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Oxidative Dinuclear Addition of a Pd^I-Pd^I Moiety to Arenes: Generation of μ-η^3:η^3-Arene-Pd^{II}_2 Species

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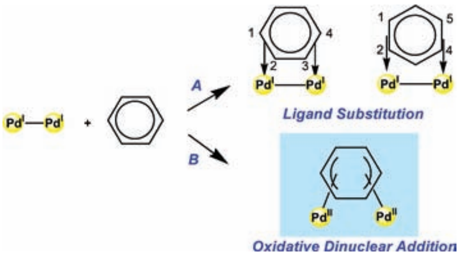
Supporting Information

ABSTRACT: We report the oxidative dinuclear addition of a Pd^I-Pd^I bond to arenes. The oxidative dinuclear addition products, which have a bi-π-allyl-type arene dipalladium(II) structure, were obtained from [2.2]paracyclophane, anthracene, tetracene, and pentacene. A systematic study of the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ with benzene and polyacenes showed that the larger polyacenes, tetracene and pentacene, afforded the oxidative dinuclear addition products, while benzene, naphthalene, and anthracene gave the π-sandwich Pd^I-Pd^I complexes.

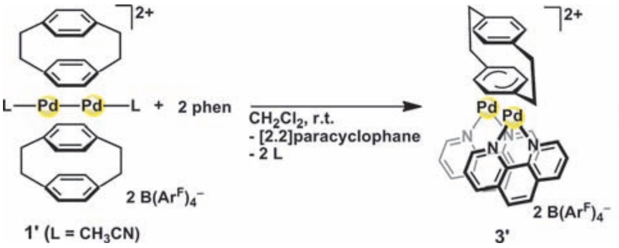
In organopalladium chemistry, arenes which lack a chelating functionality are uncommon as auxiliary ligands, mainly due to the substitutionally labile nature of arenes on a mononuclear Pd^0, Pd^{II}, or Pd^{IV} center,[1,2] while η^1- or η^2-coordination of an arene moiety in a chelating ligand has been thought to be involved in the reactions of highly active mononuclear Pd catalysts.[3−5] Recently, increasing attention has been paid to arene coordination to a Pd−Pd moiety. The arene−Pd_n ($n \geq 2$) interaction is expected to be more robust than the mononuclear arene−Pd interaction in view of the involvement of a higher number of arene carbons in the bridging coordination. In fact, several reports have shown that arenes which lack a chelating functionality are able to act as the effective binder of multiple Pd atoms.[2,6−10] As the binder of a dinuclear Pd moiety, arenes which lack a chelating functionality are known to serve as neutral π-donors to a Pd^I-Pd^I bond (Scheme 1A) to afford sandwich-type complexes, such as $Pd_2(\mu\text{-benzene})_2(ECl_4)_2$ (E = Al, Ga)[6] and $[Pd_2(\mu\text{-[2.2]paracyclophane})_2(CH_3CN)_2][B(Ar^F)_4]_2$ ($\mathbf{1'}$, Ar^F = 3,5-$(CF_3)_2C_6H_3$).[7] Herein, we report another binding mode of arene−Pd_2, namely μ-η^3:η^3-(arene)-Pd^{II}_2, via unprecedented oxidative dinuclear addition of the Pd−Pd moiety to arenes (Scheme 1B).

Scheme 1. (A) Ligand Substitution To Form μ-Arene Pd^I-Pd^I Complexes[a] and (B) Oxidative Dinuclear Addition To Form μ-Arene-Pd^{II}_2 Complexes



[a] Two representative coordination modes are shown: left, (C1,2,3,4)-coordination; right, (C1,2,4,5)-coordination.

Our group has shown that a substitutionally labile Pd^I-Pd^I complex $[Pd_2(CH_3CN)_6][BF_4]_2$ (**2**)[11] reacts with several arenes in CH_2Cl_2 or $ClCH_2CH_2Cl$ to afford di- and multinuclear sandwich complexes either with or without assistance of a Pd^0 source.[2,7,8] $\mathbf{1'}$ can be isolated by treatment of **2** with [2.2]-paracyclophane in CH_2Cl_2 in the presence of $NaB(Ar^F)_4$.[7,12] Interestingly, addition of 1,10-phenanthroline (2 equiv) to $\mathbf{1'}$ resulted in the liberation of one of the cyclophane ligands, to afford the oxidative dinuclear addition product $[Pd_2(\mu\text{-[2.2]paracyclophane})(phen)_2][B(Ar^F)_4]_2$ ($\mathbf{3'}$) in 58% yield after recrystallization (eq 1).



(1)

The structure of BF_4 salt **3** was determined by X-ray crystallographic analysis (Figure 1). The cyclophane ligand coordinates to two Pd moieties in a μ-η^3:η^3-mode. The C−C single bond character of C3−C4 and C1−C6 bonds (1.506(9) and 1.526(9) Å) is consistent with the bi-η^3-allyl structure of the coordinated phenylene moiety. Although the Pd···Pd distance in **3** (2.7789(6) Å) is within the range of normal Pd−Pd bond lengths,[13] it is attributed to the Pd^{II}_2 complexes.[14] The oxidative dinuclear addition product $\mathbf{3'}$ or **3** is stable in CD_3CN, while the π-sandwich complex $\mathbf{1'}$ released cyclophane ligands in CD_3CN.

Although **2** is poorly soluble in dichloromethane or 1,2-dichloroethane, it is fairly soluble in nitromethane, allowing us to examine the binding mode of several arenes, including fused arenes, in this solvent without addition of phenanthroline. Benzene (10 equiv) showed no sign of the formation of benzene complexes in CD_3NO_2. However, repeated precipitation from the CH_3NO_2 solution of **2** by addition of excess benzene gave the bis-benzene dipalladium sandwich complex $[Pd_2(\mu\text{-benzene})_2(CH_3CN)_2][BF_4]_2$ (**4**). **4** showed a high-field-shifted ^{13}C NMR signal at 112.9 ppm for the benzene carbons in CD_3NO_2. The

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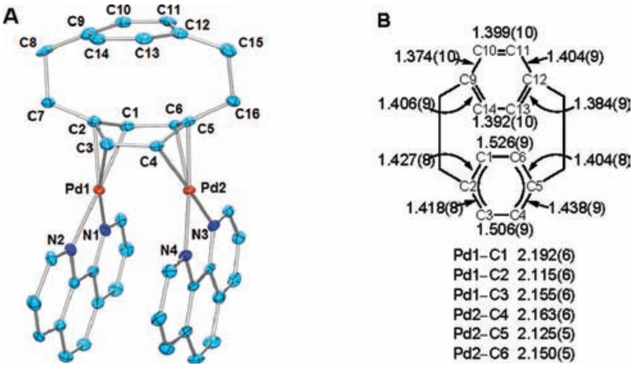
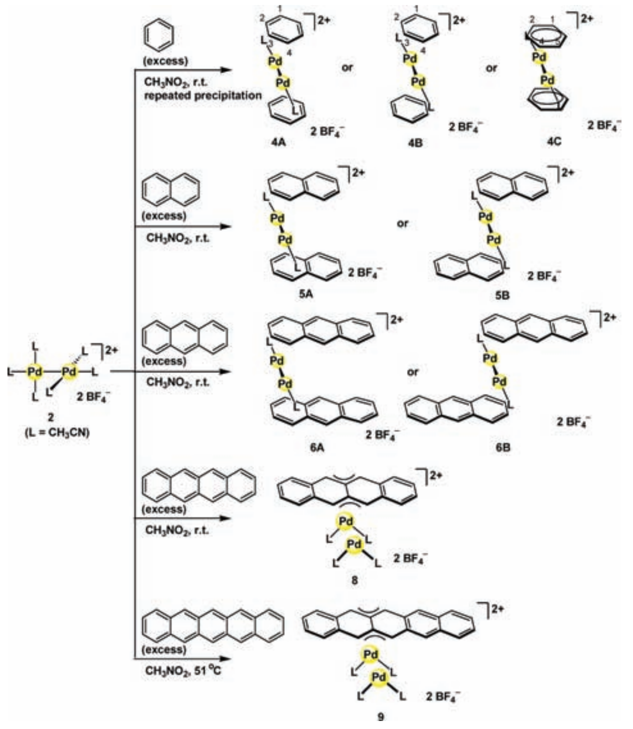


Figure 1. (A) ORTEP drawing of $[Pd_2(\mu\text{-}C_{16}H_{16})(phen)_2][BF_4]_2$ (**3**) (30% probability ellipsoids; BF_4 anions omitted for clarity). One of two independent molecules in a unit cell is shown. (B) Selected bond lengths (Å).

Scheme 2. Reactions of $[Pd_2(CH_3CN)_6][BF_4]_2$ with Benzene, Naphthalene, Anthracene, Tetracene, and Pentacene



sharp singlet ^1H NMR signal of the benzene ligands (7.35 ppm) at 25 °C was almost unchanged at −20 °C in CD_3NO_2, indicating fast fluxional behavior of the benzene ligands on the Pd−Pd moiety. Three possible structures for **4** are shown in Scheme 2 (**4A**, superposed η^2(C1,2):η^2(C3,4); **4B**, non-superposed η^2(C1,2):η^2(C3,4); **4C**, η^2(C1,2):η^2(C4,5)).[6]

The reaction of **2** with 1 equiv of naphthalene or anthracene did not afford the oxidative dinuclear addition product. Instead, it gave an equilibrated mixture of **2** and the π-sandwich complex $[Pd_2(\mu\text{-naphthalene})_2(CH_3CN)_2][BF_4]_2$ (**5**) or $[Pd_2(\mu\text{-anthracene})_2(CH_3CN)_2][BF_4]_2$ (**6**), while for anthracene, a small amount of a double sandwich complex $[Pd_2Pd_2(\mu_4\text{-anthracene})_2(CH_3CN)_4][BF_4]_4$ (**7**) was also formed (**2**/**5** = 68/32 at 25 °C; **2**/**6**/**7** = 43/55/2 at 25 °C). Yellow-orange **5** or dark purple **6** was isolated by reaction of **2** with excess naphthalene or anthracene at room temperature (Scheme 2).[15] X-ray structure analysis showed that **5** in the crystalline state has the structure **5A**, in which two μ-η^2:η^2-naphthalene ligands flanking a Pd−Pd moiety (Pd−Pd = 2.5892(7) Å) are in a superposed arrangement (Figure 2A). In solution, **5** or **6** exists as a single isomer, showing the high-field-shifted $^{13}C\{^1H\}$ NMR chemical shifts of the 1,2,3,4-carbons of naphthalene or anthracene. Dark brown **7** was isolated by treatment of **6** with **2** in CH_3NO_2, followed by evaporation under vacuum.[16] $^{13}C\{^1H\}$ NMR analysis of **7** showed that 1,2,3,4,5,6,7,8-carbons of anthracene ligands are high-field-shifted due to the involvement of these carbons in the double sandwich coordination (Scheme 3).[17,18]

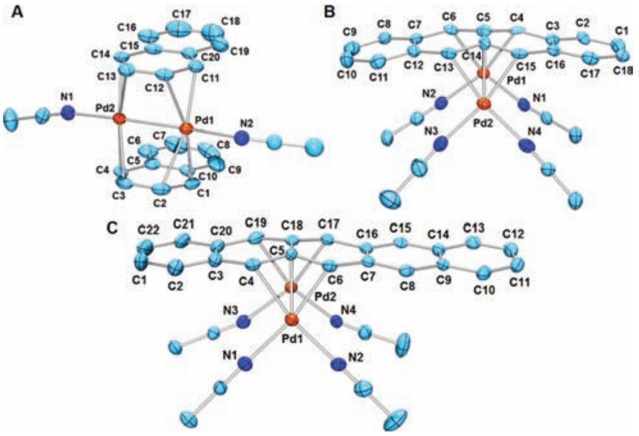
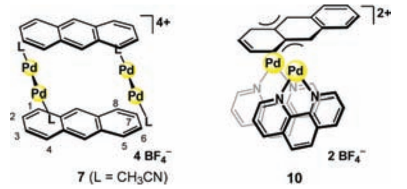


Figure 2. ORTEP drawings of (A) $[Pd_2(\mu\text{-}C_{10}H_8)_2(CH_3CN)_2][BF_4]_2$ (**5**), (B) $[Pd_2(\mu\text{-}C_{18}H_{12})(CH_3CN)_4][BF_4]_2$ (**8**; one of two independent molecules in a unit cell is shown), and (C) $[Pd_2(\mu\text{-}C_{22}H_{14})(CH_3CN)_4][BF_4]_2$ (**9**) (30% probability ellipsoids; BF_4 anions omitted for clarity).

Scheme 3. Double Sandwich Complex and Dinuclear Oxidative Addition Product of Anthracene



In contrast, treatment of **2** with tetracene at room temperature or pentacene at 51 °C afforded the yellow oxidative dinuclear addition product $[Pd_2(\mu\text{-tetracene})(CH_3CN)_4][BF_4]_2$ (**8**) or $[Pd_2(\mu\text{-pentacene})(CH_3CN)_4][BF_4]_2$ (**9**).[19,20] The structures of **8** and **9** were determined by X-ray crystallographic analyses (Figure 2B,C). In **8** or **9**, the two synfacial $Pd^{II}(CH_3CN)_2$ moieties are bound to the arene plane in a μ-η^3:η^3-coordination mode, where the Pd···Pd distance is out of the range of the normal Pd−Pd bond lengths (Pd···Pd = 3.25 Å for **8**, 3.22 Å for **9**). While **9** showed seven ^1H NMR resonances for pentacene protons at −20 °C, warming to 90 °C caused the three pairs among those resonances to coalesce (Figure S5), indicating slippage of the $[Pd(CH_3CN)_2]$ units to the neighboring sites in CD_3NO_2 solution; i.e., a slippage from the η^3(C4,5,6):η^3(C17,18,19) position in Figure 2C to the η^3(C6,7,8):η^3(C15,16,17) position. **8** and **9** are stable even in aerobic conditions. It was also confirmed that the tetracene ligand in **8** can be facilely replaced with pentacene to afford **9** by treatment of **8** with pentacene (5 equiv) in CD_3NO_2 at 80 °C.

Addition of phenanthroline (2 equiv) to the benzene or naphthalene π-sandwich complex **4** or **5** did not afford the oxidative dinuclear addition product, while the [2.2]paracyclophane analogue gave **3′** facilely as mentioned above. The distorted arene ring and the interannular interaction between two phenylene rings in the [2.2]paracyclophane ligand may contribute to the thermodynamic stability of the oxidative dinuclear addition product.[21] On the other hand, the anthracene complex **6** can be converted to oxidative dinuclear addition product $[Pd_2(\mu\text{-anthracene})(phen)_2][BF_4]_2$ (**10**) in CD_3NO_2 in 27% NMR yield. The μ-η^3:η^3-coordinated structure of **10** (Scheme 3) is consistent with the high-field-shifted ^{13}C NMR signals of the carbons involved in the η^3:η^3-coordination.[22]

Thus, the present results show that the bi-η^3-allyl-type arene dipalladium(II) species is accessible via oxidative dinuclear syn-addition of a Pd^I-Pd^I moiety. The oxidative dinuclear addition of an M−M species to mono- and polycyclic arenes has rarely been reported.[23−25] For group 10 metals, it was recently reported that a Ni^I-Ni^I moiety adds to an arene moiety of a chelating ligand 1,4-$(C_6H_4PPr^i{}_2)_2(C_6H_4)$ or 1,3,5-$(C_6H_4PPr^i{}_2)_3(C_6H_3)$ during the transmetalation or chloride addition process.[23] Several antifacial μ-η^3:η^3-arene $Ni^{II}{}_2$ or $Pt^{II}{}_2$ complexes were isolated by different routes, i.e., reduction of Ni^{II} complexes in the presence of arenes[26] or the bimolecular coupling of a cationic $ArPt^{II}$ species.[27] The facile oxidative dinuclear addition of a Pd−Pd bond to arenes is thus quite interesting.[28]

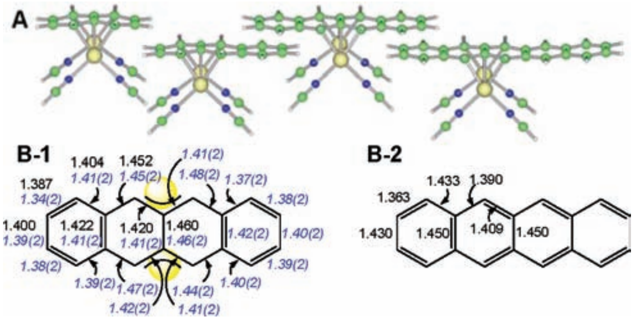
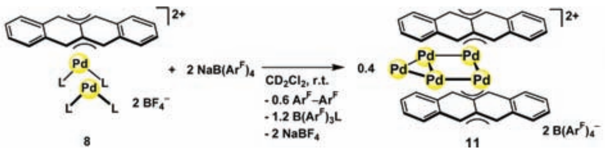


Figure 3. (A) Optimized structures of model compounds $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-polyacene})(HCN)_4]^{2+}$ (polyacene = naphthalene, anthracene, tetracene, and pentacene) at the DFT B3LYP level. (B) Calculated C−C bond lengths (Å) of the coordinated (1, black) and free tetracene (2) and experimental C−C bond lengths (Å) for **8** (1, blue).

The present results also show that increasing the number of fused rings in polyacenes affects the reaction course, yielding either sandwich complexes or oxidative dinuclear addition products. In fact, as mentioned, equimolar reactions of **2** with naphthalene and anthracene afforded not the oxidative dinuclear addition product but an equilibrium mixture of **2** and sandwich complex **5** or **6**, while those with tetracene or pentacene gave the oxidative dinuclear addition product **8** or **9**. We note that the observed trend might be related to the increasing Diels−Alder reactivity of larger polyacenes.[29] The isolobal analogy between the $[4\pi+2\pi]$ Diels−Alder reaction and the formal $[4\pi+2\sigma]$ oxidative dinuclear addition of a Pd−Pd moiety to 1,3-diene or 1,3,5-triene has been proposed by our group on the basis of the stereoretentive nature of the oxidative dinuclear addition and reductive dinuclear elimination.[11b,30] The formation of syn-adducts in the present oxidative dinuclear additions to arenes is consistent with the concerted $[4\pi+2\sigma]$ addition mechanism. The origin of the increasing Diels−Alder reactivity of larger polyacenes has been a subject of theoretical work, and it was claimed that the HOMO−LUMO gaps, ionization potentials, electron affinities, and aromaticity of the products affect the reactivity.[31] It is noted that polyacenes maintain their planarity in the oxidative dinuclear addition products in the present cases, while the Diels−Alder reactions result in bent geometry at the sp^3-carbons generated after the addition reaction. However, this does not immediately mean that the aromatic stabilization energy possessed by free polyacenes is conserved after dinuclear addition reactions. Indeed, decreased π-conjugation of the polyacene ligand compared to the free polyacene is indicated by the increase of C3−C4 (or C6−C7) bond length in the DFT-optimized dinuclear oxidative addition products $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-polyacene})(HCN)_4]^{2+}$ (polyacene = tetracene, pentacene) (Figure 3A) [1.452 Å for $[Pd_2(\mu\text{-}C_{18}H_{12})(HCN)_4]^{2+}$ vs 1.390 Å for free tetracene (Figure 3B-1,2); 1.452 and 1.450 Å for $[Pd_2(\mu\text{-}C_{22}H_{14})(HCN)_4]^{2+}$ vs 1.386 and 1.400 Å for free pentacene]. The trend of the calculated C−C lengths for $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-polyacene})(HCN)_4]^{2+}$ (polyacene = tetracene, pentacene) is consistent with the experimental C−C lengths for **8** (Figure 3B-1) or **9**. In addition, the electronic influence of the fused rings in the polyacene−Pd interactions should also be taken into consideration. Natural Population Analyses of the model compounds $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-polyacene})(HCN)_4]^{2+}$ (polyacene = naphthalene, anthracene, tetracene, pentacene) (Figure 3A) showed that there is a significant charge transfer from the polyacene ligand to the Pd moieties in each oxidative dinuclear addition product through the donating interactions,[32] where the charge transfer is more efficient for larger polyacenes (i.e., the calculated natural charge of the polyacene ligand (q_{ligand}): $q_{\text{naphthalene}}$ = +0.333; $q_{\text{anthracene}}$ = +0.397; $q_{\text{tetracene}}$ = +0.445, $q_{\text{pentacene}}$ = +0.489).[33] As was established in the (η^3-allyl)-Pd^{II} bonds, which become stronger with more-electron-donating allyl moieties,[32] the larger polyacenes with higher donating ability form stronger η^3:η^3-polyacene−$Pd^{II}{}_2$ bonds.

Finally, we note that the reaction mode of **2** with tetracene at ambient temperature affording **8** is in sharp contrast to the previously reported formation of a pentapalladium sheet complex $[Pd_5(\mu5\text{-tetracene})_2][B(Ar^F)_4]_2$ (**11**), which was obtained by reaction of **2** with tetracene in 1,2-dichloroethane under refluxing condition in the presence of $NaB(Ar^F)_4$.[2] It was confirmed that **8** can be converted to sandwich complex **11** by treatment with $NaB(Ar^F)_4$ at ambient temperature (eq 2).



(2)

In this reaction, $NaB(Ar^F)_4$ may serve as a reducing reagent to generate Pd^0 and tetracene from a portion of **8**, as indicated by the formation of a biaryl, Ar^F-Ar^F (0.69 equiv from **8** (1 equiv) after 6 days). Thus, the oxidative dinuclear addition product would behave as the intermediate in the formation of intriguing multinuclear sandwich complexes of arenes. The possible formation of Pd sheet sandwich complexes from pentacene complex **9** is now under investigation.

In summary, it has been proven that a $\mathrm{Pd^I{-}Pd^I}$ moiety undergoes oxidative dinuclear addition to arenes lacking a chelating functionality. Systematic analysis of the dipalladium complexes obtained from polyacenes showed that the reaction mode is dependent on the size of the polyacene: naphthalene and anthracene gave π-sandwich complexes, but tetracene and pentacene gave dinuclear syn-adducts. This trend is similar to the trend in the Diels−Alder reactions of polyacenes. The present results give not only a method for using arenes as auxiliary ligands for dinuclear Pd moieties but also an implication for use of a Pd−Pd moiety in activation of arenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and product characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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■ REFERENCES

(1) There are a few reports on isolation of Pd complexes bearing nonchelating arenes on a mononuclear Pd center: (a) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 294. (b) Stromnova, T. A.; Dayneko, M. V.; Churakov, A. V.; Kuz'mina, L. G.; Campora, J.; Palma, P.; Carmona, E. *Inorg. Chim. Acta* **2006**, *399*, 1613. (c) Walter, M. D.; Moorhouse, R. A.; Urbin, S. A.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131*, 9055.

(2) Murahashi, T.; Fujimoto, M.; Oka, M.; Hashimoto, Y.; Uemura, T.; Tatsumi, Y.; Nakao, Y.; Ikeda, A.; Sakaki, S.; Kurosawa, H. *Science* **2006**, *313*, 1104.

(3) (a) Barder, T.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685. (b) Barder, T. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 12003.

(4) (a) Lloyd-Jones, G. C.; Stephen, S. C.; Murray, M.; Butts, C. P.; Vyskocil, S.; Kocovsky, P. *Chem.—Eur. J.* **2000**, *6*, 4348. (b) Kumar, P. G. A.; Dotta, P.; Hermatschweiler, R.; Pregosin, P. S. *Organometallics* **2005**, *24*, 1306.

(5) (a) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreno, E.; Pregosin, P. S. *J. Am. Chem. Soc.* **2002**, *124*, 4336. (b) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323.

(6) (a) Allegra, G.; Casagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289. (b) Gorlov, M.; Fischer, A.; Kloo, L. *Inorg. Chim. Acta* **2003**, *350*, 449. (c) Gorlov, M.; Fischer, A.; Kloo, L. *Inorg. Chim. Acta* **2009**, *362*, 605. (d) Akerstedt, J.; Gorlov, M.; Fischer, A.; Kloo, L. *J. Organomet. Chem.* **2010**, *695*, 1513.

(7) Murahashi, T.; Fujimoto, M.; Kawabata, Y.; Inoue, R.; Ogoshi, S.; Kurosawa, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5440.

(8) (a) Murahashi, T.; Uemura, T.; Kurosawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 8436. (b) Murahashi, T.; Kato, N.; Uemura, T.; Kurosawa, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 3509.

(9) (a) Barder, T. E. *J. Am. Chem. Soc.* **2006**, *128*, 898. (b) Christmann, U.; Pantazis, D. A.; Benet-Buchholz, J.; McGrady, J. E.; Maseras, F.; Vilar, R. *J. Am. Chem. Soc.* **2006**, *128*, 6376.

(10) (a) Dupont, J.; Pfeffer, M.; Rotieveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116. (b) Dotta, P.; Kumar, P. G. A.; Pregosin, P. S. *Organometallics* **2004**, *23*, 4247.

(11) (a) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *Chem. Commun.* **2000**, 1689. (b) Murahashi, T.; Nakashima, H.; Nagai, T.; Mino, Y.; Okuno, T.; Jalil, M. A.; Kurosawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 4377.

(12) The structure of **1′** has not been determined by X-ray crystallographic analysis. In eq 1, one possible structure, a superimposed η^2(C1,2):η^2(C3,4) sandwich coordination, is shown.

(13) The $d^8{-}d^8$ $\mathrm{Pd^{II}{-}Pd^{II}}$ interaction with a Pd−Pd distance comparable to that in **3** is known: Bercaw, J. E.; Durrell, A. C.; Gray, H. B.; Green, J. C.; Hazari, N.; Labinger, J. A.; Winkler, J. R. *Inorg. Chem.* **2010**, *49*, 1801 and references therein.

(14) Another formal oxidation state $\mathrm{Pd^0_2}$ is also possible when the arene ligand is attributed to the dication.

(15) **5** and **6** in either structure **A** or **B** (Scheme 2) would have shown a dynamic behavior probably due to the sliding of naphthalene or anthracene ligands (see Figures S1 and S2 for VT ^{1}H NMR spectra).

(16) CH_3CN was removed by evaporation under vacuum from CH_3NO_2, with a higher b.p. than CH_3CN, in order to shift the equilibrium to the formation of **7** and make its isolation easier.

(17) (a) Schneider, J. J.; Wolf, D.; Lehmann, C. W. *Inorg. Chim. Acta* **2003**, *350*, 625. (b) Woolf, A.; Chaplin, A. B.; McGrady, J. E.; Alibadi, M. A. M.; Rees, N.; Draper, S.; Murphy, F.; Weller, A. S. *Eur. J. Inorg. Chem.* **2011**, 1614.

(18) The naphthalene sandwich complex **5** did not afford the corresponding double sandwich complex by similar treatment with **2**.

(19) The solubility of tetracene and pentacene in CH_3NO_2 is low.

(20) In ^{1}H NMR monitoring of the reaction of **2** and tetracene or pentacene in CD_3NO_2 at ambient temperature, another product showing a signal pattern similar to that of **8** or **9** was observed in the initial stage. The final product was **8** or **9**.

(21) (a) Papoyan, G. A.; Butin, K. P.; Hoffmann, R.; Rozenberg, V. I. *Russ. Chem. Bull.* **1998**, *47*, 153. (b) Bond, A. M.; Dyson, P. J.; Humphrey, D. G.; Lazarev, G.; Suman, P. *J. Chem. Soc., Dalton Trans.* **1999**, 443.

(22) The syn product is shown for **10** in Scheme 3. However, the anti dinuclear addition structure cannot be ruled out at this stage.

(23) (a) Verian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296. (b) Chao, S. T.; Lara, N. C.; Lin, S.; Day, M. W.; Agapie, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 7529.

(24) Begley, M. J.; Puntambekar, S. G.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1251.

(25) Jones, C.; McDyre, L.; Murphy, D. M.; Stasch, A. *Chem. Commun.* **2010**, *46*, 1511.

(26) (a) Schneider, J. J.; Wolf, D.; Denninger, U.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1999**, *579*, 139. (b) Bai, G.; Wei, P.; Stephen, D. W. *Organometallics* **2005**, *24*, 5901.

(27) (a) Konze, W. V.; Scott, B. L.; Kubas, G. *J. Am. Chem. Soc.* **2002**, *124*, 12550. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870.

(28) Selected examples of μ-η^3:η^3-arene dinuclear complexes of other metals: (a) Jonas, K.; Koepe, G.; Schieferstein, L.; Mynott, R.; Kruger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed.* **1983**, *22*, 620. (b) Muller, J.; Gaede, P. E.; Quiao, K. *Angew. Chem., Int. Ed.* **1993**, *32*, 1697. (c) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600. (d) Blake, A. J.; Dyson, P. J.; Ingham, S. L.; Johnson, B. F. G.; Martin, C. M. *Organometallics* **1995**, *14*, 862.

(29) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163.

(30) (a) Murahashi, T.; Nagai, T.; Nakashima, H.; Tomiyasu, S.; Kurosawa, H. *Chem. Lett.* **2006**, *35*, 754. (b) Murahashi, T.; Kato, N.; Ogoshi, S.; Kurosawa, H. *J. Organomet. Chem.* **2008**, *693*, 894.

(31) (a) Schleyer, P. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643. (b) Cheng, M.-F.; Li, W.-K. *Chem. Phys. Lett.* **2003**, *368*, 630.

(32) Sakaki, S.; Takeuchi, K.; Sugimoto, M.; Kurosawa, H. *Organometallics* **1997**, *16*, 2995.

(33) Ionization potentials of polyacenes are in the following order: naphthalene > anthracene > tetracene > pentacene. Chen, E. S.; Chen, E. C. M.; Sane, N.; Talley, L.; Kozanecki, N.; Shulze, S. *J. Chem. Phys.* **1999**, *110*, 9319.