Host–Guest Chemistry

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Diphosphinite Ag^I and Pd^{II} Dinuclear Complexes as Adaptable Anion Receptors: An Unprecedented Bridging Mode for the PF_6^- Ion **

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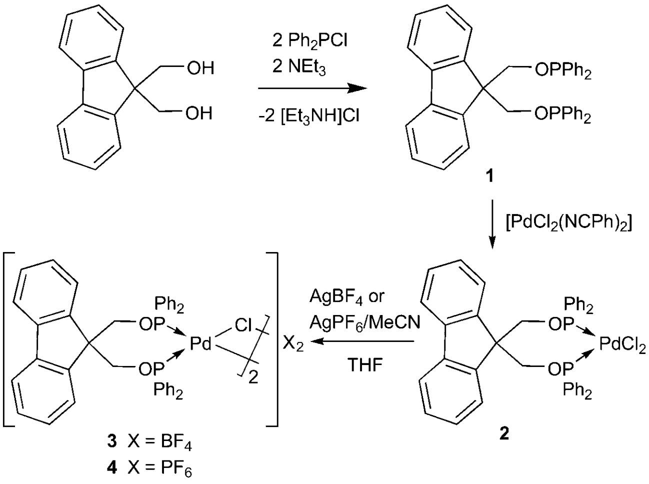
The coordination chemistry of anions has attracted much attention, as the supramolecular host–guest chemistry involving their binding is relevant to ion-pairing effects,[1] which play an important role in the reactivity and catalytic properties of metal complexes.[2] Herein we describe host–guest interactions between transition-metal complexes bearing the new diphosphinite ligand **1** (Scheme 1) and weakly coordinating anions such as PF_6^- and BF_4^-, which exert a remarkable structural effect on the conformation of the cationic complex owing to specific metal–anion interactions.



Scheme 1.

Ligand **1** was reacted with $[PdCl_2(NCPh)_2]$ to give the mononuclear, chelated complex $[PdCl_2(\mathbf{1})]$ (**2**). Chloride abstraction by $AgBF_4$ or $AgPF_6$ afforded the dinuclear, chloro-bridged complexes $[Pd(\mu\text{-}Cl)(\mathbf{1})]_2[BF_4]_2$ (**3**) and $[Pd(\mu\text{-}Cl)(\mathbf{1})]_2[PF_6]_2$ (**4**), respectively, in which **1** remains chelated to the metal centers (Scheme 1, for experimental details see the Supporting Information). Their molecular structure was determined by single-crystal X-ray diffraction (Figure 1 and Figure 2).[4]

The anions of complexes **3** and **4** occupy cavities above and below the metal coordination planes. The nature of these pockets depends on the size of the accommodated anion. In **3**, one BF_4^- ion occupies a cavity below the Pd_2Cl_2 core which is delimited by four phenyl groups (Scheme 2). The second BF_4^-

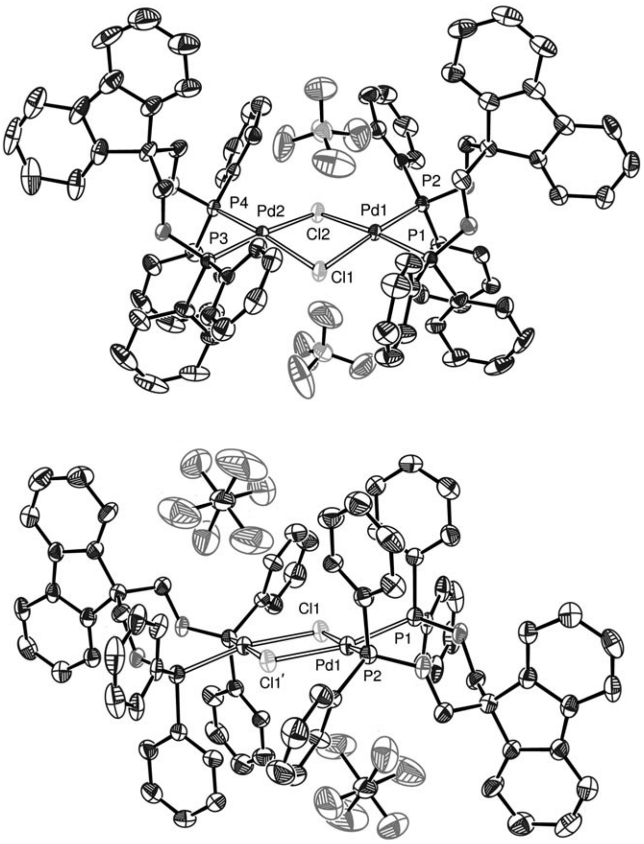


Figure 1. ORTEP plots of complex **3** in $\mathbf{3}\cdot 3\,CH_2Cl_2$ (top) and **4** in centrosymmetric $\mathbf{4}\cdot 2\,CH_2Cl_2\cdot C_5H_{12}$ (bottom). Selected distances [Å] and angles [°] for **3**: Pd1–P1 2.2480(1), Pd1–P2 2.2422(9), Pd2–P3 2.2660(9), Pd2–P4 2.234(1), Pd1–Cl1 2.3922(9), Pd1–Cl2 2.3893(9), Pd2–Cl1 2.3944(9), Pd2–Cl2 2.3866(8); P2-Pd1-P1 90.71(3), P4-Pd2-P3 91.19(3); For **4**: Pd1–P1 2.236(2), Pd1–P2 2.244(2), Pd1–Cl1 2.400(2), Pd1–Cl1′ 2.4140(16); P1-Pd1-P2 91.53(7).

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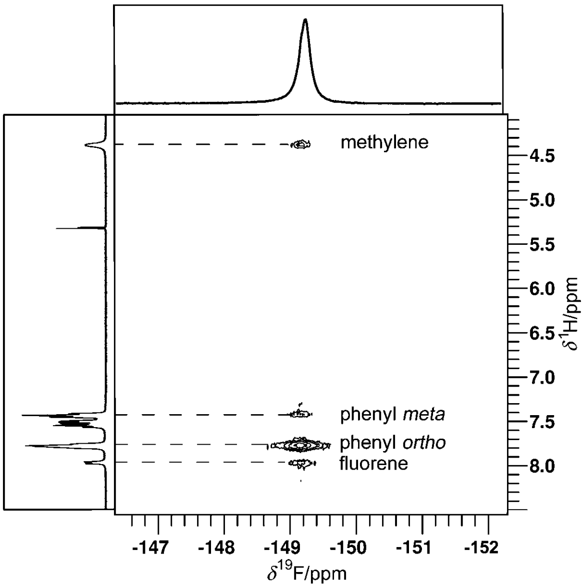
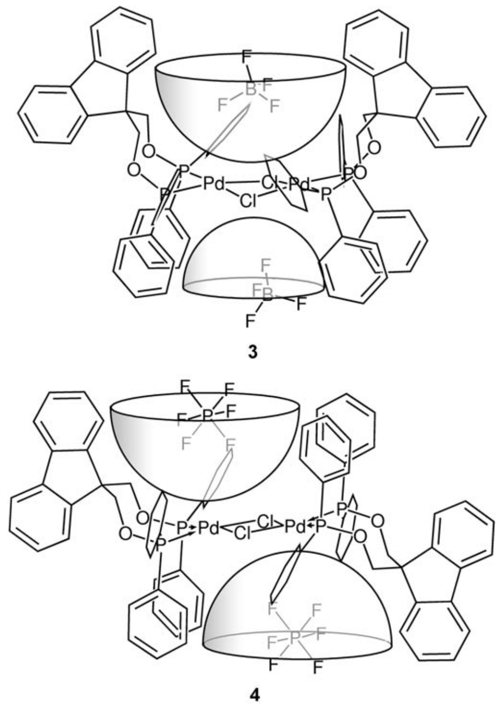


Figure 2. ^{19}F,^{1}H HOESY NMR spectrum of complex **3** in CD_2Cl_2. $T = 298$ K, d1 = 3 s, mixing time = 250 ms, 2 K × 256 real data points.



Scheme 2.

ion lies in the upper pocket generated by four phenyl and the two fluorene groups, the latter being almost orthogonal with respect to the P1-Pd-P2 plane. In contrast, the larger PF_6^- ions in **4** occupy two centrosymmetric pockets that are formed by one fluorene and four phenyl moieties. The anion thus exerts a remarkable effect on the conformation of the dipalladium complex (Scheme 2).

In each case, the structural data indicate that the cation–anion couple is stabilized by multiple H···F contacts (see the Supporting Information). These contacts are retained in solution, as demonstrated by ^{19}F,^{1}H HOESY (heteronuclear Overhauser enhancement spectroscopy) NMR spectroscopy (Figure 2, see details in the Supporting Information).[3]

The strongest signal in the HOESY spectrum of **3** consistently corresponds to the interactions between the fluorine atoms of the BF_4^- ion and the *ortho* protons of the phenyl groups. Other couplings with the fluorine atoms involve both the methylene groups, the *meta* protons of the phenyl groups, and the fluorene hydrogen atoms that point towards the anion (Scheme 2). The absence of couplings with, for example, the *para* protons of the phenyl groups indicates that the HOESY signals do not originate from the formation of extended aggregates in solution. Further evidence for the existence of discrete anion–cation couples is provided by the ^{19}F{^{1}H} NMR spectrum at 193 K, which shows two resonances for the BF_4^- ion, at $\delta = -143.7$ and -151.6 ppm (Figure 3). These resonances coalesce to form a singlet at room temperature ($\delta = -149.2$ ppm). The peak at -151.6 ppm corresponds to free BF_4^-, the signal at -143.7 ppm should correspond to the anion involved in the host–guest couple. Indeed, addition of $[NEt_4]BF_4$ to a solution of **3** resulted in a shift of the peak at -149.2 ppm towards the usual value for free tetrafluoroborate.

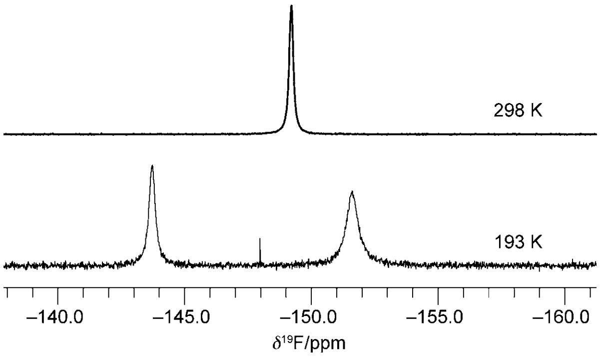


Figure 3. ^{19}F NMR spectrum of complex **3** in CD_2Cl_2 at 298 and 193 K.

The reaction of **1** with $AgPF_6$ afforded in good yields the complex $[Ag(\mathbf{1})(PF_6)]_2$ (**5**), which was characterized by X-ray crystallography (Figure 4). The metal centers of **5**·2 CH_2Cl_2 are bridged by two molecules of **1**, leading to a 16-membered dimetallocycle. Their coordination geometry can be described as distorted tetrahedral, and the metal centers are further bridged by a fluorine atom of each of the PF_6^- ions [Ag–F1 2.639(3), Ag–F2 2.638(1) Å]. To the best of our knowledge,[5] this type of M···F···M (M = transition metal) interaction involving the PF_6^- ion is unprecedented. Although complexes featuring terminally coordinated PF_6^- are not rare,[6] the few examples of intramolecular[7] or intermolecular[8] bridging PF_6^- ions reported are of the type M···F–P–F···M, and generally display rather long mean F···M distances (minimum = 2.804(4) Å).[8d] In one case, a very short Cu–F interaction (2.345(2) Å) was observed.[8c]

The metal–anion interactions are probably rather weak and no evidence for Ag···F contacts could be found in solution by multinuclear 1D NMR spectroscopy. A fast dynamic

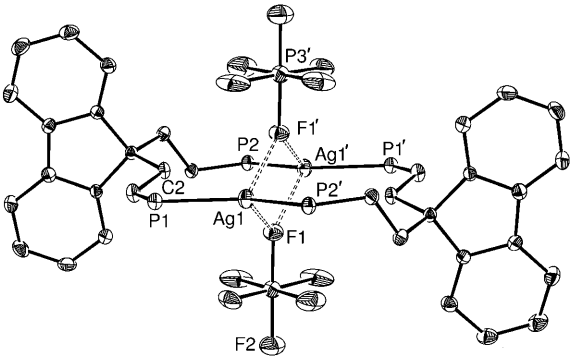


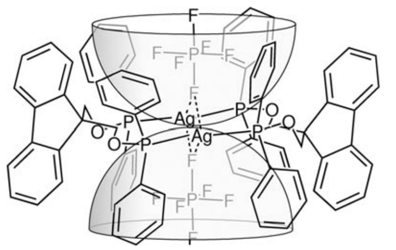
Figure 4. ORTEP plot of centrosymmetric complex **5** in $5{\cdot}2\,CH_2Cl_2$. Phenyl groups are omitted for clarity. Selected distances [Å] and angles [°]: Ag1–P1 2.419(1), Ag1–P2 2.413(1), Ag1–F1 2.639(3), Ag1–F2 2.638(1); P1-Ag1-P2′ 140.62(4), F1-Ag1-F1′ 62.18(9).

process is likely to take place in solution, resulting in the equivalence of the fluorine atoms on the NMR timescale.

A comparison between the unprecedented metal–anion interaction in **5** and the related situations in **3** and **4** very clearly illustrates the mutual influence of the metal cation and the anion on such host–guest features. The aryl groups synergistically cooperate in **5** to form hemispherical cavities situated on opposite sides of the Ag_2P_4 moiety (Scheme 3).

The steric complementarity and resulting affinity between the anion and the cationic complex is emphasized in the space-filling model shown in Figure 5.

We have shown herein that the synergy between axial planar groups and phenyl groups in the coordination complexes of functional ligands can induce the formation of cavities with dimensions of supramolecular relevance, which can 1) be modified by the size of the anion, resulting in major conformational changes (compounds **3** and **4**) and 2) give rise to unprecedented bonding modes for the guest, including commonly used anions (compound **5**). The fact that the PF_6^- ion was found to be less coordinatively "innocent" than previously assumed may have broader implications in the field of coordination chemistry.



Scheme 3.

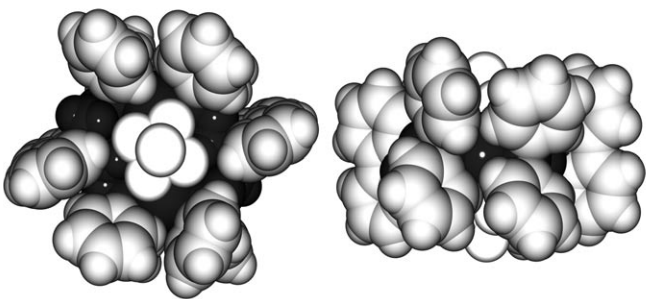


Figure 5. Orthogonal views of space-filling diagrams of the molecular structure of **5** in $5{\cdot}2\,CH_2Cl_2$. Color code: aryl groups: gray, PF_6: white.

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[4] X-ray diffraction data: $\mathbf{3}{\cdot}3\,CH_2Cl_2$: $C_{81}H_{70}B_2Cl_8F_8O_4P_4Pd_2$, $T = 173$ K, $M = 1901.27$, triclinic $P\bar{1}$, $a = 13.7361(4)$, $b = 16.0504(4)$, $c = 20.0595(4)$ Å, $\alpha = 103.023(1)$, $\beta = 106.833(1)$, $\gamma = 98.008(1)°$, $V = 4023.69(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.569\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 8.61\,mm^{-1}$, $F(000) = 1916$, $2\theta_{max} = 53°$, $R_1 = 0.0477$, $wR_2 = 0.1252$, $R(int) = 0.0544$ parameters = 1018, observed reflections = 12085 (16670 measured); $\mathbf{4}{\cdot}2\,CH_2Cl_2{\cdot}C_5H_{12}$: $C_{85}H_{78}Cl_8F_{12}O_4P_6Pd_2$, $T = 173$ K, $M = 2073.69$, triclinic $P\bar{1}$, $a = 11.3740(13)$, $b = 14.1500(17)$, $c = 15.905(2)$ Å, $\alpha = 114.812(5)$, $\beta = 99.373(7)$, $\gamma = 97.914(8)°$, $V = 2231.0(5)$ Å^3, $Z = 1$, $\rho_{calcd=}1.543\,g\,cm^{-3}$, μ-$(Mo_{K\alpha}) = 8.24\,mm^{-1}$, $F(000) = 1046$, $2\theta_{max} = 52°$, $R_1 = 0.0755$, $wR_2 = 0.1444$, $R(int) = 0.0879$ parameters = 525, observed reflections = 3839 (8475 measured); $\mathbf{5}{\cdot}2\,CH_2Cl_2$: $C_{80}H_{68}Ag_2Cl_4F_{12}O_4P_6$, $T = 173$ K, $M = 1864.70$, triclinic $P2_1/c$, $a = 14.1605(5)$, $b = 13.6956(5)$, $c = 23.8959(8)$ Å, $\beta = 123.245(2)$, $V = 3875.8(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.598\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 8.46\,mm^{-1}$, $F(000) = 1880$, $2\theta_{max} = 55°$, $R_1 = 0.0500$, $wR_2 = 0.1003$, $R(int) = 0.0674$ parameters = 523, observed reflections = 4663 (8856 measured). CCDC 685553 (**3**), 685554 (**4**), and 685555 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[5] CCDC database, November **2006** update.

[6] For a recent example see: N. Muresan, K. Chlopek, T. Weyhermueller, F. Neese, K. Wieghardt, *Inorg. Chem.* **2007**, *46*, 5327–5337.

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