL of demineralized water was solidified upon cooling to −78 °C. A solution of 1.00 g (1.40 mmol) of $Na[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$ in 25 mL of EtOH was layered on top, and the mixture was allowed to warm to room temperature. A precipitate formed, which was filtered off and washed with water and ethanol. Drying in vacuo yielded 0.70 g (70%) of a white solid. Anal. Calcd for $C_{36}H_{52}AgBSi_4$: C, 60.40; H, 7.32; Ag, 15.07. Found: C, 59.92; H, 7.40; Ag, 14.18. IR (KBr, cm^{-1}): 3045, 2953, 2895, 1575, 1359, 1248, 1143, 1087, 841, 804, 756.

Silver Tetrakis[4-{dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl}phenyl]borate (3b). A solution of 0.12 g (0.70 mmol) of $AgNO_3$ in 5 mL of demineralized water and 5 mL of EtOH was solidified at −78 °C. A solution of 1.55 g (0.80 mmol) of $Na[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]$ in 10 mL of EtOH was layered on top, and the mixture was allowed to warm to room temperature. The solid products isolated were separated by centrifugation and washed with water and EtOH. Drying in vacuo yielded 1.50 g (95%) of a white solid. Anal. Calcd for $C_{64}H_{56}AgBF_{52}Si_4$: C, 37.61; H, 2.76; Ag, 5.28. Found: C, 37.64; H, 2.94; Ag, 5.20. IR (KBr, cm^{-1}): 3049, 2960, 1575, 1456, 1361, 1244, 1211, 1143, 1068, 1018, 896, 841, 810, 734, 707.

μ-Chlorobis[2,6-bis{(dimethylamino)methyl}phenylpalladium(II)] Tetrakis[4-(trimethylsilyl)phenyl]borate (4a). To a solution of 0.13 g (0.40 mmol) of **1** in acetone (20 mL) were added 0.30 g (0.40 mmol) of $Na[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$ and H_2O (0.25 mL, 13.8 mmol). The resulting suspension was stirred for 16 h, filtered over Celite, and evaporated to dryness. The solid product was dissolved in acetone (1 mL), and pentane was added (20 mL). Centrifugation was used to remove small amounts of insolubles, and the resulting solution was dried in vacuo, yielding 0.51 g (95%) of a light yellow solid. Slow diffusion of pentane into a concentrated solution of **4a** in MeOH yielded crystals suitable for X-ray analysis. ^1H NMR (acetone-d_6, 300.1 MHz): δ 0.17 (s, 36H), 2.94 (s, 24H), 4.08 (s, 8H), 6.80 (dd, 4H), 6.97 (dd, 2H), 7.15 (d, 8H), 7.43 (m, 8H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.5 MHz): δ −1.1 (s), 52.8 (s), 74.4 (s), 119.9 (s), 124.8 (s), 130.7 (s), 136.0 (s), 145.7 (s), 165.4 (q, $^1J_{BC} = 49.3$ Hz). Anal. Calcd for $C_{60}H_{90}BClN_4Pd_2Si_4$: C, 58.17; H, 7.32; N, 4.52. Found: C, 56.50; H, 7.21; N, 3.89.

μ-Chlorobis[2,6-bis{(dimethylamino)methyl}phenylpalladium(II)] Tetrakis[4-(trimethylsilyl)phenyl]borate (4a) Using $Ag[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$ (3a). Using a procedure similar to the preparation of **4a** from **1** and $Na[B\{C_6H_4(SiMe_3)\text{-}4\}_4]$, 0.25 g (0.76 mmol) of **1** and 0.54 g (0.76 mmol) of **3a** yielded 0.60 g (64%) of a light yellow solid. ^1H NMR (acetone-d_6, 300.1 MHz): δ 0.17 (s, 36H), 2.94 (s, 24H), 4.08 (s, 8H), 6.80 (dd, 4H), 6.97 (dd, 2H), 7.15 (d, 8H), 7.43 (m, 8H).

μ-Chlorobis[2,6-bis{(dimethylamino)methyl}phenylpalladium(II)] Tetrakis[4-{dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl}phenyl]borate (4b). Using a procedure similar to the preparation of **4a**, 0.30 g (1.00 mmol) of $[PdCl\{C_6H_3(CH_3NMe_2)_2\text{-}2,6\}]$ and 2.25 g (1.00 mmol) of $Na[B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}4\}_4]$ yielded 0.90 g (80%) of a light yellow solid. ^1H NMR (acetone-d_6, 300.1 MHz): δ 0.27 (s, 24H), 0.93 (m, 8H), 2.15 (m, 8H), 2.93 (s, 24H), 4.13 (s, 8H), 6.83 (dd, 4H), 7.00 (dd, 2H), 7.10 (d, 8H), 7.40 (m, 8H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.5 MHz): δ −3.7 (s), 5.5 (s), 26.2 (t), 52.7 (s), 74.0 (s), 108.2 (m), 111.2 (m), 115.6 (m), 115.9 (m), 119.3 (m), 120.4 (s), 122.8 (m), 125.4 (s), 128.0 (s), 130.9 (m), 136.3 (s), 145.5 (s), 154.0 (s), 165.8 (q, $^1J_{BC} = 49.3$ Hz). Anal. Calcd for $C_{88}H_{94}BClF_{52}N_4Pd_2Si_4$: C, 41.17; H, 3.69; Cl, 1.38; N, 2.18. Found: C, 41.35; H, 3.62; Cl, 1.35; N, 2.11.

μ-Chlorobis[2,6-bis{(dimethylamino)methyl}phenylpalladium(II)] Tetrakis[4-{dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl}phenyl]borate (4b) Using $Ag[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]$ (3b). Using a procedure similar to the preparation of **4b** from **1** and $Na[B(C_6H_4\{SiMe_2(CH_2CH_2C_6F_{13})\}\text{-}4)_4]$, 0.13 g (0.40 mmol) of **1** and 0.82 g (0.40 mmol) of **3b** yielded 0.46 g (93%) of a light yellow solid. ^1H NMR (acetone-d_6, 300.1 MHz): δ 0.27 (s, 24H), 0.93 (m, 8H), 2.15 (m, 8H), 2.93 (s, 24H), 4.13 (s, 8H), 6.83 (dd, 4H), 7.00 (dd, 2H), 7.10 (d, 8H), 7.40 (m, 8H).

μ-Chlorobis[2,6-bis{(dimethylamino)methyl}phenylpalladium(II)]BF_4 (4c).[7] To 0.14 g (0.70 mmol) of $AgBF_4$ was added 0.22 g (0.66 mmol) of **1** in acetone (10 mL). After stirring the resulting mixture for 1 h, it was filtered over dried Celite and all volatiles were removed in vacuo. The resulting waxy solid was taken up in CH_2Cl_2 (20 mL), all solids were separated by centrifugation, and the solution was concentrated to 5 mL. Addition of hexane resulted in the precipitation of 0.05 g (10%) of a white solid. ^1H NMR (acetone-d_6, 300.1 MHz): δ 2.83 (s, 24H), 4.13 (s, 8H), 6.84 (dd, 4H), 7.03 (dd, 2H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.5 MHz): δ 51.9 (s), 73.3 (s), 120.1 (s), 124.4 (s), 146.2 (s), 150.9 (s). Anal. Calcd for $C_{24}H_{38}BClF_4N_4Pd_2$: C, 40.17; H, 5.54. Found: C, 39.94; H, 5.54.

[2,6-Bis{(dimethylamino)methyl}phenylpalladium(II)-aqua]BF_4 (5c).[6] Using a procedure similar to the preparation of **4a**, 0.20 g (0.66 mmol) of **1** and 0.14 g (0.71 mmol) of $AgBF_4$ yielded 0.27 g (97%) of a white solid. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **5c** in the presence of water. ^1H NMR (acetone-d_6, 300.1 MHz): δ 2.86 (s, 12H), 3.30 (s, H_2O), 4.18 (s, 4H), 6.85 (dd, 2H), 7.04 (dd, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.5 MHz): δ 51.8 (s), 73.4 (s), 120.5 (s), 125.9 (s), 145.6 (s), 150.9 (s).

Reaction of μ-Chlorobis[{2,6-bis[(dimethylamino)methyl]phenyl-*N,C,N′*}palladium(II)] Tetrakis[4-{dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]borate (4b) with $AgBF_4$. To a solution of 0.05 g (0.02 mmol) of **4b** in acetone (5 mL) was added 3.8 mg (0.02 mmol) of $AgBF_4$. The formed suspension was filtered over Celite and evaporated to dryness. A light yellow solid was obtained that was analyzed by ^1H and ^{11}B NMR to be a 2:1 molar mixture of **5c** and **4b**. The material was redissolved, and an additional equivalent of $AgBF_4$ was added following the above procedure to afford **5c**. ^1H NMR (acetone-d_6, 300.1 MHz): δ 7.04 (dd, 1H), 6.85 (dd, 2H), 4.18 (s, 4H), 2.86 (s, 12H). ^{11}B NMR (acetone-d_6, 96.3 MHz): δ 4.37 (s, BF_4).

Crystal Structure Determination of 4a. $[C_{24}H_{38}ClN_4Pd_2]^+\cdot[C_{36}H_{52}BSi_4]^-$, $M_r = 1238.82$. A colorless, plate-shaped crystal ($0.05 \times 0.15 \times 0.35$ mm^3) was fixed to a glass capillary and transferred into the cold nitrogen stream on a Nonius KappaCCD area detector diffractometer with rotating anode. The measured crystal was monoclinic, space group $P2_1/c$ (no. 14) with $a = 16.8686(15)$, $b = 20.674(3)$, $c = 25.349(5)$ Å, $\beta = 129.298(12)°$, $V = 6841.3(17)$ Å^3, $Z = 4$, $D_x = 1.203$ g cm^{-3}, $F(000) = 2592$, μ(Mo Kα) = 0.671 mm^{-1}. A total of 116 887 reflections were measured, 15 709 of which were independent, ($R_\sigma = 0.0468$, $R_{int} = 0.0874$, $1.0° < \theta < 27.5°$, $T = 150$ K, Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å, ϕ scan and ω scans with κ offset, distance crystal to detector 50 mm, data reduction by DENZO,[33] refined mosaicity 0.381(1)°, no absorption correction). The structure was solved by direct methods (SHELXS-86)[34] and refined on F^2 using SHELXL-97-2.[35] The disorder in one of the NCN ligands was described with a two-site disorder model. The occupancy factor of the major component refined to 0.710(7). A total of 327 distance restraints were introduced to ensure equal geometries in chemically equivalent bonds and 1,3-distances in the NCN ligands. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All ordered non-hydrogen atoms were refined with anisotropic displacement parameters. The non-hydrogen atoms in the major disorder component were refined with isotropic displacement parameters; the displacement parameters of the minor component atoms were equated to the parameters of the corresponding major component atoms. Hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms. Refinement of 618 parameters converged at $wR2 = 0.1548$, $w = 1/[\sigma^2(F^2) + (0.0568P)^2 + 21.76P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$, R1 = 0.0643 (for 12 285 $I > 2\sigma(I)$), $S = 1.045$, and $-0.97 < \Delta\rho < 1.76$ e Å^{-3} (near a disordered SiMe$_3$ group).

Crystal Structure Determination of 5c. $[C_{12}H_{21}N_2OPd]^+\cdot[BF_4]^-$, $M_r = 402.52$. Intensity data were collected for a colorless, needle-shaped crystal ($0.30 \times 0.12 \times 0.12$ mm^3) using the same procedure as for the structure determination of **4a**. Of the 19 397 reflections measured, 3820 were unique, 3179 with $I > 2\sigma(I)$ ($R_{int} = 0.0460$). An absorption correction was considered unnecessary ($\mu = 1.150$ mm^{-1}). The structure was solved by automated Patterson methods using DIRDIF99.[36] Refinement of 202 parameters was performed as for **4a**, except that the hydrogen atoms of the coordinated water molecule were refined with isotropic displacement parameters. Structure validation and molecular graphics preparation were performed with the PLATON package.[37] The measured crystal was monoclinic, space group $P2_1/c$ (no. 14) with $a = 9.0800(2)$, $b = 18.5226(4)$, $c = 12.1707(2)$ Å, $\beta = 125.423(1)°$, $V = 1668.03(6)$ Å^3, $Z = 4$, $D_x = 1.603$ g cm^{-3}, $R(F)$ [$I > 2\sigma(I)$] = 0.0273, $wR(F^2) = 0.0634$, $S = 1.084$, and $-0.86 < \Delta\rho < 0.70$ e Å^{-3}.

Theoretical Studies. The relative energies of complexes and their separate components were evaluated using density functional calculations (DFT). Initial molecular conformations were calculated using the semiempirical (PM3(tm)) method as implemented in the Spartan 5.1.1 (SGI) molecular modeling software package. The geometry of the thus obtained structures was further optimized using Becke's three-parameter hybrid functional and the Lee, Yang, and Parr correlation functional (B3LYP)[38] as implemented in both the Gamess-UK SGI (version 6.3)[23] and the Gaussian 98[22] programs. All atoms are described with the double-ζ basis set LANL2DZ,[24] with effective core potentials being used for the atoms Si, Cl, and Pd. Due to the size of the calculations on the structures containing the $[B\{C_6H_4(SiMe_3)\text{-}4\}_4]^-$ anion, frequency analyses could not be completed within an acceptable time span. Therefore only the electronic energies were taken into account in this study. Absolute energies and atomic coordinates for the calculated molecules can be supplied on request from the author.

Table 4. Comparative Data for the Geometry of 4a, 4c, and 5c Obtained from Crystallographic Studies and DFT Studies

bond distances[a]			bond angles[a]		
	X−ray	DFT		X−ray	DFT
			4a		
Pd(1)−C(9)	1.906	1.947	Pd(1)−Cl(1)−Pd(2)	121.11	137.48
Pd(1)−N(1)	2.102	2.149	N(1)−Pd(1)−N(2)	162.97	162.82
Pd(1)−N(2)	2.091	2.174	C(9)−Pd(1)−Cl(1)	176.87	176.12
Pd(1)−Cl(1)	2.453	2.630			
B(1)−C(25)	1.653	1.657	C(25)−B(1)−C(34)	110.1	109.1
B(1)−C(34)	1.644	1.654	C(25)−B(1)−C(43)	110.4	110.7
			4c		
Pd(1)−C(9)	1.929	1.946	Pd(1)−Cl(1)−Pd(2)	134.8	139.9
Pd(1)−N(1)	2.105	2.174	N(1)−Pd(1)−N(2)	162.6	161.4
Pd(1)−N(2)	2.100	2.168	C(9)−Pd(1)−Cl(1)	174.5	173.3
Pd(1)−Cl(1)	2.463	2.656			
B(1)−F(1)	1.318	1.467	F(1)−B(1)−F(2)	114.6	110.5
B(1)−F(2)	1.356	1.452	F(1)−B(1)−F(3)	107.2	106.9
			5c		
Pd(1)−C(1)	1.909	1.940	N(1)−Pd(1)−N(2)	162.7	162.0
Pd(1)−N(1)	2.107	2.155	C(1)−Pd(1)−O(1)	176.8	175.0
Pd(1)−N(2)	2.108	2.170			
Pd(1)−O(1)	2.192	2.220	F(1)−B(1)−F(2)	110.7	112.7
B(1)−F(3)	1.401	1.495	F(2)−B(1)−F(4)	107.2	105.7
B(1)−F(4)	1.386	1.441			
F(3)−H(1a)	1.92	1.602	O(1)−H(1a)−F(3)	176	170.7

[a] Numbering according to the scheme applied in the crystallographic studies.

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Supporting Information Available: Crystal data and structure refinement details for **4a** and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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