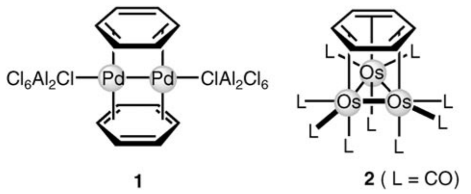
Sandwich Complexes

DOI: 10.1002/anie.200701665

Discrete Triangular Tripalladium Sandwich Complexes of Arenes**

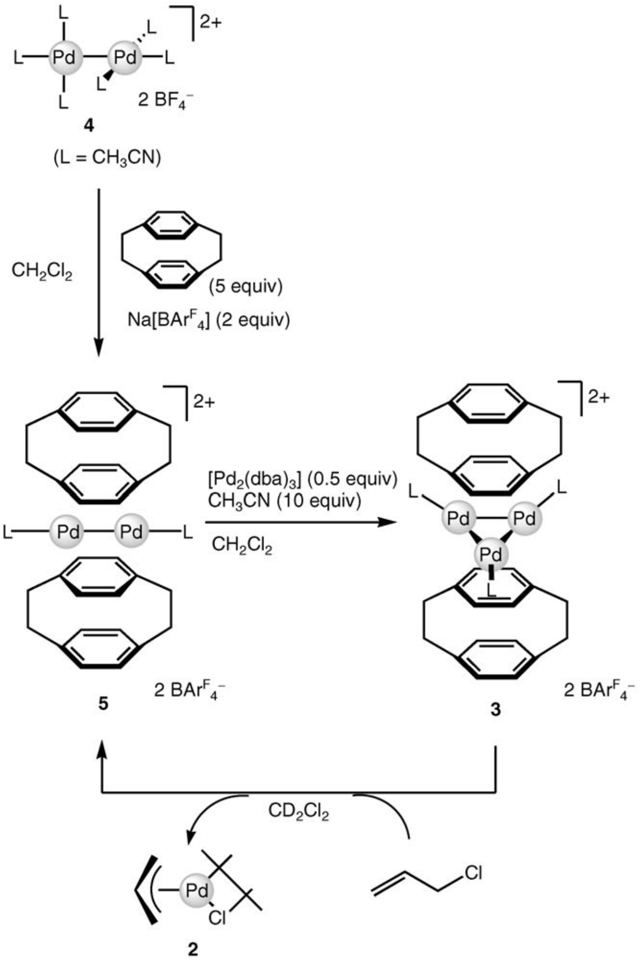
Tetsuro Murahashi, Mayu Fujimoto, Yurika Kawabata, Ryou Inoue, Sensuke Ogoshi, and Hideo Kurosawa*

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 corresponding 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 [Pd$_3$([2.2]paracyclophane)$_2$(CH$_3$CN)$_3$][BAr$^F_4$]$_2$ (**3**, BAr$^F_4$ = B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$)[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]paracyclophane and 1,3,5,7-cyclooctatetraene (cot).



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

The homoleptic acetonitrile dipalladium(I) complex [Pd$_2$(CH$_3$CN)$_6$][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]paracyclophane[11–13] was employed, however, the desired dipalladium sandwich complex [Pd$_2$([2.2]paracyclophane)$_2$(CH$_3$CN)$_2$][BAr$^F_4$]$_2$ (**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.

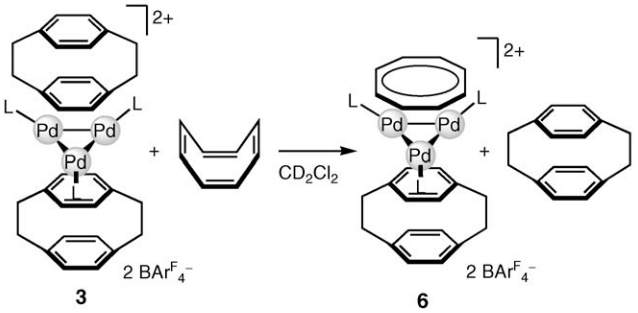
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

confirmed by elemental analysis. In the $^{13}C\{^1H\}$ NMR spectrum of **5**, resonances due to one of the two phenylene rings in the [2.2]paracyclophane ligands appeared at higher field ($\delta_{ipso} = 126.8$ ppm and $\delta_{ortho} = 115.0$ ppm) than those of the other phenylene ring ($\delta_{ipso} = 140.1$ ppm and $\delta_{ortho} = 133.5$ ppm) and of the phenylene rings in free [2.2]paracyclophane ($\delta_{ipso} = 139.8$ ppm and $\delta_{ortho} = 134.5$ 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 $[Pd_2(dba)_3]$ (0.5 equiv; dba = *trans,trans*-dibenzylideneacetone) in the presence of acetonitrile (10 equiv), the trinuclear sandwich complex $[Pd_3([2.2]paracyclophane)_2(CH_3CN)_3][BAr^F_4]_2$ (**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 $^{13}C\{^1H\}$ NMR spectrum of **3** showed upfield-shifted resonances for the coordinated phenylene ring ($\delta_{ipso} = 118.6$ ppm and $\delta_{ortho} = 93.3$ ppm) relative to those of **5**, whereas the chemical shifts of the noncoordinated phenylene rings ($\delta_{ipso} = 140.0$ ppm and $\delta_{ortho} = 133.1$ 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 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 $[Pd_3([2.2]paracyclophane)(cot)(CH_3CN)_3]X_2$ (**6**, $X = BAr^F_4$; **6′**, $X = BF_4$). 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 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)°) is slightly larger than the Pd1-Pd2-Pd3 (58.00(2)°) and Pd2-Pd3-Pd1 angles (59.35(2)°). 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



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

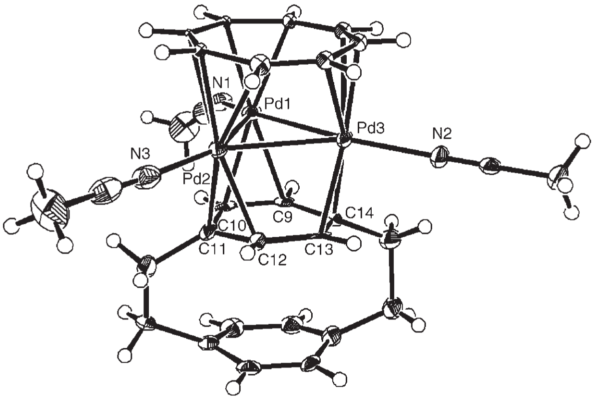


Figure 1. Molecular structure of **6′**; probability ellipsoids set at 50%; BF_4^- counterions, solvent molecule, and other set of disordered cot carbon atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.7406(8), Pd2–Pd3 2.8296(9), Pd3–Pd1 2.7016(8), Pd1–N1 2.169(8), Pd2–N3 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).

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 ^{1}H 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}C{^{1}H} NMR chemical shifts of the [2.2]paracyclophane ligand of **6** at −80 °C ($\delta_{ipso} = 89.7$ ppm, $\delta_{ortho} = 69.8$ ppm, $\delta_{ortho'} = 69.0$ ppm for coordinated phenylene; $\delta_{ipso} = 139.6$ ppm, $\delta_{ortho} = 133.2$ ppm, $\delta_{ortho'} = 133.0$ 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

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. Bleeke, 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 μ-(η^2:η^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. Rotteveel, 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. Wadepohl, *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. Wadepohl, *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 $[Pd_3(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ 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 ^{1}H 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 $Hg_3\{\mu_3\text{-}(\eta^1{:}\eta^1)\text{-}C_6F_4\}_3$ by μ_3-(η^2:η^2:η^2:η^2:η^2:η^2) coordination in the crystalline state, whereby $Hg_3(C_6F_4)_3$ 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] $[Pd_3(C_7H_7)_2(CH_3CN)_3][BF_4]_2$,[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), $[Pd_2(dba)_3]$ (0.5 equiv), and cot (1 equiv) in CH_2Cl_2/CH_3CN (20:1) (57% yield of isolated product).

[21] Crystal data for **6'**$\cdot C_6H_6$: $C_{36}H_{39}Pd_3N_3B_2F_8$, $M = 1006.53$, space group $P2_1/n$ (No. 14), $a = 11.8602(6)$, $b = 17.2197(7)$, $c = 18.153(1)$ Å, $\beta = 90.7617(7)°$, $V = 3707.1(3)$ Å^3, $Z = 4$, $F(000) = 1984$, $\rho_{calcd} = 1.803\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 15.12\ \mathrm{cm^{-1}}$, 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 μ_4-(η^2:η^2:η^2:η^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.