A stable zerovalent palladium chain enveloped by a π-electron sheath of conjugated polyene ligands†

Yasuki Tatsumi, Tetsuro Murahashi,* Mitsue Okada, Sensuke Ogoshi and Hideo Kurosawa

Received (in Cambridge, UK) 20th September 2007, Accepted 31st October 2007
First published as an Advance Article on the web 13th November 2007
DOI: 10.1039/b714530f

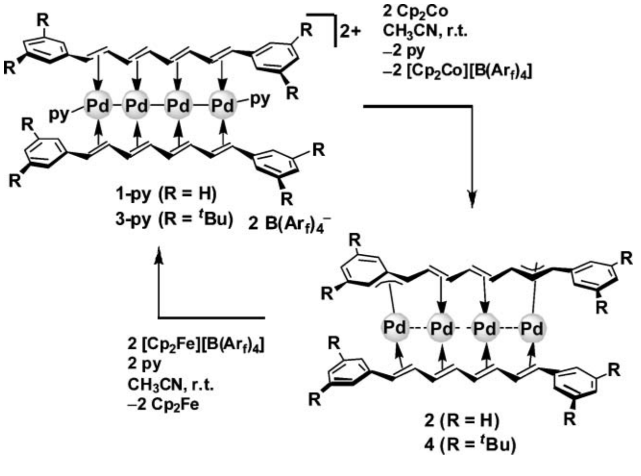
A surprisingly stable homoleptic $Pd^0{}_4$ chain complex of non-activated olefins was isolated and structurally characterized by X-ray crystallographic analysis, and the unique structure and bonding are compared to those of the corresponding dicationic $[Pd_4]^{2+}$ chain sandwich complex.

Small Pd clusters have been proposed to act as the active catalytic species by themselves or the source of mononuclear Pd^0 species in heterogeneous Pd catalyzed reactions.[1] However, it has not been understood how small aggregates of Pd^0 atoms are stabilized in the absence of strong π-acceptor ligands such as CO, isocyanide, or electron-deficient olefin ligands.[2] Actually, without such strong π-acceptor ligands, only a limited number of polynuclear Pd^0 complexes with intermetallic distances close to that of bulk Pd metal (2.76 Å) have been isolated; *e.g.* $Pd_2(Cy_2P(CH_2)_2PCy_2)_2$ (Pd–Pd = 2.761 Å).[3,4] In light of the fact that graphenes or other sp^2-carbon frameworks are widely used as the catalyst support for palladium, "non-activated" olefins and arenes[5] may be capable of stabilizing small Pd^0 clusters. However, this has not been proven at the molecular level. Indeed, the corresponding homoleptic mononuclear Pd^0 complexes such as Pd(1,6-cyclooctadiene)$_2$ and Pd(norbornene)$_3$ are thermally unstable, and usually decompose in solution at around ambient temperature.[6,7] Herein, we report the isolation and structural characterization of a surprisingly stable homoleptic olefin Pd^0 cluster in which "non-activated" conjugated polyene ligands flank a linear array of Pd^0 atoms with Pd–Pd separations shorter than 2.7 Å. The bonding nature of the unique Pd^0 cluster was studied using quantum calculations.

Our group recently reported that a dicationic palladium chain or sheet, which is generally formulated as $[Pd_n]^{2+}$, can be formed and stabilized between parallel π-conjugated polyenes or aromatic hydrocarbons in a discrete complex.[8,9] Typically, a stable sandwich chain complex $[Pd_n(\alpha,\omega\text{-diphenylpolyene})_2]^{2+}$ (n = 3–5) is obtained from a dicationic precursor $[PdL_4]^{2+}$ or $[Pd_2L_6]^{2+}$ (L = CH_3CN) and a Pd^0 complex in the presence of α,ω-diphenylpolyene ligands.[8] On the other hand, the polyene-polypalladium(0) complexes were not formed from a mixture of the Pd^0 complex $Pd_2(dba)_3$ and α,ω-diphenylpolyenes. A recent theoretical study showed that the dicationic charge is important in maintaining the high stability of sandwich chain complexes where charge delocalization over the Pd chain as well as over the polyene ligands takes place.[8g]

Interestingly, treatment of the $[Pd_4]^{2+}$ complex $[Pd_4(\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^2{:}\eta^3\text{-DPOT})_2][B(Ar_f)_4]_2$ (DPOT = 1,8-diphenyl-1,3,5,7-octatetraene and $B(Ar_f)_4$ = $B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$) (**1**)[8a] or $[Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-DPOT})_2(py)_2][B(Ar_f)_4]_2$ (**1-py**)[8a] with Cp_2Co (2 equiv.) in CH_3CN gave a brown precipitate **2**, which is insoluble in most organic solvents. The composition of **2** was confirmed as "$Pd_4(DPOT)_2$" by the elemental analysis. Oxidation of **2** with $[Cp_2Fe][B(Ar_f)_4]$ (2 equiv.)[10] in the presence of pyridine gave **1-py** almost quantitatively. The reduction of $[Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}{}^t\text{Bu-DPOT})_2(py)_2][B(Ar_f)_4]_2$ (**3-py**, ^{t}Bu-DPOT = 1,8-bis(3,5-di-*t*-Bu)phenyl-1,3,5,7-octatetraene) gave complex **4** which is soluble in benzene or THF (Scheme 1). It was confirmed that oxidation of **4** with $[Cp_2Fe][B(Ar_f)_4]$ (2 equiv.) in the presence of pyridine gave **3-py** almost quantitatively.

The molecular structure of **4** was determined from X-ray crystallographic analysis (Fig. 1).‡ The Pd_4 chain is retained in **4**. The Pd–Pd distances (Pd1–Pd2 = 2.6272(8) Å, Pd2–Pd3 = 2.6048(7) Å, Pd3–Pd4 = 2.6662(8) Å) are shorter than the Pd–Pd distance in bulk Pd metal (2.76 Å) or those in the $[Pd_4]^{2+}$ complexes **3-py(BF$_4$)** (2.7580(2) Å, 2.7448(2) Å)[11] and **1** (2.7322(8) Å, 2.654(1) Å).[8a] The linear $Pd^0{}_n$ ($n > 2$) chain cluster with Pd–Pd separation shorter than 2.7 Å is unprecedented.[12] Interestingly, two ^{t}Bu-DPOT ligands in **4** coordinate to the Pd_4 chain in different coordination modes: *i.e.* μ_4-$\eta^3{:}\eta^2{:}\eta^2{:}\eta^3$ and μ_4-$\eta^2{:}\eta^2{:}\eta^2{:}\eta^2$ modes. On the other hand, in the dicationic complexes, the two 1,8-diaryltetraene ligands bind a $[Pd_4]^{2+}$ chain in an identical mode: μ_4-$\eta^3{:}\eta^2{:}\eta^2{:}\eta^3$-mode to the $[Pd_4]^{2+}$ chain in the absence of capping ligands at the Pd chain ends, or



Scheme 1

Department of Applied Chemistry, Osaka University, & PRESTO, Japan Science and Technology Agency (JST), Suita, Osaka, 565-0871, Japan. E-mail: tetsu@chem.eng.osaka-u.ac.jp; Fax: (+81)6 6879 7394; Tel: (+81)6 6879 7374

† Electronic supplementary information (ESI) available: Experimental details of the preparation and characterization of **2**, **3-py**, **4** and **4′**, details of the X-ray single crystal structural analyses for **4** and **3-py(BF$_4$)**, and computational details. See DOI: 10.1039/b714530f

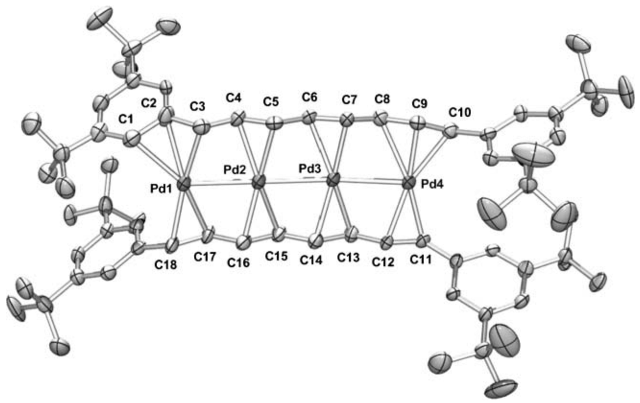


Fig. 1 ORTEP drawing of **4** (50% probability thermal ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity). Selected bond lengths (Å) and angles (°): Pd1–Pd2 2.6272(8), Pd2–Pd3 2.6048(7), Pd3–Pd4 2.6662(8), Pd1–C1 2.413(9), Pd1–C2 2.311(11), Pd1–C3 2.175(8), Pd1–C18 2.206(8), Pd1–C17 2.223(7), Pd2–C4 2.227(10), Pd2–C5 2.192(8), Pd2–C16 2.152(9), Pd2–C15 2.205(8), Pd3–C6 2.232(10), Pd3–C7 2.187(8), Pd3–C14 2.173(9), Pd3–C13 2.207(8), Pd4–C8 2.358(10), Pd4–C9 2.122(8), Pd4–C10 2.250(7), Pd4–C12 2.155(7), Pd4–C11 2.169(8), Pd1–Pd2–Pd3 176.33(2), Pd2–Pd3–Pd4 176.00(3).

μ_4-η^2:η^2:η^2:η^2-mode in the presence of capping ligands. Thus, during the reduction, the pyridine ligands dissociate and one of the ^{t}Bu-DPOT ligands slips on the Pd_4 chain by changing the hapticity, stabilizing the formally zerovalent Pd_4 chain. It is noticeable that the total electron counting for **4** (58 e) is the same as that for the dicationic complexes **1**, **1-py**, and **3-py**.

Complex **4** isomerized slowly to **4′** at 25 °C under N_2 atmosphere within 2 days. The isomerization was promoted by the presence of free ^{t}Bu-DPOT (1 h at 20 °C). The structure of the isomer **4′** is assumed to be the eclipsed sandwich with respect to the zigzag polyene part of ^{t}Bu-DPOT ligands.[13,14] No decomposition of **4′** was observed even upon heating to 95 °C in toluene-d_8 under N_2 atmosphere, while complex **4** or **4′** is air-sensitive.[15] Such a high thermal stability of **4** is surprising because known homoleptic "non-activated" olefin Pd^0 complexes decompose in solution upon heating.

Obvious differences in the reactivity toward electrophilic substrates was observed between lower valent **4** and higher valent **3-py**, **1-py**, or **1**. Complex **4** reacted with dibenzylideneacetone (dba) or allyl chloride immediately to form $Pd_2(dba)_3$ or $[Pd(\eta^3\text{-allyl})Cl]_2$. On the other hand, **3-py**, **1-py**, or **1** did not react with these substrates under the same conditions. These results in reactivity emphasize the zerovalent character of the palladium chain in **4**.

To gain an insight into the bonding of **4**, we carried out quantum calculations at the MP2 level on the model compound $Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_8H_{10})(\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^2{:}\eta^3\text{-}C_{10}H_{12})$.[16] The optimized geometry agrees well with the structure of **4**, where calculated Pd–Pd distances are 2.65 Å for outer bonds and 2.59 Å for inner. Natural charge analysis shows that the Pd_4 moiety possesses a considerable positive charge (+1.68), and the negative charge is shared by the C_8H_{10} ligand (−0.83) and $C_{10}H_{12}$ ligand (−0.85). The polyene ligands in the corresponding dicationic model $[Pd_4(\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^2{:}\eta^3\text{-}C_{10}H_{12})_2]^{2+}$ are charged positively (+0.21 for each), while the dominant positive charge is located on the Pd_4 moiety (+1.57). For another dicationic model $[Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_8H_{10})_2(py)_2]^{2+}$, the polyene ligands are nearly neutral (−0.08 for each), while positive charge is mainly on the Pd_4 moiety (+1.83). Thus, the wide range of charge capacities for the π-conjugated polyene from negative to positive values is important in stabilizing the Pd chain in different oxidation states. The MO analysis showed that back-donating interactions from the bonding dπ orbital to the tetraene LUMO and from the antibonding dσ orbital to the pentaene LUMO are responsible for the bonding between the polyene ligand and the polypalladium moiety in $Pd_4(C_8H_{10})(C_{10}H_{12})$ (Scheme 2). However, these interactions do not cause a direct Pd–Pd interaction;[4,17] Wiberg bond indices (WBIs)[18] (0.095 for the inner Pd–Pd and zero for the outer Pd–Pd) are much smaller than those for the corresponding dicationic model compounds.[19]

Scheme 2 **A**: Back-donating interactions between the tetraene LUMO and bonding dπ orbital; **B**: Back-donating interactions between pentaene LUMO and antibonding dσ orbital.

In summary, the homoleptic Pd^0 cluster of a "non-activated" olefin was isolated for the first time. The surprisingly stable structure is mainly due to the variable hapticity as well as the charge capacity of the conjugated polyene ligands. The present results provide molecular evidence of the concept that sp^2-carbon frameworks could serve as excellent supports for small *zerovalent* Pd clusters. Further study on the π-complexes of Pd^0 clusters is now underway in our laboratory.

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. Y. T. thanks the research fellowships for young scientists from the Japan Society for the Promotion of Science (JSPS).

Notes and references

‡ Crystal data for **4**: $C_{78}H_{111}NOPd_4$, $M_r = 1504.34$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.8260(5)$, $b = 15.3256(5)$, $c = 18.6303(5)$ Å, $\alpha = 71.3570(8)°$, $\beta = 83.1230(9)°$, $\gamma = 71.5490(9)°$, $V = 3547.44(19)$ Å^3, $Z = 2$, $F(000) = 1556$, $D_c = 1.408$ g cm^{-3}, μ(Mo Kα) = 10.414 cm^{-1}, $T = 123$ K, 44 531 reflections collected, 21 391 unique ($R_{int} = 0.072$), 797 variables refined with 11 296 reflections with $I > 2\sigma(I)$ to $R1 = 0.099$. CCDC 661329. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b714530f

1 For selected recent reviews: (*a*) D. Astruc, *Inorg. Chem.*, 2007, **46**, 1884; (*b*) A. M. Trzeciak and J. Ziolkowski, *Coord. Chem. Rev.*, 2007, **251**, 1281; (*c*) J. G. de Vries, *Dalton Trans.*, 2006, 421; (*d*) M. T. Reetz and J. G. de Vries, *Chem. Commun.*, 2004, 1559.

2 Most of the previously isolated molecular Pd^0 clusters are stabilized by the bridging coordination of strong π-acceptor ligands such as CO and isocyanides. For a review: A. D. Burrows and D. M. P. Mingos, *Transition Met. Chem. (Dordrecht, Neth.)*, 1993, **18**, 129 and references therein.

3 (*a*) Y. Pan, J. T. Mague and M. J. Fink, *J. Am. Chem. Soc.*, 1993, **115**, 3842; (*b*) A. Döhring, R. Goddard, G. Hopp, P. W. Jolly, N. Kokel and C. Krüger, *Inorg. Chim. Acta*, 1994, **222**, 179; (*c*) R. A. Klein, P. Witte, R. van Belzen, J. Fraanje, K. Goubitz, M. Numan, H. Schenk, J. M. Ernsting and C. J. Elsevier, *Eur. J. Inorg. Chem.*, 1998, 319.

4 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.

5 The term "non-activated" olefin is used for an olefin containing no strong electron-withdrawing substituents.

6 (*a*) M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1975, 449; (*b*) M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 271; (*c*) J. Krause, G. Cestaric, K.-J. Haack, K. Seevogel, W. Storm and K.-R. Pörschke, *J. Am. Chem. Soc.*, 1999, **121**, 9807; (*d*) M. Schwalbe, D. Walther, H. Schreer, J. Langer and H. Görls, *J. Organomet. Chem.*, 2006, **691**, 4868.

7 The Pd^0 complexes of "activated" olefins, such as $Pd_2(dba)_3$ (dba = dibenzylideneacetone), are stable even under heating.

8 (*a*) T. Murahashi, E. Mochizuki, Y. Kai and H. Kurosawa, *J. Am. Chem. Soc.*, 1999, **121**, 10660; (*b*) T. Murahashi, Y. Higuchi, T. Katoh and H. Kurosawa, *J. Am. Chem. Soc.*, 2002, **124**, 14288; (*c*) T. Murahashi, T. Uemura and H. Kurosawa, *J. Am. Chem. Soc.*, 2003, **125**, 8436; (*d*) Y. Tatsumi, T. Nagai, H. Nakashima, T. Murahashi and H. Kurosawa, *Chem. Commun.*, 2004, 1430; (*e*) T. Murahashi, H. Nakashima, T. Nagai, Y. Mino, T. Okuno, M. A. Jalil and H. Kurosawa, *J. Am. Chem. Soc.*, 2006, **128**, 4377; (*f*) Y. Tatsumi, K. Shirato, T. Murahashi, S. Ogoshi and H. Kurosawa, *Angew. Chem., Int. Ed.*, 2006, **45**, 5799; (*g*) P. Lebéguerie, M. Bénard and M.-M. Rohmer, *Inorg. Chem.*, 2007, **46**, 5283.

9 (*a*) T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki and H. Kurosawa, *Science*, 2006, **313**, 1104; (*b*) T. Murahashi, N. Kato, T. Uemura and H. Kurosawa, *Angew. Chem., Int. Ed.*, 2007, **46**, 3509; (*c*) T. Murahashi, M. Fujimoto, Y. Kawabata, R. Inoue, S. Ogoshi and H. Kurosawa, *Angew. Chem., Int. Ed.*, 2007, **46**, 5440.

10 I. Chávez, A. Alvarez-Carene, E. Molins, A. Roig, W. Maniukiewicz, A. Arancibia, V. Arancibia, H. Brand and J. M. Manriquez, *J. Organomet. Chem.*, 2000, **601**, 126.

11 The structure of $[Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}{}^t\text{Bu-DPOT})_2(py)_2][BF_4]_2$ (**3-py(BF$_4$)**) was characterized by X-ray structure analysis. CCDC 661330. See ESI†.

12 The known $Pd^0{}_4$ clusters are tetrahedral $[Pd_4(CO)_6(P^nBu_3)_4]$, distorted tetrahedral $[Pd_4(CO)_5(PR_3)_4]$ ($PR_3 = PPh_3$ or PPh_2Me), or butterfly $[Pd_4(SO_2)_3(CH_3CN)(PPh_3)_4]$. (*a*) E. G. Mednikov, N. K. Eremenko, S. P. Gubin, Y. L. Slovokhotov and Y. T. Struchkov, *J. Organomet. Chem.*, 1982, **239**, 401; (*b*) J. Dubrawski, J. C. Kriege-Simondsen and R. D. Feltham, *J. Am. Chem. Soc.*, 1980, **102**, 2089; (*c*) R. D. Feltham, G. Elbaze, R. Ortega, C. Eck and J. Dubrawski, *Inorg. Chem.*, 1985, **24**, 1503; (*d*) A. D. Burrows, J. C. Machell and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1992, 1991.

13 The presence of two isomers for the dicationic polyene-polypalladium complexes is due to the two stacking modes of the zigzag polyenes. See ref. 8*b*.

14 The ^1H or $^{13}C\{^1H\}$ NMR signal pattern of **4′** is similar to that of **4**. ^1H NMR spectra of **4** or **4′** were temperature dependent due to the dynamic sliding behavior of the ^{t}Bu-DPOT ligands on the Pd_4 chain. In THF-d_8 (25 °C) or toluene-d_8 at 25–95 °C, complex **4** exhibited one set of 8 olefin proton resonances for the two ^{t}Bu-DPOT ligands. ^1H NMR (C_6D_6, 25 °C) of the *–(CH=CH)$_4$–* part of **4**: $\delta = 5.11$ (1H, d, $J = 12.7$ Hz), 4.34 (1H, t, $J = 11.8$ Hz), 3.74 (1H, d, $J = 12.5$ Hz), 3.57 (1H, t, $J = 11.6$ Hz), 2.33 (1H, t, $J = 12.2$ Hz), 2.28 (1H, t, $J = 12.3$ Hz), 1.55 (2H, overlapped). Cooling the THF-d_8 solution sample down to −105 °C resulted in decoalescence of these resonances. Although we are unable to obtain well-characterized resonances at temperatures lower than −105 °C, the spectral aspects suggest occurrence of synchronous sliding of the ^{t}Bu-DPOT ligands ($\eta^3{:}\eta^2{:}\eta^2{:}\eta^3 \rightarrow \eta^2{:}\eta^2{:}\eta^2{:}\eta^2$ and $\eta^2{:}\eta^2{:}\eta^2{:}\eta^2 \rightarrow \eta^3{:}\eta^2{:}\eta^2{:}\eta^3$) where the relative direction of these two slidings is either parallel or antiparallel without intercrossing of the two different directional movements. For details of the proposed dynamic behavior, see ESI†.

15 The complex **4** or **4′** gradually decomposed in C_6D_6 under air within 10 h to unidentified products. In contrast, the dicationic complex **3-py** is air-stable even in solution.

16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

17 The d^{10}–d^{10} interactions in $Pt_2(PH_3)_4$ and $Pd_2(PH_3)_4$ were theoretically investigated: (*a*) A. Dedieu and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2074; (*b*) S. Sakaki, M. Ogawa and Y. Musashi, *J. Phys. Chem.*, 1995, **99**, 17134.

18 K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

19 For $[Pd_4(C_{10}H_{12})_2]^{2+}$: WBI = 0.269 for the inner Pd–Pd; WBI = 0.096 for the outer Pd–Pd. For $[Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_8H_{10})_2(py)_2]^{2+}$: WBI = 0.269 for the inner Pd–Pd; WBI = 0.315 for the outer Pd–Pd.