

Remarkably Wide Range of Bond Distance Adjustment of d⁹–d⁹ Pd–Pd Interactions to Change in Coordination Environment

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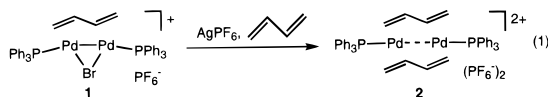
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The bond order, bond strength, and bond distance of metal–metal interactions, which are key factors in designing multi-metallic catalyses or polymetallic functional materials,¹ depend on not only the d-electron configuration of each metal but also the electronic and steric properties of the auxiliary ligands.² With regard to d⁹–d⁹ M₂L₆ complexes,³ the M–M length is expected to be especially variable with even a small change in ligand steric and/or electronic requirements, because of its single bond-order nature,^{2c} but there have been no precedents to demonstrate this expectation. We report here that, when sandwiched between two *s-trans*-1,3-diene ligands, the Pd(I)–Pd(I) bond can be elongated to an unprecedented length (3.19 Å) for an open bi-square planar L₃–Pd–Pd–L₃ complex.

A diamagnetic, sandwich-type bis-1,3-butadiene dipalladium complex **2** (a mixture of two isomers in solution, possibly *meso* and *racemic* arising from chiral mode of Pd₂–(*s-trans*-diene) association; major/minor = 75/25 in CDCl₃ at 25 °C)⁴ was prepared from the cationic complex **1**⁵ as yellow crystals in 50% yield (eq 1).



The X-ray analysis⁶ (Figure 1) of **2** showed the *meso* arrangement of two *s-trans*-dienes with C–C distances (1.37(1) Å {1.33–(1) Å} and 1.41(1) Å) being within the range of those for μ - η^2 : η^2 -1,3-diene ligands of dinuclear complexes of late transition

(1) Selected recent examples: (a) Matthews, R. C.; Howell, D. K.; Peng, W.-J.; Laneman, S. A.; Stanley, G. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2253 and references therein. (b) Finnis, G. M.; Canadell, E.; Campana, C.; Dunbar, K. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2772 and references therein.

(2) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, New York, 1993. (b) Mingos, D. M. P.; May, A. S., In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 2. (c) Boeyens, J. C. A.; Cotton, F. A.; Han, S. *Inorg. Chem.* **1985**, *24*, 1750.

(3) (a) Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543. (b) Kostic, N. M.; Fenske, R. F. *Inorg. Chem.* **1983**, *22*, 666. (c) Harvey, P. D.; Murtaza, Z. *Inorg. Chem.* **1993**, *32*, 4721 and references therein. (d) Provencher, R.; Harvey, P. D. *Inorg. Chem.* **1996**, *35*, 2113. (e) Sakaki, S.; Takeuchi, K.; Sugimoto, M.; Kurosawa, H. *Organometallics* **1997**, *16*, 2995. (f) Sugimoto, M.; Horiuchi, F.; Sakaki, S. *Chem. Phys. Lett.* **1997**, *274*, 543.

(4) The identity of major and minor isomers was not determined. Major: ¹H NMR (CDCl₃) δ 7.7–7.5 (PPh₃), 4.84 (br d, *cis*-CH₂), 3.42 (br d, *trans*-CH₂), 2.71 (br m, CH), ¹³C NMR (CDCl₃ with the aid of C–H COSY) δ 134.04–129.78 (Ph), 89.16 (CH), 78.40 (CH₂), ³¹P NMR (CDCl₃) δ –111.38 (s). Minor: ¹H NMR (CDCl₃) δ 7.7–7.5 (PPh₃), 4.54 (br d, *cis*-CH₂), 3.26 (br d, *trans*-CH₂), 2.82 (br m, CH), ¹³C NMR (CDCl₃) δ 134.04–129.78 (Ph), 90.07 (CH), 75.99 (CH₂), ³¹P NMR (CDCl₃) δ –112.56 (s). Anal. Calcd (found) for C₄₄H₄₂P₄F₁₂Pd₂: C, 46.54 (46.30); H, 3.73 (3.79).

(5) Murahashi, T.; Kanehisa, N.; Kai, Y.; Otani, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1996**, 825.

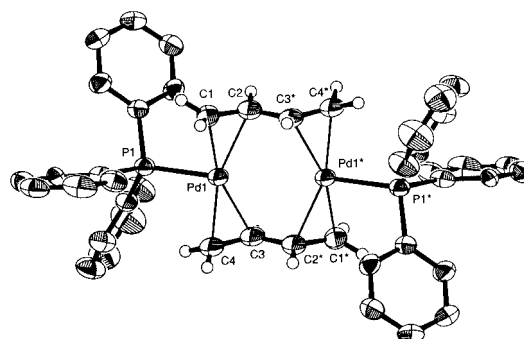


Figure 1. ORTEP drawing of **2**. Selected bond distances (Å) and angles (deg): Pd1–Pd1*, 3.1852(6); Pd1–P1, 2.3060(9); Pd1–C1, 2.154(4); Pd1–C2, 2.264(4); Pd1–C3, 2.305(4); Pd1–C4, 2.170(4); C1–C2, 1.368–(7); C2–C3*, 1.410(6); C3–C4, 1.331(7); Pd1*–Pd1–P1, 163.46(3); C1–C2–C3*, 125.4(5); C2–C3*–C4*, 126.9(5).

metals,⁷ and these were bound to Pd–Pd through π -bonding distances (2.15(1) Å {2.17(1) Å} and 2.26(1) Å {2.30(1) Å}). The P1–Pd1–Pd1*–P1* skeleton forms a zigzag structure on the pseudo mirror plane of the molecule (P1–Pd1–Pd1* angle is 163.5(1)°) so as to reduce the steric repulsion between PPh₃ and the –CH=CH₂ part of a diene oriented nearly in a square coordination plane.⁸ However, the most striking feature is the Pd–Pd distance (3.1852(6) Å) which is by far longer⁹ than those in the previously reported Pd(I)–Pd(I) single bond, 2.500(1)^{10a}–2.834(4) Å,^{10b} and is near the sum of van der Waals radii, 3.26 Å.

The steric congestion about the olefin ligand mentioned above would be relieved considerably not only by the zigzag P–Pd–Pd–P skeleton but also by the Pd–Pd bond elongation observed. However, such elongation would be apparently disfavored in terms of Pd–Pd σ -bond energy.¹¹ To obtain a further insight, preliminary theoretical calculations at Hartree–Fock (HF) and MP2 levels were undertaken¹² on a model compound [Pd₂(μ -C₄H₆)₂(PH₃)₂]²⁺ (**2'**) mimicking the crystallographically determined geometries of **2** except that the Pd–Pd distance was changed from 2.8 to 3.7 Å. The total energy minimum was observed at 3.44 Å in HF and 3.19 Å in MP2 calculations. Although the former is somewhat longer than the experimental value, a Walsh diagram seems useful for qualitative understanding of the long Pd–Pd distance of **2'**. As the Pd–Pd distance lengthens up to 3.5 Å, the energy levels of the occupied orbitals remain almost unchanged except that the orbital mainly involving the donation from diene HOMO to ($d\sigma$ – $d\sigma$)^a (Chart 1) slightly lowers in energy.¹³

(6) Crystal data for **2**·(CH₂Cl₂): C₄₆H₄₆Cl₄P₄F₁₂Pd₂, *M* = 1305.36, space group P2₁/c (no. 14), *a* = 13.988(4) Å, *b* = 14.274(2) Å, *c* = 14.596(2) Å, β = 116.69(1)°, *U* = 2603(1) Å³, *Z* = 2, *F*(000) = 1216, *D_c* = 1.556 g cm^{–3}, μ (Mo K α) = 9.90 cm^{–1}, 307 variables refined with 6487 reflections with *I* > 3 σ (*I*) to *R* = 0.054, *R_w* = 0.062.

(7) (a) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (b) Spetsers, N.; Norton, J. R.; Rithner, C. D. *Organometallics* **1995**, *14*, 603 and references therein.

(8) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 2.2.

(9) A reviewer pointed out that some A-frame-type dipalladium complexes with a similar electronic count showed relatively long Pd–Pd separations, for example, Pd–Pd of 2.9933(7) Å for [(μ -H)Pd₂(Et)₂(dppm)₂]⁺; Stockland, R. A.; Anderson, G. K.; Rath, N. P. *Inorg. Chim. Acta* **1997**, *259*, 173. However, these are corner-sharing bi-square planar L₃–Pd–L'–Pd–L₃ complexes having a 3-centered 2-electron bond, while **2** is an open bi-square planar L₃–Pd–Pd–L₃ complex formally having a 2-centered 2-electron bond.

(10) (a) Tani, K.; Nakamura, S.; Yamagata, T.; Kataoka, Y. *Inorg. Chem.* **1993**, *32*, 5398. (b) Leoni, P.; Pasquali, M.; Sommogio, M.; Albinati, A.; Lianza, F.; Pregosin, P.; Rügger, H. *Organometallics* **1994**, *13*, 4017.

(11) By using the DFT^{3d} or MP2^{3f} calculation, the Pd^I–Pd^I or Pt^I–Pt^I bond energy was theoretically estimated to be considerably large with the metal–metal length well reproduced within the experimental value.

Chart 1

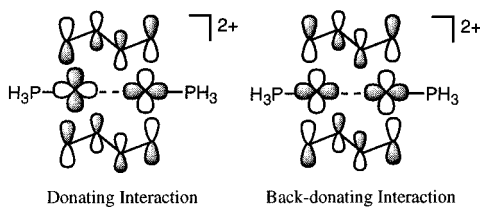
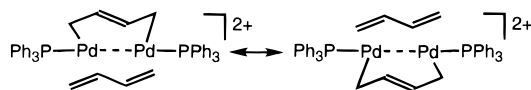


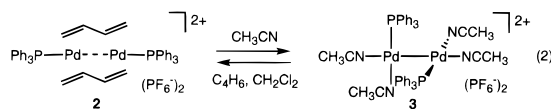
Chart 2



This is probably because the overlap between diene HOMO and $(d\sigma-d\sigma)^a$ slightly increases¹⁴ and $(d\sigma-d\sigma)^a$ of $[\text{Pd}_2(\text{PH}_3)_2]^{2+}$ lowers in energy upon the Pd–Pd elongation. Particularly notable is the near constancy of the orbital involving the back-donation from $(d\sigma-d\sigma)^b$ to diene LUMO (Chart 1).¹³ This is in a clear contrast to the considerable destabilization in energy of $(d\sigma-d\sigma)^b$ of $[\text{Pd}_2(\text{PH}_3)_2]^{2+}$ upon the Pd–Pd elongation.¹⁵ This contrast suggests an important role of the back-donation in effectively preventing $(d\sigma-d\sigma)^b$ from rising in energy with the Pd–Pd elongation. Thus, a coherent picture of the long Pd–Pd distance is obtained as follows: the Pd–Pd lengthening decreases the steric congestion, where the concomitant Pd–Pd bond weakening is compensated by both back-donation and donation interactions between diene and the Pd dinuclear unit.

An extreme formalism involving the Pd(II) state with one of butadienes having the enediyl structure (Chart 2) may not contribute to a large extent, if any, since the structural parameters and ¹³C NMR shifts for the 1,3-butadiene ligand in **2** do not show so significant differences from those of the free diene as observed in the typical enediyl complexes.⁷ Neither do the Pd–C distances discussed above appear consistent with the enediyl representation.¹⁶ It is notable that the above-mentioned steric and electronic origins of the unusual Pd–Pd elongation are at work particularly when two *s-trans*-dienes having the extended geometry coordinate parallel to the Pd–Pd axis.^{17,18}

Dissolution of **2** in acetonitrile resulted in removal of both 1,3-diene ligands to give the reddish-orange unbridged complex **3** in 91% yield (eq 2). Interestingly, the X-ray crystal structure¹⁹ of

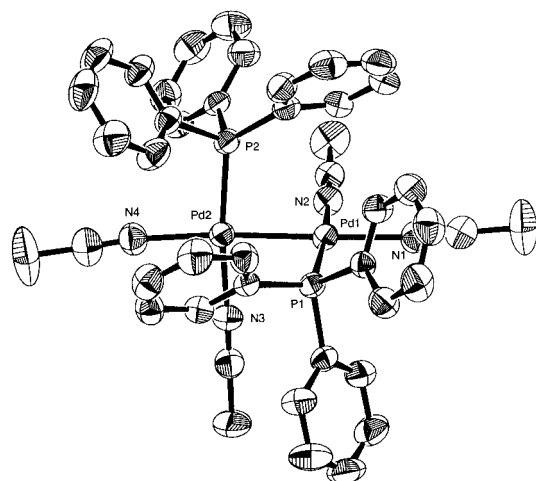


3 (Figure 2) showed the shortest Pd–Pd bond distance (2.4878(7) Å) in the previously reported L_3 –Pd–Pd– L_3 dipalladium(I) complexes,¹⁰ which possibly reflects a very weak trans influence of CH_3CN . When **3** was treated with 1,3-butadiene in CH_2Cl_2 , **2** was regenerated almost quantitatively. It should be also mentioned that the reactivity of **2** with CH_3CN is in sharp contrast to the inertness of **1** to CH_3CN .

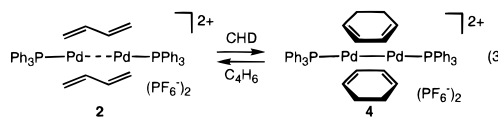
When **2** was treated with 5 equiv of 1,3-cyclohexadiene (CHD), an “*s-cis*” diene, in CH_2Cl_2 , facile diene ligand exchange occurred

(12) (a) Gaussian 94 program was used (Gaussian Inc., Pittsburgh, PA, 1995), where core electrons of P and Pd were replaced with effective core potentials,^{12b,c} and $(3s3p)/[2s2p]$ and $(5s5p4d)/[3s3p2d]$ were employed for valence electrons of P and Pd, respectively. MIDI-3^{12d} and $(4s)/[2s]$ were used for C and H, respectively. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (d) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(13) The superscripts “a” and “b” mean antibonding and bonding, respectively.

Figure 2. ORTEP drawing of **3**.

to yield yellow microcrystals of **4** (90%) (one isomer) (eq 3).



Again, **1** was inert to even a large excess of 1,3-cyclohexadiene.⁵ In view of the fact that the related bis-benzene complex $[\text{Pd}_2(\mu-\eta^2-\eta^2-\text{C}_6\text{H}_6)_2(\text{ClAlCl}_2)_2]$ shows the Pd–Pd bond distance of 2.57 Å,²⁰ determination of the Pd–Pd distance in **4** is awaited.

In conclusion, the sandwich ligation of two “*s-trans*” 1,3-dienes to a Pd–Pd bond has been experimentally and theoretically proven effective in stabilizing the unprecedentedly elongated geometry of Pd–Pd.²¹ Further studies of the unique bonding and structural nature arising from π -complexation between the conjugated π -system and the metal–metal bond are under investigation.

Supporting Information Available: Characterization data, theoretical calculation results, and crystallographic data (26 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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(14) Note that the p_π orbitals of terminal C atoms contribute more to the diene HOMO than those of internal C atoms.

(15) Pd–Pd elongation from 2.8 to 3.5 Å raised back-donation orbital energy in **2** by only 0.038 eV, but $(d\sigma-d\sigma)^b$ in $[\text{Pd}_2(\text{PH}_3)_2]^{2+}$ by 1.2 eV. Beyond the minimum point, several occupied orbitals including back-donation orbital started to rise in energy.

(16) A possible alternative suggested by a reviewer is a μ - π -allyl- CH_2 structure ($\eta^3:\eta^1$ type) having two Pd(II). However, we can ignore this contribution since the relevant distances (Pd1–C2*, 3.051(4) Å; Pd1–C3*, 3.027(4) Å) are far from those^{7b} of μ - π -allyl- CH_2 structures.

(17) (a) Normal Pd–Pd lengths were observed in mono- μ -1,3-diene dipalladium complexes of anionic and neutral type,⁵ as well as in $[(\mu-\eta^2:\eta^2\text{-isoprene})\text{Pd}_2(\text{P}(\text{tol-}i\text{-}p)_3)_2(\mu\text{-Br})][\text{PF}_6]$ (Pd–Pd, 2.713(2) Å)^{17b} and $[(\mu-\eta^2:\eta^2\text{-isoprene})\text{Pd}_2(\text{PBu}_2\text{H})_2(\mu\text{-PBu}_2)][\text{OTf}]$ (Pd–Pd, 2.751(2) Å).^{17c} (b) Murahashi, T.; Otani, T.; Kurosawa, H., unpublished result. (c) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rügger, H. *Organometallics* **1993**, *12*, 4503.

(18) The normal Pd–Pd length found on the optimized geometry of $[\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_6\text{H}_6)(\mu\text{-Br})]^+$ (2.75 Å) is rationalized as follows: acceptor/donor orbitals on each Pd of $[\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})]^+$ point opposite to the Pd–Br bond (to the outer space of the Pd–Pd bond), so as to overlap well with 1,3-butadiene HOMO/LUMO having larger lobes at the terminal carbons than at the inner carbons even when the Pd–Pd length is considerably shorter than the C(terminal)–C(terminal) length. Also, the steric congestions between PPh_3 and diene termini in **1** are less than those in **2**.

(19) Crystal data for **3**· CH_3CN : $\text{C}_{46}\text{H}_{45}\text{N}_5\text{P}_4\text{F}_{12}\text{Pd}_2$, $M = 1232.57$, space group $P1$ (no. 2), $a = 12.929(4)$ Å, $b = 18.158(4)$ Å, $c = 12.507(3)$ Å, $\alpha = 99.02(2)^\circ$, $\beta = 108.67(2)^\circ$, $\gamma = 104.48(2)^\circ$, $U = 2601(1)$ Å³, $Z = 2$, $F(000) = 1232$, $D_c = 1.573$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 8.95$ cm⁻¹, 622 variables refined with 8268 reflections with $I > 3\sigma(I)$ to $R = 0.055$, $R_w = 0.042$.

(20) Allegra, G.; Casagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289.

(21) To our knowledge, **2** is the first example in which the metal–metal bond is sandwiched between two *s-trans*-1,3-diene ligands.