Cationic Palladium Bis-carbene Carboxylate Complexes

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Cationic bis-carbene palladium acetate complexes are obtained by protonation of their neutral bis-acetate precursors and show fluxional behavior in solution, whereas the use of $NaBArF_{24}$ generates unique sodium complexes instead. The cationic palladium species can undergo dimerization, which was proven by single-crystal X-ray analysis.

Introduction

C−H bond activation and functionalization is currently one of the most active fields in organometallic chemistry.[1] Among the various transition metals that show activity in this reaction, the use of platinum compounds is well documented[2] and originates from the work of Shilov[3a] and Garnett.[3b] We reported recently on the catalytic deuteration of benzene by acetic acid-d_4 using the well-defined cationic platinum(II)−κ^2-acetate complex **1**, in which over 1500 turnovers are seen.[4] In subsequent work, the related neutral (*N*,*O*-picolinate)platinum trifluoroacetate complex was also shown to be competent in this reaction using CF_3CO_2D as solvent.[5] In the latter case, the C−H cleavage occurs through a six-membered transition state where the κ^1-acetate serves as the proton acceptor.[6] Alternatively, the use of $Pd(OAc)_2$ together with additional oxidants has recently attracted much interest for the conversion of inert C−H bonds into functional groups by means of coordination-directed metalation.[7] Structural knowledge on these palladium acetate catalysts is essential to clarify the mechanism and is crucial for further catalyst design. Protasiewicz et al. reported on the cationic palladium phosphine carboxylate complexes **2**, which show reversible cyclometalation (R = *i*Pr), and by adding CH_3CO_2D incorporation of deuterium into the ligand was found.[8] Similar complexes bearing bidentate phosphine ligands are suggested to be active polymerization catalysts, but these species, obtained from the neutral (P−P)$Pd(OAc)_2$ and acid, often generate complex catalyst mixtures due to autoionization processes.[8,9] Stable catalyst structures are therefore needed, and the use of *N*-heterocyclic carbenes for this purpose is already a proven concept.[10] Herrmann et al. demonstrated that the bis-carbene palladium complexes **3** (X = F, Cl, Br, $OCOCF_3$) can activate methane catalytically, using CF_3COOH and its anhydride, under strongly oxidizing conditions ($K_2S_2O_8$), where the trifluoroacetate derivative is the general precatalyst formed during the reaction.[11] Bis-carbene palladium acetates are also reported to be highly active in Heck-type coupling reactions.[12,13]

We herein present the first cationic bis-carbene palladium(II) acetate complexes and report on their structure and reactivity in solution and in the gas phase.

Results and Discussion

Reaction of the bis-carbene palladium(II) acetate complexes **4a**,**b**[14] with *p*-toluenesulfonic acid (HOTs·H_2O) in dichlo-

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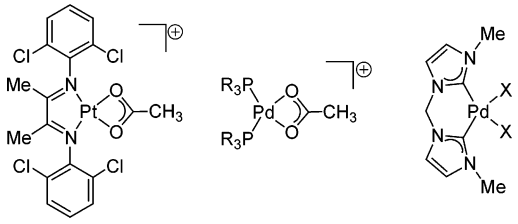

1 **2** **3**

romethane (RT, 17−24 h) results in elimination of (trifluoro)-acetic acid and the formation of the cationic mono-acetate complexes **5a**,**b**[OTs], which are isolated as colorless, crystalline products in high yield (**5a**[OTs] 89%, **5b**[OTs] 85%; Scheme 1). To increase solubility, the tosylate anion was exchanged for the weakly coordinating tetrakis[(3,5-trifluoromethyl)phenyl]-borate ($BArF_{24}^-$),[15] by reacting **5a**,**b**[OTs] with $NaBArF_{24}$[16] in dichloromethane (RT, 0.5 h). This yields, after removal of NaOTs and evaporation of the solvent, the desired **5a**,**b**[$BArF_{24}$] as colorless solids (**5a**[$BArF_{24}$] 83%, **5b**[$BArF_{24}$] 77%).[17,18] Indicative for the formation of the cationic complexes is the downfield shift in the ^{1}H NMR of the acetate-CH_3 group in **5a**[OTs] and **5a**[$BArF_{24}$] (both δ ^{1}H (CD_2Cl_2) = 2.05 ppm) compared to the neutral precursor **4a**[14a] (δ ^{1}H (CD_2Cl_2) = 1.88 ppm).[8,19] This effect is also observed for the acetate-O_2C resonances in the ^{13}C NMR (**5a**[$BArF_{24}$] δ ^{13}C = 184.0 ppm;[20] **4a** δ ^{13}C (DMSO-d_6) = 175.0 ppm[14a]). The presence of the fluoro substituents in **5b** causes the acetate-O_2C resonances to shift upfield compared to **5a** (**5b**[$BArF_{24}$] δ ^{13}C = 167.4 ppm, ^2J(C,F) = 41.5 Hz), and this also accounts for the corresponding carbene resonances[12,14c] (**5a**[$BArF_{24}$] δ ^{13}C = 149.8 ppm; **5b**[$BArF_{24}$] δ ^{13}C = 145.0 ppm).

Single crystals suitable for X-ray analysis were obtained of **5a**[OTs], which reveals that **5a**[OTs] exhibits a dimeric structure in the solid state (Figure 1). The molecular structure of (**5a**[OTs])$_2$ shows an open-book type structure with a close Pd−Pd contact (Pd1−Pd18 3.1683(6) Å), where the two bowl-shaped bis-carbene palladium(II) fragments are bridged by the two acetates. Related, neutral carboxyl-bridged structures are known,[21] but to our knowledge this is the first structurally characterized bis-cationic palladium carboxylate complex.

For comparison we calculated the structures of the monocationic κ^2-acetates **5** (labeled **A** and **B**, Figure 2) and their corresponding dimers (**5**)$_2$ at the B3PW91/6-31+G** (LANL2DZ for Pd) level of theory.[22,23] The X-ray structure of (**5a**[OTs])$_2$ closely resembles the calculated (**5A**)$_2$ (C_s symmetry), except it bears a shorter Pd−Pd contact ((**5a**[OTs])$_2$ 3.1683(6) Å vs (**5A**)$_2$ 3.541 Å), which we attribute to crystal-packing effects, and contains slightly shorter Pd−C bond lengths ((**5a**[OTs])$_2$ av 1.960 Å; (**5A**)$_2$ 1.988 Å). The cationic monomers **5A** and **B** show longer Pd−O bond lengths (e.g., **5A** 2.123 Å) compared to (**5a**[OTs])$_2$ (Pd1−O15 2.071(4) Å, Pd1−O21 2.076(4) Å) and the calculated dimers (e.g., (**5A**)$_2$ 2.091 Å), which indicates that the κ^2-acetates are more weakly bound to palladium than the μ-acetates.

Variable-temperature (VT) ^{1}H NMR experiments (CD_2Cl_2) show that the NCH_3 (δ ^{1}H (23 °C) = 3.56 ppm), the CH_2 (δ ^{1}H (23 °C) = 5.88 ppm), and the olefinic resonances (δ ^{1}H (23 °C) = 6.91 and 7.16 ppm, ^3J(H,H) = 2.18 Hz) of **5a**[$BArF_{24}$] split up at −70 °C, displaying two different NCH_3 signals (δ ^{1}H = 2.96 and 3.95 ppm), two AB patterns (δ ^{1}H = 5.57, 5.61, 5.78, 5.82 and 5.80, 5.84, 6.25, 6.30 ppm; CH_2), and four olefinic signals (δ ^{1}H = 6.82, 6.98, 7.18, and 7.22 ppm), but only one acetate signal (δ ^{1}H = 2.02 ppm). The predominant species in solution is therefore not monomer **5a**[$BArF_{24}$], but its dimer (**5a**[$BArF_{24}$])$_2$. In addition, trifluoroacetate analogue **5b**[$BArF_{24}$] shows a more complex behavior and gives, already at ambient temperature, two broad NCH_3 resonances at δ ^{1}H 3.74 and 3.87 ppm (ratio 3:1), which become one at 50 °C (δ ^{1}H = 3.77 ppm). At −40 °C, the spectrum shows a range of NCH_3 resonances (δ ^{1}H = 3.50, 3.75, 3.80, 3.81, 3.86, and 3.88 ppm) and in the ^{19}F NMR various O_2CCF_3 resonances (δ ^{19}F = −73.45, −73.48, −73.77, −74.12, −74.24, and −75.37 ppm) are observed, which we attribute to a rapid interchange of the monomeric κ^2-acetate,[24] the κ^1-acetate complex stabilized by ion paring or van der Waals contacts with the anion, and the bis-cationic dimer (Scheme 2).

We tested the novel acetate complexes **5a**,**b**[$BArF_{24}$] for C−H activation of benzene by either CD_3COOD or CF_3COOD at 85 °C for 24−48 h, in analogy with our experimental setup for diimine complex **1**.[4] Unfortunately, no catalytic activity was

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(17) This protocol is preferred over the direct use of $[H(Et_2O)_2]^+[BArF_{24}]^-$.[16b]

(18) The corresponding [(1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pt(OCOCH_3)][$BArF_{24}$] can be prepared in an analogous manner, whereas [(1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pt($OCOCF_3$)]-[$BArF_{24}$] cannot be synthesized starting from (1,1′-dimethyl-3,3′-methyl-enediimidazol-2,2′-diylidene)Pt($OCOCF_3$)$_2$: Slootweg, J. C.; Chen, P. Unpublished results.

(19) *trans*-[(R_3P)$_2$Pd(O_2CCH_3)$_2$]: δ ^{1}H (CD_2Cl_2) = 1.84 (R = Cy) and 1.77 (R = *i*Pr) ppm, [(R_3P)$_2$Pd(κ^2-*O*,*O*′-O_2CCH_3)][$B(C_6F_5)_4$]: δ ^{1}H ($CDCl_3$) = 2.04 (R = Cy) and 2.02 (R = *i*Pr) ppm; see ref 8.

(20) A ^{13}C{^{1}H} NMR of **5a**[OTs] was not obtained due to its poor solubility in CD_2Cl_2.

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(23) On the potential energy surface we found a sterically less encumbered isomer for dimeric **5A** ((**5A**)$_2$*_anti*), in which the two bis-carbene palladium fragments are oriented *anti* to each other, that is 1.6 kcal·mol^{-1} more stable in the gas phase, but not favored in the experiment. For dimeric **5B**, only (**5B**)$_2$*_anti* exists and (**5B**)$_2$ is not a minimum; see Supporting Information.

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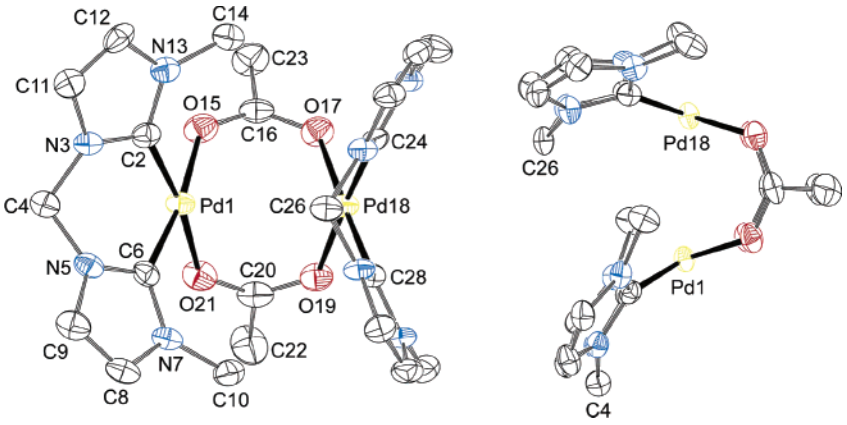
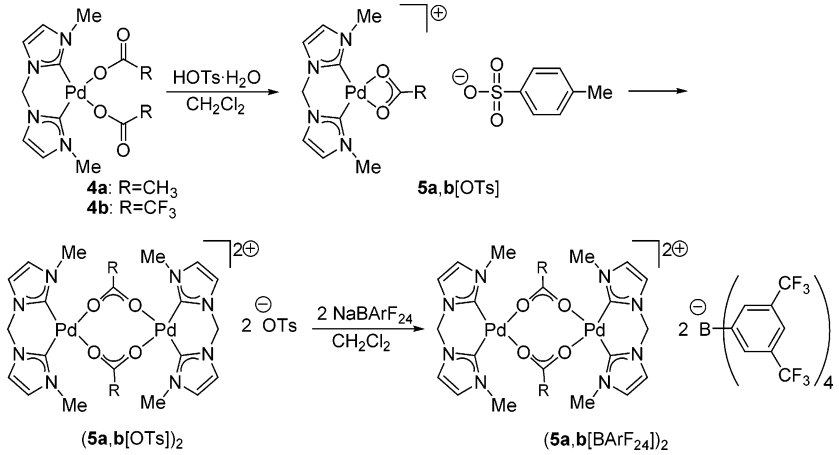


Figure 1. Displacement ellipsoid plot of (**5a**[OTs])$_2$ with ellipsoids drawn at the 50% probability level. Hydrogen atoms, the two tosylate anions, and the two water molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−Pd18 3.1683(6), Pd1−O15 2.071(4), Pd1−O21 2.076(4), Pd1−C2 1.975(5), Pd1−C6 1.960(5), Pd18−O17 2.064(4), Pd1−O19 2.054(4), Pd1−C24 1.953(5), Pd1−C24 1.952(5), O15−C16 1.260(7), O17−C16 1.272(7), C2−N3 1.355(7), C2−N13 1.329(7), C4−N3 1.441(7), C4−N5 1.458(6), C6−N5 1.370(7), C6−N7 1.334(6); O15−Pd1−O21 86.67(15), O15−Pd1−C6 171.1(2), O21−Pd1−C2 170.4(2), C2−Pd1−C6 85.8(2), N3−C2−N13 104.2(4), N3−C4−N5 109.2(5), N5−C6−N7 105.4(4).

Scheme 1. Synthesis of the Cationic Palladium Acetate Complexes 5



observed, not even at 120 °C, which was ascribed to the unfavorable dimerization process that renders the concentration of the bis-carbene palladium(II)−κ^2-acetates to be low.[25]

Analysis of the acetate complexes **5** by ESI-MS shows that the dimeric structure is not retained in the spray process and only the monocationic species **5a**,**b** were detected. Interestingly,

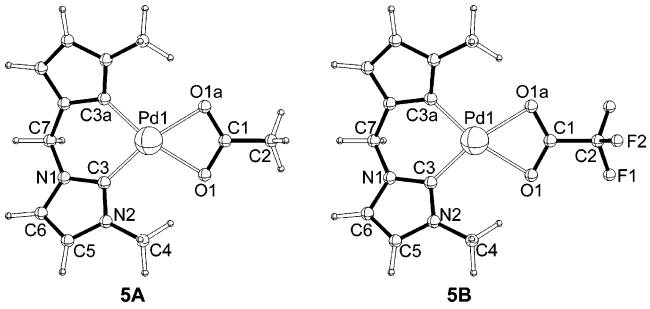
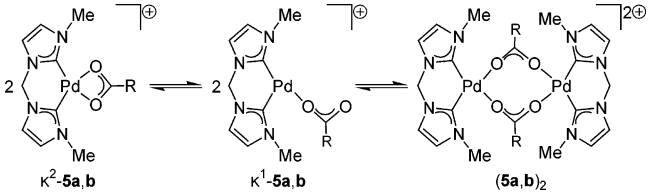


Figure 2. Calculated structures of (1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(κ^2*O*,*O*′-OCOCH$_3$)$^+$ (**5A**) and (1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(κ^2*O*,*O*′-OCOCF$_3$)$^+$ (**5B**) (both C_s symmetry) at B3PW91/6-31+G** (LANL2DZ for Pd). Selected bond lengths [Å] and angles [deg] for **5A** [**5B**]: Pd1−O1 2.123 [2.158], Pd1−C3 1.978 [1.971], O1−C1 1.279 [1.264], C1−C2 1.491 [1.543], C3−N1 1.355 [1.355], C3−N2 1.348 [1.347], C4−N2 1.462 [1.464], C7−N1 1.451 [1.450]; O1−Pd1−O1a 62.04 [61.43], O1−Pd1−C3a 167.98 [167.80], C3−Pd1−C3a 86.06 [85.82], N1−C3−N2 105.42 [105.61].

Scheme 2. Dynamic Behavior of Cationic Palladium Acetate Complexes 5



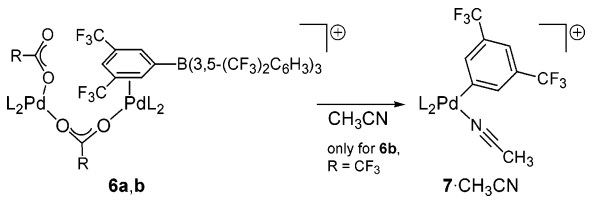
in CH_2Cl_2 **5a**,**b**[$BArF_{24}$] shows, besides **5a**,**b** (100%), also a new complex with the composition [2M − $BArF_{24}$]$^+$ (3−10%) that we attribute to $L_2Pd(\kappa^1$-acetate$)(\mu$-acetate$)PdL_2$[B(3,5-$(CF_3)_2C_6H_3)_4$] (**6a**,**b**) (L_2 = bis-carbene), where the anion is connected to Pd presumably via a π-bond or electrostatic interactions with a CF_3 group. The spectrum changes in CH_3CN, but only for **5b**[$BArF_{24}$], which bears the labile trifluoroacetate ligand,[24] and additionally the cationic bis-carbene palladium−$C_6H_3(CF_3)_2$-3,5 (**7**) with CH_3CN (55%) and without (100%) is observed, due to transmetalation of the aryl group from boron to palladium (Scheme 3).[26]

It is reported that π-arene species are intermediates in transmetalation,[27] and also the need for a nucleophile for the

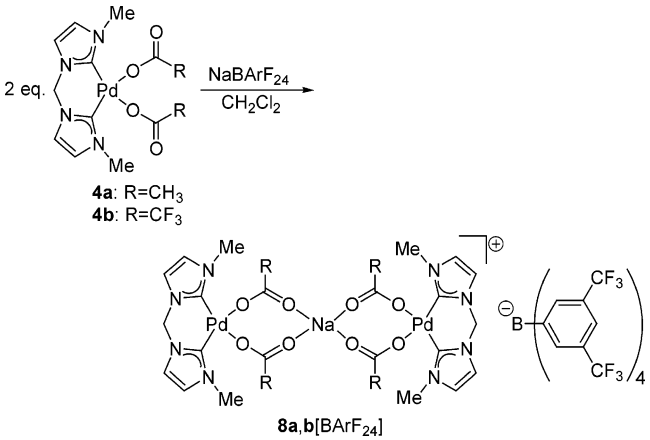
(25) The corresponding Pt−acetate complex[18] does not activate benzene either under these reaction conditions.

(26) Transmetalation from B to Pt in solution: Konze, W. V.; Scott, B. L.; Kubas, G. J. *Chem. Commun.* **1999**, 1807−1808.

Scheme 3. Transmetalation from B to Pd



Scheme 4. Synthesis of Cationic Sodium Complexes 8



transmetalation to proceed is established.[28] This is indeed what we observe for **5b**[$BArF_{24}$] in the gas phase when using the coordinating solvent acetonitrile, where the acetate in **6b** can act as an internal nucleophile. One should note that this phenomenon is not observed in solution, as **6** is only formed in the gas phase, and **5b**[$BArF_{24}$] is stable at 80 °C for at least 24 h. Nonetheless, it demonstrates that more insight into the poorly understood process of transmetalation, which is *the* key process in all Suzuki-type coupling reactions, can be obtained.

Besides the synthesis of **5a**,**b**[$BArF_{24}$] using HOTs·H_2O *and* $NaBArF_{24}$, also the direct reaction with $NaBArF_{24}$, by elimination of sodium (trifluoro)acetate, was investigated.[8,29] Surprisingly, the reaction of the neutral bis-acetates **4a**,**b**[14] with $NaBArF_{24}$[16] in a 1:1 ratio (CD_2Cl_2, 50 °C, 1 h) yielded not only **5a**,**b**[$BArF_{24}$], but also a new species (**8**), which according to ESI-MS consists of a cationic fragment bearing two molecules of **4** and one Na atom (**8a** $[M]^+ = 825$, **8b** $[M]^+ = 1041$). Reaction of **4a**,**b** with $NaBArF_{24}$ in a 2:1 ratio (CH_2Cl_2, 50 °C, 2 h) leads selectively to the self-assembly of the unique cationic sodium complexes **8a**,**b**[$BArF_{24}$], which are isolated as crystalline products (**8a**[$BArF_{24}$]: yellow, 85%; **8b**[$BArF_{24}$]: colorless, 82%; Scheme 4). To our knowledge this is the first example of a bis-acetate complex that coordinates to a sodium cation. Alternatively, **8a**,**b**[$BArF_{24}$] can be constructed by mixing **4a**,**b**, sodium (trifluoro)acetate and **5a**,**b**[$BArF_{24}$] in a 1:1:1 ratio (CH_2Cl_2, 60 °C, 0.5 h), which illustrates that sodium complex **8a**,**b**[$BArF_{24}$] is the thermodynamically favored product.

VT ^1H NMR experiments (CD_2Cl_2) show that the isolated **8a**[$BArF_{24}$] is in equilibrium with its factors at ambient temperature (**4a**+**5a**[$BArF_{24}$]:**8a**[$BArF_{24}$] = ∼1:3; 23 °C), whereas at −50 °C almost no **4a** or **5a**[$BArF_{24}$] could be detected. In contrast, the structure of trifluoroacetate analogue **8b**[$BArF_{24}$] is retained in solution over a wide temperature range (−50 to 50 °C). The presence of the sodium atom in **8a**,**b**-[$BArF_{24}$] has a noticeable effect on the NMR features compared to **5a**,**b**[$BArF_{24}$]. The acetate-C*H*$_3$ group of **8a**[$BArF_{24}$] is shifted upfield (δ ^1H = 1.88 ppm) compared to **5a**[$BArF_{24}$] as well as the acetate-O_2C resonances of both species in the ^{13}C NMR (**8a**[$BArF_{24}$] δ ^{13}C = 177.8 ppm; **8b**[$BArF_{24}$] δ ^{13}C = 162.9 ppm, $^2J(C,F)$ = 37.2 Hz), whereas the carbene resonances are shifted downfield (**8a**[$BArF_{24}$] δ ^{13}C = 156.3 ppm; **8b**[$BArF_{24}$] δ ^{13}C = 150.3 ppm). The molecular structure of **8b**[$BArF_{24}$] was determined unequivocally by single-crystal X-ray analysis and shows that in the solid state (C_2-symmetry) the $BArF_{24}$ anion coordinates to sodium via two of its CF_3 groups (Figure 3). The geometry around Na is a distorted trigonal prism with typical Na−O bond lengths (Na5−O4 2.323(4) Å, Na5−O6 2.320(4) Å) and a Na−F separation of 2.492(4) Å.[30] Further-

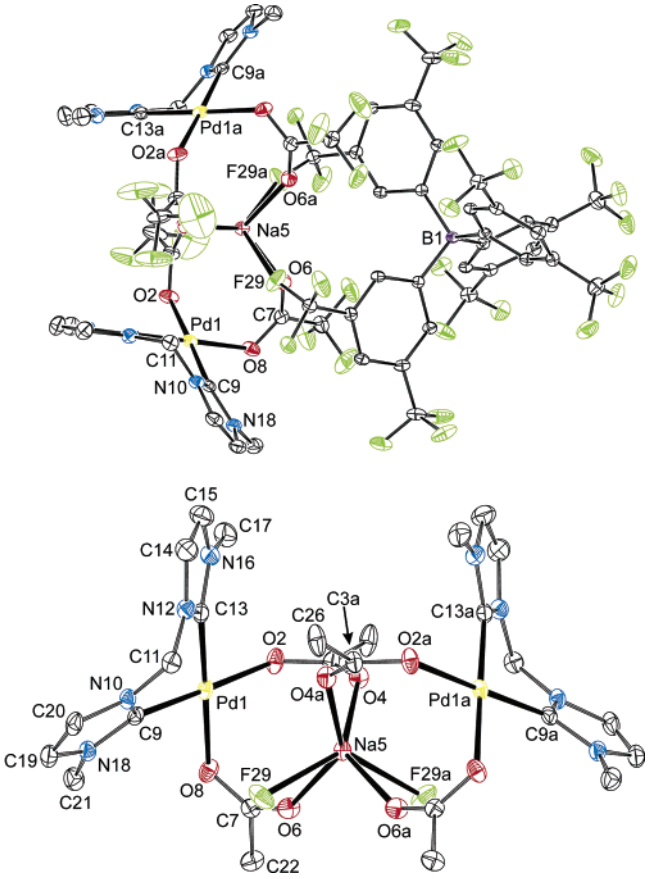


Figure 3. Displacement ellipsoid plot of **8b**[$BArF_{24}$] (C_2-symmetry; top: full, bottom: core) with, for clarity, ellipsoids drawn at the 20% probability level. Hydrogen atoms, two CD_2Cl_2 solvent molecules, and the three water molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Na5−O4 2.323(4), Na5−O6 2.320(4), Na5−F29 2.492(4), Pd1−Na5 3.6679(11), Pd1−O2 2.079(4), Pd1−O8 2.083(4), Pd1−C9 1.968(5), Pd1−C13 1.960(6), O2−C3 1.256(6), O4−C3 1.199(6), O8−C7 1.260(6), O6−C7 1.212(6), C9−N10 1.350(7), C9−N18 1.344(7), C11−N10 1.443(7), C11−N12 1.450(7), C13−N12 1.350(7), C13−N16 1.342(7); O4−Na5−O4a 92.3(2), O6−Na5−O6a 113.7(2), F29−Na5−F29a 132.0(2), O2−Pd1−O8 85.56(17), O2−Pd1−C9 176.78-(17), O8−Pd1−C13 179.16(17), C9−Pd1−C13 85.8(2), N10−C9−N18 105.3(4), N10−C11−N12 109.0(4), N12−C13−N16 104.5(5).

(27) Siegmann, K.; Pregosin, P. S.; Venanzi, L. M. *Organometallics* **1989**, *8*, 2659−2664, and references therein.

(28) (a) Suzaki, Y.; Osakada, K. *Organometallics* **2004**, *23*, 5081−5084. (b) Pantcheva, I.; Nishihara, Y.; Osakada, K. *Organometallics* **2005**, *24*, 3815−3817. (c) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317−4324.

(29) Treatment of [3-Me-1-{C(C_6H_5)N(C_6H_5)}-$C_3H_2N_2$]Pt($OAc)_2$ with 1 equiv of $NaBArF_{24}$ gives [[3-Me-1-{C(C_6H_5)N(C_6H_5)}-$C_3H_2N_2$]Pt(OAc)]-[$BArF_{24}$] as the sole product: Slootweg, J. C.; Keller, S. F.; Chen, P. Unpublished results.

(30) Pascu, S. I.; Jarrosson, T.; Naumann, C.; Otto, S.; Kaiser, G.; Sanders, J. K. M. *New J. Chem.* **2005**, *29*, 80−89.

more, the Pd−C bonds in **8b**[$BArF_{24}$] are slightly longer (Pd1−C9 1.968(5) Å, Pd1−C13 1.960(6) Å) than in precursor **4b**[14b] (1.954(3) and 1.955(3) Å), and the C−Pd−C angle of **8b**[$BArF_{24}$] is slightly larger (C9−Pd1−C13 85.8(2)°; **4b**[14b] 84.25(11)°), whereas the Pd−O, the C═O, and the C−O bonds are almost identical.[31]

Conclusions

We have reported a facile synthesis and full characterization of the novel cationic bis-carbene palladium(II) acetate complexes. The resulting materials exhibit fluxional behavior in solution and can undergo dimerization, as was demonstrated by low-temperature ^{1}H NMR and single-crystal X-ray analysis. These palladium species are not active in the catalytic deuteration of benzene, and further studies using larger *N*-substituents to prevent the unfavorable dimerization process and generate active catalyst species are underway.

Experimental Section

Computations. The density functional theory calculations (B3PW91) were performed with the Gaussian03 suite of programs,[22] using the LANL2DZ basis and pseudopotentials for palladium and the 6-31+G** basis for all other atoms.

General Procedures. All experiments were performed under an atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded on a Varian Mercury 300 (^{1}H, ^{13}C, and ^{19}F; CCl_3F) and referenced internally to residual solvent resonances (CD_2Cl_2: ^{1}H: δ 5.32 ppm, ^{13}C{^{1}H}: 53.8 ppm; DMSO-d_6: ^{1}H: δ 2.49 ppm, ^{13}C{^{1}H}: 39.5 ppm). ESI-MS measurements were performed on either a Finnigan MAT LCQ Deca ion trap or a Finnigan MAT TSQ Quantum triple-quad mass spectrometer, both equipped with electrospray sources. Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich. Melting points were measured on samples in unsealed capillaries and are uncorrected.

1,1′-Dimethyl-3,3′-methylenediimidazolium Dibromide.[32] 1,1′-Dimethyl-3,3′-methylenediimidazolium dibromide was prepared according to Herrmann et al.[32] at 140 °C in 84% yield. ^{1}H NMR (299.9 MHz, DMSO-d_6): δ 3.90 (s, 6H; CH_3), 6.81 (s, 2H; CH_2), 7.83 (s, 2H; C*H*(imid)), 8.13 (s, 2H; C*H*(imid)), 9.61 (s, 2H; NC*H*N).

(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene) $PdBr_2$.[33] A DMSO solution (50 mL) of 1,1′-dimethyl-3,3′-methylenediimidazolium dibromide (1.33 g, 3.93 mmol) and $Pd(OAc)_2$ (0.88 g, 3.93 mmol) was stirred at room temperature for 4 h, then heated at 40 °C for 14 h and then at 120 °C for a further 2 h, after which an orange solution was obtained. Subsequent removal of the solvent in vacuo at 80 °C yielded a yellowish solid, which was washed with acetonitrile (3 × 10 mL) and dried in vacuo to yield (1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)$PdBr_2$ as a white powder (1.68 g, 97%). ^{1}H NMR (299.9 MHz, DMSO-d_6): δ 3.89 (s, 6H; NCH_3), 6.26 (s, 2H; CH_2), 7.32 (d, ^3J(H,H) = 1.7 Hz, 2H; C*H*(imid)), 7.58 (d, ^3J(H,H) = 1.7 Hz, 2H; C*H*(imid)).

(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OAc)$_2$ (4a).[14a] **4a** was obtained according to Herrmann et al.[14a] as a white solid in 90% yield starting from (1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)$PdBr_2$ and 2 equiv of AgOAc in CH_3CN (60 °C, 8 h). ^{1}H NMR (299.9 MHz, DMSO-d_6): δ 1.72 (s, 6H; O_2CCH_3), 3.72 (s, 6H; NCH_3), 6.16 (s, 2H; CH_2), 7.25 (d, ^3J(H,H) = 1.87 Hz, 2H; C*H*(imid)), 7.53 (d, ^3J(H,H) = 1.87 Hz, 2H; C*H*(imid)). ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 1.88 (s, 6H; O_2CCH_3), 3.82 (s, 6H; NCH_3), 6.23 (s, 2H; CH_2), 6.82 (d, ^3J(H,H) = 1.87 Hz, 2H; C*H*(imid)), 7.50 (d, ^3J(H,H) = 1.87 Hz, 2H; C*H*(imid)). MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 341 (100) $[M - O_2CCH_3]^+$, 743 (20) $[2M - O_2CCH_3]^+$, 1143 (5) $[3M - O_2CCH_3]^+$.

(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(O-COCF$_3$)$_2$ (4b).[14b] **4b** was obtained according to Herrmann et al.[14b] as a white solid in 97% yield starting from (1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)$PdBr_2$ and 2 equiv of silver trifluoroacetate in CH_3CN (60 °C, 8 h). ^{1}H NMR (299.9 MHz, 60 °C, CD_2Cl_2): δ 3.89 (s, 6H; NCH_3), 6.31 (br s, 2H; CH_2), 6.94 (d, ^3J(H,H) = 2.0 Hz, 2H; C*H*(imid)), 7.30 (d, ^3J(H,H) = 2.0 Hz, 2H; C*H*(imid)). ^{19}F{^{1}H} NMR (282.2 MHz, CD_2Cl_2): δ − 74.0 (br s; CF_3). MS (ESI, positive ions, CH_3CN) *m*/*z* (%): 395 (100) $[M - O_2CCF_3]^+$, 904 (10) $[2M - O_2CCF_3]^+$, 1413 (2) $[3M - O_2CCF_3]^+$.

[(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OAc)][OTs] (5a[OTs]). (1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)$Pd(OAc)_2$ (**4a**)[14a] (664 mg, 1.66 mmol) and HOTs·H_2O (315 mg, 1.66 mmol) were dissolved in CH_2Cl_2 (15 mL), and the resulting mixture was stirred for 24 h at room temperature. Subsequent removal of the solvent from the precipitate yielded a white solid, which was washed with CH_2Cl_2 (1 × 10 mL) and dried in vacuo to yield **5a**[OTs] as a white solid (759 mg, 89%). Mp ≥ 218 °C (dec). ^{1}H NMR (299.9 MHz, 50 °C, CD_2Cl_2): δ 2.05 (s, 3H; O_2CCH_3), 2.35 (s, 3H; ArCH_3), 3.60 (s, 6H; NCH_3), 6.58 (s, 2H; CH_2), 6.99 (s, 2H; C*H*(imid)) (22 °C: d, ^3J(H,H) = 2.18 Hz), 7.15 (d, ^3J(H,H) = 7.9 Hz, 2H; Ar*H*) (22 °C: m), 7.68 (d, ^3J(H,H) = 7.9 Hz, 2H; Ar*H*) (22 °C: m), 8.00 (s, 2H; C*H*(imid)) (22 °C: d, ^3J(H,H) = 2.18 Hz). A ^{13}C{^{1}H} NMR of **5a**[OTs] was not obtained due to its poor solubility in CD_2Cl_2. MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 341 (100) $[M - OTs]^+$, 855 (12) $[2M - OTs]^+$. Anal. Found: C, 42.03; H, 4.32; N, 10.96. Calcd for $C_{18}H_{22}N_4O_5PdS$: C, 42.15; H, 4.32; N, 10.92. Colorless crystals suitable for X-ray crystallography were obtained by dissolving **4a**[14a] (81.3 mg, 0.20 mmol) and HOTs·H_2O (38.5 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) at room temperature.

[(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OCOCF$_3$)][OTs] (5b[OTs]). (1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)$Pd(OCOCF_3)_2$ (**4b**)[14b] (504 mg, 0.99 mmol) and HOTs·H_2O (189 mg, 0.99 mmol) were suspended in CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 17 h at room temperature. Filtration and removal of the solvent in vacuo yielded **5b**[OTs] as a white solid (478 mg, 85%). Mp: 70−80 °C, pale yellow wax; ≥150 °C (dec). ^{1}H NMR (299.9 MHz, 50 °C, CD_2Cl_2): δ 2.37 (s, 3H; ArCH_3), 3.83 (s, 6H; NCH_3), 6.22 (s, 2H; CH_2), 6.87 (d, ^3J(H,H) = 1.9 Hz, 2H; C*H*(imid)), 7.18 (d, ^3J(H,H) = 8.1 Hz, 2H; Ar*H*), 7.45 (s, 2H; C*H*(imid)), 7.67 (d, ^3J(H,H) = 8.1 Hz, 2H; Ar*H*). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 21.3 (s; Ar*C*H_3), 37.5 (s; N*C*H_3), 62.5 (s; *C*H_2), 115.7 (q, ^1J(C,F) = 286.3 Hz; *C*F_3), 122.2 (br s; ═*C*H), 123.3 (br s; ═*C*H), 126.0 (s; *m*-Ar), 129.1 (s; *o*-Ar), 140.9, and 141.6 (s; *C*SO_3^-, and *C*Me), 148.5 (br s; N*C*N), 160.4 (br s, ^2J(C,F) = unresolved; O*C*O). ^{19}F{^{1}H} NMR (282.2 MHz, 50 °C, CD_2Cl_2): δ −75.0 (br s; CF_3). MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 395 (100) $[M - OTs]^+$.

[(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OAc)][$BArF_{24}$] (5a[$BArF_{24}$]). A mixture of **5a**[OTs] (393 mg, 0.77 mmol) and $NaBArF_{24}$[16] (679 mg, 0.77 mmol) was suspended in CH_2Cl_2 (10 mL) and stirred for 0.5 h at 0 °C and then for 0.5 h at room temperature. The resulting suspension was filtered, to remove the precipitated NaOTs, yielding a pale yellow solution. Then, the solvent was removed in vacuo to yield **5a**[$BArF_{24}$] as a white solid (769 mg, 83%). Mp: 74−78 °C, pale yellow wax; ≥95 °C (dec). ^{1}H NMR (299.9 MHz, CD_2Cl_2): δ 2.05 (s, 3H; O_2CCH_3), 3.56 (br s, 6H; NCH_3), 5.88 (br s, 2H; CH_2), 6.91 (d, ^3J(H,H) =

(31) **4b**: Pd−O (2.078 and 2.084 Å), C═O (1.214 and 1.217 Å), C−O (1.261 and 1.263 Å); see ref 14b.

(32) Muehlhofer, M.; Strassner, T.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *660*, 121−126.

(33) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239−247.

2.18 Hz, 2H; C*H*(imid)), 7.16 (d, ^3J(H,H) = 2.18 Hz, 2H; C*H*(imid)), 7.56 (br s, 4H; *p*-Ar*H*), 7.73 (br s, 8H; *o*-Ar*H*). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 24.0 (s; O_2CCH_3), 36.8 (s; NCH_3), 63.0 (s; CH_2), 117.8 (br s; *p*-Ar), 121.9 (s; =*C*H), 124.7 (s; =*C*H), 124.8 (q, ^1J(C,F) = 271.6 Hz; CF_3), 129.1 (br q, ^2J(C,F) = 31.1 Hz; CCF_3), 135.0 (s; *o*-Ar), 149.8 (s; N*C*N), 161.9 (q, ^1J(C,B) = 49.6 Hz; *ipso*-Ar), 184.0 (s; O*C*O). ^{19}F{^{1}H} NMR (282.2 MHz, CD_2Cl_2): δ − 62.12 (s, 24F; CF_3). MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 341 (100) [M − $BArF_{24}$]$^+$, 1547 (10) [2M − $BArF_{24}$]$^+$. MS (ESI, positive ions, CH_3CN) *m*/*z* (%): 341 (82) [M − $BArF_{24}$]$^+$, 1547 (3) [2M − $BArF_{24}$]$^+$. Anal. Found: C, 42.95; H, 2.49; N, 4.72. Calcd for $C_{43}H_{27}BF_{24}N_4O_2Pd$: C, 42.86; H, 2.26; N, 4.65. Reacting **4a**[14a] (11.8 mg, 29.4 μmol) directly with 1 equiv of $NaBArF_{24}$[16] (26.1 mg, 29.4 μmol) in CD_2Cl_2 (0.7 mL) at 50 °C for 1 h gives a mixture of **5a**[$BArF_{24}$] and sodium complex **8a**[$BArF_{24}$].

[(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OCOCF$_3$)][BArF$_{24}$] (5b[BArF$_{24}$]). A mixture of **5b**[OTs] (239 mg, 0.42 mmol) and $NaBArF_{24}$[16] (365 mg, 0.42 mmol) was dissolved in CH_2Cl_2 (8 mL) and stirred for 0.5 h at 0 °C and then for 1 h at room temperature. The resulting suspension was filtered, to remove the precipitated NaOTs, yielding a pale yellow solution. Then, the solvent was removed in vacuo to yield **5b**[$BArF_{24}$] as a white solid (410 mg, 77%). Mp: 70−80 °C, gives pale yellow wax; ≥124 °C (dec). ^{1}H NMR (299.9 MHz, 50 °C, CD_2Cl_2): δ 3.77 (br s, 6H; NCH_3) (22 °C: 3.74 and 3.87, br s), 5.92 (br s, 2H; CH_2), 6.93 (d, ^3J(H,H) = 1.7 Hz, 2H; C*H*(imid)), 7.18 (d, ^3J(H,H) = 1.7 Hz, 2H; C*H*(imid)), 7.56 (br s, 4H; *p*-Ar*H*), 7.73 (br s, 8H; *o*-Ar*H*). ^{1}H NMR (299.9 MHz, 50 °C, CD_3CN): δ 3.83 (s, 6H; NCH_3), 6.11 (s, 2H; CH_2), 7.09 (d, ^3J(H,H) = 1.87 Hz, 2H; C*H*(imid)), 7.37 (d, ^3J(H,H) = 1.87 Hz, 2H; C*H*(imid)), 7.64−7.74 (m, 12H; Ar*H*). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 37.6 (s; NCH_3), 63.1 (s; CH_2), 115.5 (q, ^1J(C,F) = 286.3 Hz; O_2CCF_3), 117.9 (br s; *p*-Ar), 122.4 (s; =*C*H), 124.9 (q, ^1J(C,F) = 271.6 Hz; ArCF_3), 125.4 (s; =*C*H), 129.2 (br q, ^2J(C,F) = 31.1 Hz; ArCCF_3), 135.1 (s; *o*-Ar), 145.0 (s; N*C*N), 162.0 (q, ^1J(C,B) = 49.8 Hz; *ipso*-Ar), 167.4 (br q, ^2J(C,F) = 41.5 Hz; O*C*O). ^{19}F{^{1}H} NMR (282.2 MHz, CD_2Cl_2): δ −62.3 (s, 24F; CF_3), −73.7 (s, 3F; CF_3). ^{19}F{^{1}H} NMR (282.2 MHz, CD_3CN): δ −61.8 (s, 24F; CF_3), −73.5 (br s, 3F; CF_3). MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 395 (100) [M − $BArF_{24}$]$^+$, 1655 (10) [2M − $BArF_{24}$]$^+$. MS (ESI, positive ions, CH_3CN) *m*/*z* (%): 395 (82) [M − $BArF_{24}$]$^+$, 495 (100) [bisNHCPd−$C_6H_3(CF_3)_2$-3,5]$^+$, 536 (55) [bisNHCPd−$C_6H_3(CF_3)_2$-3,5 + CH_3CN]$^+$, 1655 (7) [2M − $BArF_{24}$]$^+$. Anal. Found: C, 41.14; H, 1.73; N, 4.25. Calcd for $C_{43}H_{24}BF_{27}N_4O_2Pd$: C, 41.03; H, 1.92; N, 4.45. In CD_3CN, **5b**[$BArF_{24}$] is stable at 80 °C for at least 24 h. Reacting **4b**[14b] (26.2 mg, 51.5 μmol) directly with $NaBArF_{24}$[16] (45.6 mg, 51.5 μmol) in CD_2Cl_2 (0.7 mL) at room temperature for 1 h gives a mixture of **5b**[$BArF_{24}$] and sodium complex **8b**[$BArF_{24}$].

[{(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OAc)$_2$}$_2$Na][BArF$_{24}$] (8a[BArF$_{24}$]). A mixture of **4a**[14a] (251 mg, 0.63 mmol) and $NaBArF_{24}$[16] (278 mg, 0.31 mmol) in CH_2Cl_2 (8 mL) was reacted at 50 °C for 2 h. After filtration, yielding a brown solution, the solvent was removed in vacuo to yield **8a**[$BArF_{24}$] as a beige-yellow solid (445 mg, 85%). Yellow crystals were grown from a concentrated CH_2Cl_2 solution at −20 °C. Mp: 124−128 °C, yellow wax; ≥185 °C (dec). ^{1}H NMR (299.9 MHz, 50 °C, CD_2Cl_2): δ 1.88 (s, 12H; O_2CCH_3), 3.88 (s, 12H; NCH_3), 6.18 (br s, 4H; CH_2) (−20 °C: 5.60, 5.64, 6.98, and 7.02, AB-type, ^2J(H,H) = 12.6 Hz), 6.84 (d, ^3J(H,H) = 2.0 Hz, 4H; C*H*(imid)), 7.10 (d, ^3J(H,H) = 2.0 Hz, 4H; C*H*(imid)), 7.56 (br s, 4H; *p*-Ar*H*), 7.73 (br s, 8H; *o*-Ar*H*). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 24.0 (s; O_2CCH_3), 37.35 (s; NCH_3), 37.39 (s; NCH_3), 63.0 (s; CH_2), 117.8 (br s; *p*-Ar), 120.8, and 122.9 (s; =*C*H), 124.9 (q, ^1J(C,F) = 272.0 Hz; ArCF_3), 129.1 (br q, ^2J(C,F) = 31.1 Hz; CCF_3), 135.1 (s; *o*-Ar), 156.3 (s; N*C*N), 162.0 (q, ^1J(C,B) = 49.8 Hz; *ipso*-Ar), 177.8 (s; O*C*O). ^{19}F{^{1}H} NMR (282.2 MHz, CD_2Cl_2): δ − 62.3 (s, 24F; CF_3). MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 341 (100) [bisNHCPdOAc]$^+$, 743 (70) [M − NaOAc − $BArF_{24}$]$^+$, 825 (76) [M − $BArF_{24}$]$^+$. Anal. Found: C, 41.46; H, 3.07; N, 6.57. Calcd for $C_{58}H_{48}BF_{24}N_8NaO_8Pd_2$: C, 41.28; H, 2.87; N, 6.64. Alternatively, **8a**[$BArF_{24}$] can be prepared by reacting **5a**[$BArF_{24}$] (51.0 mg, 42.3 μmol) with NaOAc (3.5 mg, 42.3 μmol) and **4a**[14a] (17.0 mg, 42.3 μmol) in CD_2Cl_2 (1 mL) at 60 °C for 0.5 h.

[{(1,1′-Dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)Pd(OCOCF$_3$)$_2$}$_2$Na][BArF$_{24}$] (8b[BArF$_{24}$]). A mixture of **4b**[14b] (308 mg, 0.61 mmol) and $NaBArF_{24}$[16] (268 mg, 0.30 mmol) in CH_2Cl_2 (8 mL) was reacted at 50 °C for 2 h. After filtration, yielding a pale yellow solution, the solvent was removed in vacuo to yield **8b**[$BArF_{24}$] as a white solid (473 mg, 82%). Colorless crystals suitable for X-ray crystallography were grown from CH_2Cl_2. Mp: 72−78 °C, colorless wax; ≥166 °C (dec). ^{1}H NMR (299.9 MHz, 50 °C, CD_2Cl_2): δ 3.87 (s, 12H; NCH_3), 6.19 (br s, 4H; CH_2) (−50 °C: 5.57, 5.62, 6.76, and 6.80, AB-type, ^2J(H,H) = 13.2 Hz), 6.88 (s, 4H; C*H*(imid)), 7.14 (d, ^3J(H,H) = 1.87 Hz, 4H; C*H*(imid)), 7.56 (s, 4H; *p*-Ar*H*), 7.73 (br s, 8H; *o*-Ar*H*). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 37.5 (s; NCH_3), 37.6 (s; NCH_3), 63.4 (s; CH_2), 116.4 (q, ^1J(C,F) = 288.9 Hz; O_2CCF_3), 117.9 (br s; *p*-Ar), 121.40 (s; =*C*H), 121.44 (s; =*C*H), 123.8 (br s; =*C*H), 124.9 (q, ^1J(C,F) = 271.6 Hz; ArCF_3), 124.9 (br q, ^2J(C,F) = 31.1 Hz; ArCCF_3), 135.1 (s; *o*-Ar), 150.3 (s; N*C*N), 162.0 (q, ^1J(C,B) = 49.8 Hz; *ipso*-Ar), 162.9 (q, ^2J(C,F) = 37.2 Hz; O*C*O). ^{19}F{^{1}H} NMR (282.2 MHz, CD_2Cl_2): δ −62.3 (s, 24F; CF_3), −74.3 (s, 12F; CF_3). MS (ESI, positive ions, CH_2Cl_2) *m*/*z* (%): 395 (10) [bis-NHCPdO$COCF_3$]$^+$, 676 (35) [M − 2 $OCOCF_3$ − $NaOCOCF_3$ − $BArF_{24}$]$^+$, 905 (20) [M − $NaOCOCF_3$ − $BArF_{24}$]$^+$, 1041 (100) [M − $BArF_{24}$]$^+$. Anal. Found: C, 36.88; H, 2.01; N, 5.72. Calcd for $C_{58}H_{36}BF_{36}N_8NaO_8Pd_2$: C, 36.60; H, 1.91; N, 5.89. Alternatively, **8b**[$BArF_{24}$] can be prepared by reacting **5b**[$BArF_{24}$] (122.4 mg, 97.0 μmol) with $NaOCOCF_3$ (13.2 mg, 97.0 μmol) and **4b**[14b] (49.5 mg, 97.0 μmol) in CH_2Cl_2 (5 mL) at 60 °C for 0.5 h.

Crystal structure determination of compound (5a[OTs])$_2$: $C_{22}H_{30}N_8O_4Pd_2 \cdot 2C_7H_7O_3S \cdot 2H_2O$, fw = 1057.7, colorless cut fragment, 0.15 × 0.14 × 0.13 mm^3; monoclinic crystal system, space group $P2_1/c$. Cell parameters: a = 14.2381(5) Å, b = 22.7148(7) Å, c = 14.3902(4) Å, α = 90.00°, β = 114.763(2)°, γ = 90.00°, V = 4226.1(2) Å^3; Z = 4, ρ = 1.662 g/cm^3; 12 511 reflections were measured on a Bruker-Nonius KappaCCD (graphite monochromator, Mo Kα, λ = 0.7107 Å) at a temperature of 200 K; 8087 reflections were unique (R_{int} = 0.0518). The structure was solved by direct methods[34] and refined by full-matrix least-squares analysis[35] including an isotropic extinction correction. All non-hydrogen atoms were refined anisotropically (H atoms isotropic, whereby H-positions are based on stereochemical considerations). Final $R(F)$ = 0.0486, $wR(F^2)$ = 0.1110 for 594 parameters and 5761 reflections with $I > 2\sigma(I)$ and θ < 26.31°.

Crystal structure determination of compound 8b[BArF$_{24}$]: $C_{58}H_{36}BF_{36}N_8NaO_8Pd_2 \cdot 2CD_2Cl_2 \cdot 3H_2O$, fw = 2121.4, colorless cut fragment, 0.21 × 0.18 × 0.16 mm^3; monoclinic crystal system, space group $C2/c$. Cell parameters: a = 21.0620(4) Å, b = 21.4351(6) Å, c = 21.2069(6) Å, α = 90.00°, β = 110.104(1)°, γ = 90.00°, V = 8990.8(4) Å^3; Z = 4, ρ = 1.567 g/cm^3; 15 263 reflections were measured on a Bruker-Nonius KappaCCD (graphite monochromator, Mo Kα, λ = 0.7107 Å) at a temperature of 173 K; 8765 reflections were unique (R_{int} = 0.0543). The structure was solved by direct methods[34] and refined by full-matrix least-squares analysis[35] including an isotropic extinction correction. All non-hydrogen atoms were refined anisotropically (H atoms isotropic, whereby H-positions are based on stereochemical considerations).

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Final $R(F) = 0.0637$, $wR(F^2) = 0.1652$ for 559 parameters and 6545 reflections with $I > 2\sigma(I)$ and $\theta < 26.02°$. The drawings were made with the program PLATON.[36]

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Note Added after ASAP Publication. In the version of this paper that was published on the Web November 9, 2006, a portion of Scheme 4 was missing. The version of this scheme that now appears is correct.

Supporting Information Available: Cartesian coordinates (Å) and energies (au) of all stationary points. Cif files with crystallographic data for compounds (**5a**[OTs])$_2$ and **8b**[$BArF_{24}$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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