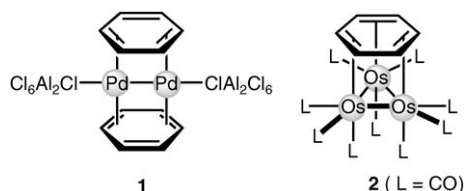


Discrete Triangular Tripalladium Sandwich Complexes of Arenes**

Tetsuro Murahashi,* Mayu Fujimoto, Yurika Kawabata, Ryou Inoue, Sensuke Ogoshi, and Hideo Kurosawa

Since the sandwich π coordination of benzene and substituted benzene was elucidated by Fischer and Hafner as well as Zeiss and Tsutsui half a century ago,^[1] the chemistry of discrete benzene π complexes has developed extensively.^[2] The η^1 or η^2 coordination of arenes to a mononuclear Pd center is important in the stabilization of active palladium catalysts.^[3,4] Furthermore, recent theoretical studies suggest that η^2 coordination of arenes to a mononuclear Pd center is involved in the palladium-catalyzed transformation of aromatic substrates.^[5] Another interesting aspect in arene–Pd chemistry is that arenes are capable of binding a Pd–Pd-bonded dipalladium moiety to form stable arene dipalladium complexes, such as **1** (Scheme 1).^[3,6] However, the corre-

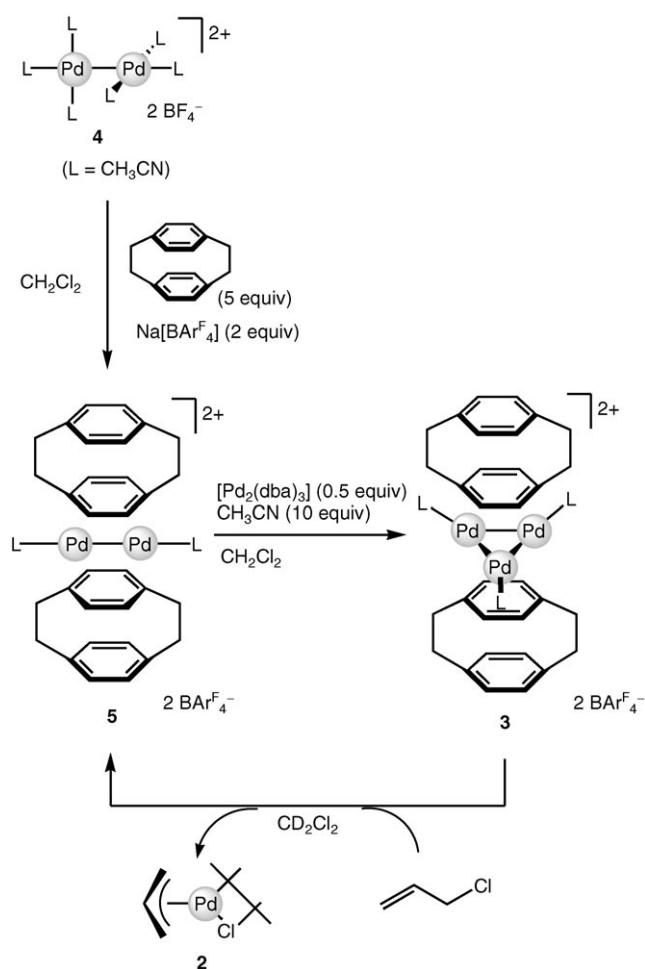


Scheme 1. Early examples of dinuclear and trinuclear arene complexes.

sponding arene tripalladium complex in which an arene ligand facially caps a triangular tripalladium core in a μ_3 -coordination manner has not been reported, although discrete μ_3 -arene trimetal complexes of Group 8 and 9 metals have been known since Lewis and co-workers isolated the half-sandwich complex **2**.^[7,8] Herein, we report the isolation of the μ_3 -arene tripalladium sandwich complex $[\text{Pd}_3\text{-(}[2.2]\text{paracyclophane)}_2(\text{CH}_3\text{CN})_3][\text{BAR}^{\text{F}}_4]_2$ (**3**, $\text{BAR}^{\text{F}}_4 = \text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4\text{)}^{[9]}$ as well as some of its properties, including its degradation to a dinuclear sandwich complex

and conversion into a mixed-sandwich complex of $[2.2]\text{paracyclophane}$ and 1,3,5,7-cyclooctatetraene (cot).

The homoleptic acetonitrile dipalladium(I) complex $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (**4**) is a useful “seed reagent” for the preparation of sandwich palladium clusters.^[9,10] Initial attempts to synthesize a bis(arene) dipalladium complex by reaction of **4** with excess benzene or *p*-xylene failed, even though Allegra’s bis(benzene)dipalladium complex **1** and its derivatives, including *p*-xylene complexes, are formed by reactions using PdCl_2 , appropriate reducing reagents, and AlCl_3 or GaCl_3 .^[6a,b,f,g] When $[2.2]\text{paracyclophane}$ ^[11–13] was employed, however, the desired dipalladium sandwich complex $[\text{Pd}_2([2.2]\text{paracyclophane})_2(\text{CH}_3\text{CN})_2][\text{BAR}^{\text{F}}_4]_2$ (**5**) was obtained in 78% yield (Scheme 2). The composition of **5** was



Scheme 2. Synthesis of the bis([2.2]paracyclophane)dipalladium and -tripalladium complexes.

[*] Prof. T. Murahashi, M. Fujimoto, Y. Kawabata, R. Inoue, Prof. S. Ogoshi, Prof. H. Kurosawa
Department of Applied Chemistry
Graduate School of Engineering, Osaka University
Suita, Osaka, 565-0871 (Japan)
Fax: (+81) 6-6879-7394
E-mail: tetsu@chem.eng.osaka-u.ac.jp

Prof. T. Murahashi
PRESTO
Japan Science and Technology Agency (Japan)

[**] This work was supported by PRESTO, Japan Science and Technology Agency (JST), and Grants-in-aid for Scientific Research, Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

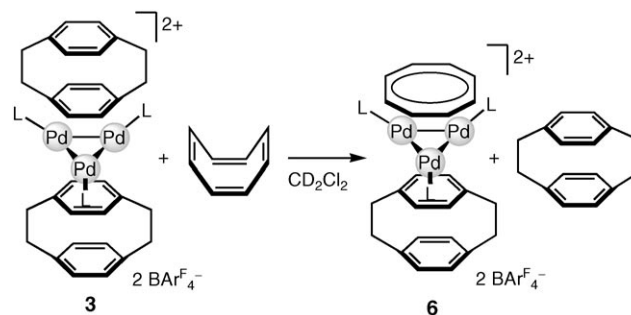
confirmed by elemental analysis. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5**, resonances due to one of the two phenylene rings in the [2.2]paracyclophane ligands appeared at higher field ($\delta_{\text{ipso}} = 126.8$ ppm and $\delta_{\text{ortho}} = 115.0$ ppm) than those of the other phenylene ring ($\delta_{\text{ipso}} = 140.1$ ppm and $\delta_{\text{ortho}} = 133.5$ ppm) and of the phenylene rings in free [2.2]paracyclophane ($\delta_{\text{ipso}} = 139.8$ ppm and $\delta_{\text{ortho}} = 134.5$ ppm). This NMR signal pattern is consistent with a sandwich structure in which each [2.2]paracyclophane ligand coordinates to the dipalladium unit through one of its phenylene rings, although the relative geometry of this ring and the Pd_2 unit is elusive.^[14] The greater reactivity of [2.2]paracyclophane than of benzene or *p*-xylene is interesting. Besides the distorted arene ring, the interannular interaction between two phenylene rings in the [2.2]paracyclophane ligand may contribute to the thermodynamic stability of [2.2]paracyclophane complexes.^[15]

When **5** was treated with $[\text{Pd}_2(\text{dba})_3]$ (0.5 equiv; dba = *trans,trans*-dibenzylideneacetone) in the presence of acetonitrile (10 equiv), the trinuclear sandwich complex $[\text{Pd}_3\text{([2.2]paracyclophane)}_2(\text{CH}_3\text{CN})_3][\text{BAR}_4^-]_2$ (**3**) was formed in 82% yield of the isolated product (Scheme 2). The composition of the deep-green complex **3** was confirmed by elemental analysis. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** showed upfield-shifted resonances for the coordinated phenylene ring ($\delta_{\text{ipso}} = 118.6$ ppm and $\delta_{\text{ortho}} = 93.3$ ppm) relative to those of **5**, whereas the chemical shifts of the noncoordinated phenylene rings ($\delta_{\text{ipso}} = 140.0$ ppm and $\delta_{\text{ortho}} = 133.1$ ppm) were similar to those of **5**. The ^1H NMR resonances for the coordinated and noncoordinated phenylene rings appeared at $\delta = 5.60$ and 6.87 ppm, respectively, as sharp singlets. Cooling a sample of **3** to -80°C resulted in almost unchanged resonances of the cyclophane protons, except that the resonance for the coordinated phenylene broadened considerably.^[16] Although [2.2]paracyclophane bound to a triangular Pd_3 moiety should show at least two proton resonances for each phenylene moiety, averaging of the resonances might occur, probably as a result of fast fluxional rotation of the [2.2]paracyclophane ligands on the Pd_3 core, as was found in the mixed-sandwich complex **6** described below. Thus, these NMR data are consistent with a sandwich structure of **3** in which each [2.2]paracyclophane ligand binds a trinuclear Pd_3 core by the μ_3 coordination of one of the phenylene moieties. Complex **3** is a very rare example of a discrete trinuclear sandwich complex with parallel face-capping unsaturated hydrocarbon ligands.^[9,17] Also, **3** is, to the best of our knowledge, the first μ_3 -arene trimetal complex of the Group 10 transition metals.

Tripalladium complex **3** can easily release a Pd atom on contact with allyl chloride; the reaction of **3** with allyl chloride (1 equiv) in CD_2Cl_2 immediately gave η^3 -allylpalladium chloride and the dinuclear sandwich complex **5** in almost quantitative yield (Scheme 2). When this reaction is combined with the facile capture of a Pd^0 atom by dipalladium complex **5** giving rise to **3**, the bis([2.2]paracyclophane) Pd_2/Pd_3 system may be regarded as a Pd^0 reservoir. These observations may provide some insights into the role of Pd clusters supported on arene-based polymers.^[18,19]

Although a single crystal of **3** suitable to X-ray diffraction analysis has not yet been obtained, the μ_3 coordination of [2.2]paracyclophane to a triangular tripalladium core was

determined through the X-ray crystallographic analysis of [2.2]paracyclophane-cot mixed-sandwich complex $[\text{Pd}_3\text{([2.2]paracyclophane)}(\text{cot})(\text{CH}_3\text{CN})_3]\text{X}_2$ (**6**, $\text{X} = \text{BAR}_4^-$; **6'**, $\text{X} = \text{BF}_4^-$). Compound **6** was obtained in 71% yield by treatment of **3** with excess cot (Scheme 3).^[20] The molecular structure of **6'** (Figure 1)^[21] shows that the triangular Pd_3 core



Scheme 3. Synthesis of the [2.2]paracyclophane-cot mixed-sandwich tripalladium complex.

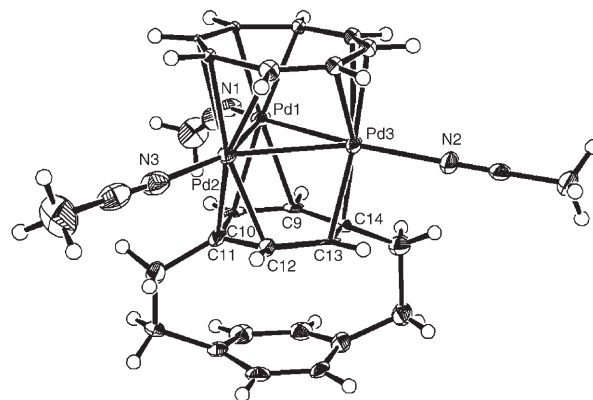


Figure 1. Molecular structure of **6'**; probability ellipsoids set at 50%; BF_4^- counterions, solvent molecule, and other set of disordered cot carbon atoms omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: Pd1–Pd2 2.7406(8), Pd2–Pd3 2.8296(9), Pd3–Pd1 2.7016(8), Pd1–N1 2.169(8), Pd2–N3 2.112(9), Pd3–N2 2.122(8), Pd1–C9 2.211(8), Pd1–C10 2.214(9), Pd2–C11 2.230(9), Pd2–C12 2.197(8), Pd3–C13 2.185(8), Pd3–C14 2.238(8); Pd1–Pd2–Pd3 58.00(2), Pd2–Pd3–Pd1 59.35(2), Pd3–Pd1–Pd2 62.65(2).

is held between the planar cot ligand^[22–24] and the [2.2]paracyclophane ligand; the coordination mode of the latter is μ_3 -(η^2 : η^2 : η^2). The Pd2–Pd3 bond (2.8296(9) Å) is longer than the Pd1–Pd2 (2.7406(8) Å) and Pd1–Pd3 bonds (2.7016(8) Å). The Pd3–Pd1–Pd2 angle (62.65(2) $^\circ$) is slightly larger than the Pd1–Pd2–Pd3 (58.00(2) $^\circ$) and Pd2–Pd3–Pd1 angles (59.35(2) $^\circ$). Complexes **6** and **6'** contain two more electrons in total than **3**. The ^1H NMR spectrum of **6** at -80°C showed two singlet resonances in a 2:1 intensity ratio for acetonitrile ligands, four singlet resonances for phenylene protons ($\delta = 7.39$, 7.36, 4.11, and 4.01 ppm), and four multiplet resonances for methylene protons of the [2.2]paracyclophane ligand. Warming the sample caused the five pairs of resonances to coalesce, leading to one singlet resonance for acetonitrile ligands, two

singlet resonances for phenylene protons, and two broad multiplet resonances for methylene protons of the [2.2]paracyclophane ligand at 25°C. In the temperature range from –80°C to 25°C, the singlet resonance for cot protons remained unchanged. This temperature-dependent ^1H NMR behavior is consistent with the fluxional ring rotations of the [2.2]paracyclophane and the cot ligands, whereby the latter ligand rotates faster than the former. The $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of the [2.2]paracyclophane ligand of **6** at –80°C ($\delta_{\text{ipso}} = 89.7$ ppm, $\delta_{\text{ortho}} = 69.8$ ppm, $\delta_{\text{ortho}'} = 69.0$ ppm for coordinated phenylene; $\delta_{\text{ipso}} = 139.6$ ppm, $\delta_{\text{ortho}} = 133.2$ ppm, $\delta_{\text{ortho}'} = 133.0$ ppm for noncoordinated phenylene) are consistent with the crystallographically determined structure, in which the coordinated phenylene carbon atoms are more upfield-shifted than those of bis([2.2]paracyclophane)tripalladium complex **3**.

In summary, it has been shown that μ_3 -arene tripalladium complexes can be prepared as stable complexes. Complex **3**, which is the first isolated discrete trimetal sandwich complex of an arene, undergoes facile release of a Pd^0 atom and ligand exchange with cot. The chemistry of arene–tripalladium complexes is being studied further in our laboratory.

Received: April 16, 2007

Published online: June 14, 2007

Keywords: π interactions · cyclophanes · palladium · sandwich complexes · structure elucidation

- [1] a) E. O. Fischer, W. Hafner, *Z. Naturforsch. B* **1955**, *10*, 665; b) E. O. Fischer, W. Hafner, *Z. Anorg. Allg. Chem.* **1956**, *286*, 146; c) H. H. Zeiss, M. Tsutsui, *J. Am. Chem. Soc.* **1957**, *79*, 3062.
- [2] For reviews, see: a) E. L. Muetterties, J. R. Bleeker, E. J. Wucherer, T. A. Albright, *Chem. Rev.* **1982**, *82*, 499; b) D. Seyferth, *Organometallics* **2002**, *21*, 1520; c) D. Seyferth, *Organometallics* **2002**, *21*, 2800.
- [3] a) P. Espinet, A. C. Albeniz, *Comprehensive Organometallic Chemistry III*, Vol. 8 (Eds.: D. M. P. Mingos, R. H. Crabtree, A. Canty), Elsevier, Oxford, **2007**, chap. 8.06, and references therein.
- [4] For selected recent examples, see: a) G. C. Lloyd-Jones, S. C. Stephen, M. Murray, C. P. Butts, S. Vyskocil, P. Kocovsky, *Chem. Eur. J.* **2000**, *6*, 4348; b) M. Catellani, C. Mealli, E. Motti, P. Paoli, E. Perez-Carreno, P. S. Pregosin, *J. Am. Chem. Soc.* **2002**, *124*, 4336; c) T. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685; d) D. Tanaka, S. P. Romeril, A. G. Myers, *J. Am. Chem. Soc.* **2005**, *127*, 10323; e) P. G. A. Kumar, P. Dotta, R. Hermatschweiler, P. S. Pregosin, *Organometallics* **2005**, *24*, 1306.
- [5] For selected recent examples, see: a) H. M. Senn, T. Ziegler, *Organometallics* **2004**, *23*, 2980; b) L. J. Goossen, D. Koley, H. L. Hermann, W. Thiel, *Organometallics* **2005**, *24*, 2398; c) S. Kozuch, C. Amatore, A. Jutand, S. Shaik, *Organometallics* **2005**, *24*, 2319.
- [6] For selected examples of $\mu(\eta^2:\eta^2)$ -arene Pd–Pd complexes, see: a) G. Allegra, L. Immirzi, L. Porri, *J. Am. Chem. Soc.* **1965**, *87*, 1394; b) G. Allegra, G. T. Casagrande, A. Immirzi, L. Porri, G. Vitulli, *J. Am. Chem. Soc.* **1970**, *92*, 289; c) J. Dupont, M. Pfeffer, M. A. Rottevel, A. de Cian, J. Fischer, *Organometallics* **1989**, *8*, 1116; d) M. Sommovigo, M. Pasquali, P. Leoni, D. Braga, P. Sabatino, *Chem. Ber.* **1991**, *124*, 97; e) S. Kannan, A. J. James, P. R. Sharp, *J. Am. Chem. Soc.* **1998**, *120*, 215; f) M. Gorlov, A. Fischer, L. Kloo, *Inorg. Chim. Acta* **2003**, *350*, 449; g) M. Gorlov, A. Fischer, L. Kloo, *J. Organomet. Chem.* **2004**, *689*, 489; h) P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2004**, *23*, 4247; i) Y. Tatsumi, T. Nagai, H. Nakashima, T. Murahashi, H. Kurosawa, *Chem. Commun.* **2004**, 1430; j) T. E. Barder, *J. Am. Chem. Soc.* **2006**, *128*, 898; k) U. Christmann, D. A. Pantazis, J. Benet-Buchholz, J. E. McGrady, F. Maseras, R. Vilar, *J. Am. Chem. Soc.* **2006**, *128*, 6376.
- [7] a) M. P. Gomez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby, A. H. Wright, *J. Chem. Soc. Chem. Commun.* **1985**, 1682; b) M. A. Gallop, M. P. Gomez-Sal, C. E. Housecroft, B. F. G. Johnson, J. Lewis, S. M. Owen, P. R. Raithby, A. H. Wright, *J. Am. Chem. Soc.* **1992**, *114*, 2502.
- [8] For selected reviews of μ_3 -benzene complexes, see: a) H. Wade, *Angew. Chem.* **1992**, *104*, 253; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 247; b) D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson, *Chem. Rev.* **1994**, *94*, 1585; c) H. Wade, *Coord. Chem. Rev.* **1995**, *143*, 535; for selected recent examples, see: d) A. Inagaki, Y. Takaya, T. Takemori, H. Suzuki, M. Tanaka, M. Haga, *J. Am. Chem. Soc.* **1997**, *119*, 625; e) J. P.-K. Lau, Z.-Y. Lin, W.-K. Wong, *Angew. Chem.* **2003**, *115*, 1979; *Angew. Chem. Int. Ed.* **2003**, *42*, 1935.
- [9] The bis(cycloheptatrienyl)tripalladium complex $[\text{Pd}_3(\text{C}_7\text{H}_7)_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$ was recently prepared as the first discrete trinuclear sandwich complex with a triangular arrangement of metal centers: T. Murahashi, M. Fujimoto, M. Oka, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science* **2006**, *313*, 1104.
- [10] a) T. Murahashi, N. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, *Chem. Commun.* **2000**, 1689; b) T. Murahashi, T. Uemura, H. Kurosawa, *J. Am. Chem. Soc.* **2003**, *125*, 8436; c) T. Murahashi, H. Nakashima, T. Nagai, Y. Mino, T. Okuno, M. A. Jalil, H. Kurosawa, *J. Am. Chem. Soc.* **2006**, *128*, 4377; d) Y. Tatsumi, K. Shirato, T. Murahashi, S. Ogoshi, H. Kurosawa, *Angew. Chem.* **2006**, *118*, 5931; *Angew. Chem. Int. Ed.* **2006**, *45*, 5799.
- [11] D. J. Cram, J. M. Cram, *Acc. Chem. Res.* **1971**, *4*, 204.
- [12] a) D. J. Cram, D. I. Wilkinson, *J. Am. Chem. Soc.* **1960**, *82*, 5721; b) C. Elschenbroich, R. Möckel, U. Zenneck, *Angew. Chem.* **1978**, *90*, 560; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 531; see also reference [2c].
- [13] The μ_3 coordination of [2.2]paracyclophane to Ru or Os clusters has been intensively studied by Johnson and co-workers: a) P. J. Dyson, B. F. G. Johnson, C. M. Martin, *Coord. Chem. Rev.* **1998**, *175*, 59; b) B. F. G. Johnson, C. M. Martin, P. Schooler, *Chem. Commun.* **1998**, 1239, and references therein.
- [14] Cooling a sample of **5** to –80°C did not result in any change of the ^1H NMR pattern, which shows two singlet resonances ($\delta = 6.77$ and 6.46 ppm) for the noncoordinated and coordinated phenylene rings of the [2.2]paracyclophane ligands.
- [15] a) G. A. Papoyan, K. P. Butin, R. Hoffmann, V. I. Rozenberg, *Russ. Chem. Bull.* **1998**, *47*, 153; b) A. M. Bond, P. J. Dyson, D. G. Humphrey, G. Lazarev, P. Suman, *J. Chem. Soc. Dalton Trans.* **1999**, 443.
- [16] The half-width (ω) is 9 Hz for the resonance of coordinated phenylene protons, and $\omega = 2$ Hz for that of noncoordinated phenylene protons at –80°C.
- [17] It was recently reported that benzene coordinates to $\text{Hg}_3\{\mu_3-(\eta^1:\eta^1)-\text{C}_6\text{F}_4\}_3$ by $\mu_3-(\eta^2:\eta^2:\eta^2:\eta^2:\eta^2:\eta^2)$ coordination in the crystalline state, whereby $\text{Hg}_3(\text{C}_6\text{F}_4)_3$ and benzene form infinitely stacked columns: M. Tsunoda, F. P. Gabbai, *J. Am. Chem. Soc.* **2000**, *122*, 8335.
- [18] Highly active Pd catalysts microencapsulated in polystyrene-based polymers were recently developed: K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida, S. Kobayashi, *J. Am. Chem. Soc.* **2005**, *127*, 2125, and references therein.

- [19] $[\text{Pd}_3(\text{C}_7\text{H}_7)_2(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$,^[9] which possesses two more electrons than the complex **3**, did not react with allyl chloride under the same conditions.
- [20] Complex **6'** was conveniently obtained by the one-pot reaction of **4**, [2.2]paracyclophane (5 equiv), $[\text{Pd}_2(\text{dba})_3]$ (0.5 equiv), and cot (1 equiv) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (20:1) (57 % yield of isolated product).
- [21] Crystal data for **6'**: $\text{C}_{36}\text{H}_{39}\text{Pd}_3\text{N}_3\text{B}_2\text{F}_8$, $M = 1006.53$, space group $P2_1/n$ (No. 14), $a = 11.8602(6)$, $b = 17.2197(7)$, $c = 18.153(1)$ Å, $\beta = 90.7617(7)^\circ$, $V = 3707.1(3)$ Å³, $Z = 4$, $F(000) = 1984$, $\rho_{\text{calcd}} = 1.803$ g cm⁻³, $\mu(\text{MoK}\alpha) = 15.12$ cm⁻¹, 520 variables refined with 6902 reflections with $I > 3\sigma(I)$ to $R = 0.062$. Two sets of disordered cot carbon atoms were refined isotropically with an occupancy ratio of 65/35. CCDC-643848 (**6'**) contains 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.
- [22] Because of disorder at the cot moiety, the structural parameters, and thus coordination mode of cot ligand can not be discussed herein.
- [23] Triangular M_3 complexes containing face-capping cot ligands have been reported. For early examples, see: a) B. H. Robinson, J. Spencer, *J. Organomet. Chem.* **1971**, 33, 97; b) J. L. Davidson, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc. Dalton Trans.* **1979**, 506.
- [24] Recently we reported $\mu_4-(\eta^2:\eta^2:\eta^2:\eta^2)$ -cot coordination of a rhombic Pd_4 sheet complex: T. Murahashi, N. Kato, T. Uemura, H. Kurosawa, *Angew. Chem.* **2007**, 119, 3579; *Angew. Chem. Int. Ed.* **2007**, 46, 3509.