Synthesis, Structure, and Unusual Reactivity of a d^{10}-d^{10} Palladium(0) Dimer

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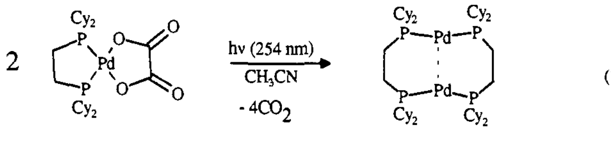
Dinuclear metal complexes possessing bonding interactions between d^{10} metal centers are very rare. A series of dinuclear complexes possessing an unsupported bond between Pt(0) centers has been reported by Otsuka,[1] but more common are complexes in which the metal centers are held in close proximity by bridging ligands.[2] Two catalytically active dinuclear palladium(0) complexes, $Pd_2(dba)_3$ and $Pd_2(dppm)_3$,[3] have three ligands bridging the tricoordinate palladium atoms. The Pd–Pd bond lengths in these complexes have been found to be in excess of 3 Å,[4] which suggests a very weak interaction. We now report the synthesis and first structure of a complex possessing two dicoordinate Pd(0) atoms bridged by two diphosphine ligands. The complex, $Pd_2(\mu_2\text{-dcpe})_2$ (**1**), despite a very short Pd–Pd distance (2.7611(5) Å), readily dissociates in solution to give highly reactive mononuclear palladium fragments.

The 254-nm photolysis of the palladium oxalate (**2**) in acetonitrile results in the formation of suspensions which upon being cooled to 0 °C give high yields of the dinuclear palladium complex **1** as an air-sensitive red precipitate (eq 1).[5] The formation



(1)

2 **1**

of **1** likely proceeds through the intermediacy of the photochemically generated intermediate (dcpe)Pd(0).[6] A similar transformation has been proposed for the dimerization of (dtbpm)Pt(0) to give $Pt_2(\mu_2\text{-dtbpm})_2$.[7]

The mass spectrum (EI, 70 eV) shows a molecular ion at 1056 amu and an abundant fragment (973 amu, 20%) corresponding to the loss of a cyclohexyl group from the parent ion. Complex **1** is soluble in most hydrocarbon solvents and shows a single resonance in the $^{31}P\{^1H\}$ NMR at 23.4 ppm.[8] The solid-state structure of **1** was determined by X-ray crystallography; an ORTEP drawing of **1** is shown in Figure 1.[9] The complex shows approximate twofold symmetry as viewed down the Pd–Pd axis with the cyclohexyl groups forming a lipophilic pocket which efficiently shields the Pd_2 core. Each palladium is bent (∠P–Pd–P ≈ 164°) toward its partner, and the two P–Pd–P fragments are twisted approximately 46° in respect to each other.[10] The Pd–Pd distance of 2.7611(5) Å suggests a significant bonding interaction when compared with palladium metal (2.751 Å) and some Pd(0) cluster compounds (2.72–2.92 Å)[11] but is significantly longer than in Pd(I)–Pd(I) dimers which have a formal bond order of 1 (2.53–2.70 Å).[12] Theoretical studies of model Pt(0)–Pt(0) systems have described the intermetallic bonding as a weak interaction due to d-p mixing in the σ bonding orbital,[13] and consequently the low-energy transition of several of d^{10}-d^{10} platinum and palladium complexes has been interpreted as being primarily dσ* → pσ in character.[14] The long-wavelength absorption (λ_{max} = 456 nm, ε = 28 100)[15] which is observed for **1** is consistent with this overall bonding model.[16]

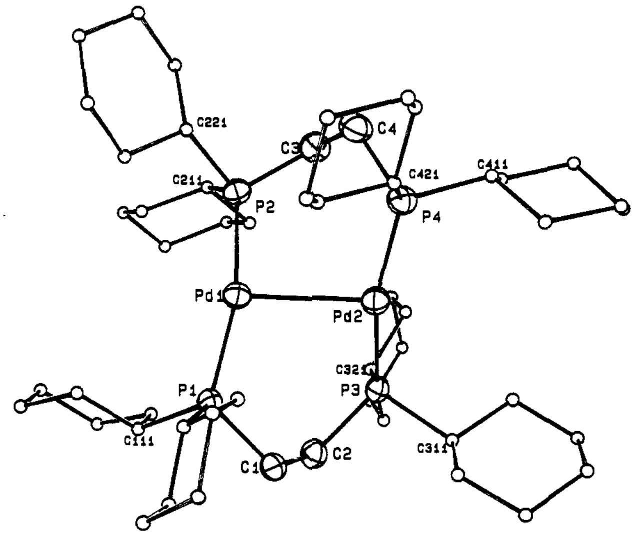


Figure 1. ORTEP drawing of **1** showing non-hydrogen atoms with thermal ellipsoids at the 45% probability level except for the cyclohexyl carbons which are shown as arbitrary spheres for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–Pd(2), 2.7611(5); Pd(1)–P(1), 2.257(1); Pd(1)–P(2), 2.257(1); Pd(2)–P(3), 2.260(1); Pd(2)–P(4), 2.260(1); P(1)–Pd(1)–P(2), 164.96(4); P(3)–Pd(2)–P(4), 162.74(5); Pd(2)–Pd(1)–P(1), 100.00(3); Pd(2)–Pd(1)–P(2), 94.35(3); Pd(1)–Pd(2)–P(3), 92.89(3); Pd(1)–Pd(2)–P(4), 100.95(3).

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(1) Yoshida, Y.; Yamagata, Y.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.

(2) (a) Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *232*, C13–C16. (b) Hofmann, P.; Heiss, H.; Neiteler, P.; Muller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880–882.

(3) dba = bis(dibenzylidene)acetone; dppm = bis(diphenylphosphino)methane; dcpe = 1,2-bis(dicyclohexylphosphino)ethane; dtbpm = bis(di-*tert*-butylphosphino)methane.

(4) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065–1066. (b) Mosely, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 982–983. (c) Stern, E. W.; Maples, P. K. *J. Catal.* **1972**, *27*, 120–133. (d) Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *232*, C13–16. (e) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266. (*f*) Pierpont, C. G.; Mazza, M. C. *Inorg. Chem.* **1974**, *13*, 1891–1895.

(5) Interestingly, oxalate **2** has been reported to be photostable in solutions containing acidic amides. Schaad, D. R.; Landis, C. R. *Organometallics* **1992**, *11*, 2024–2029.

(6) Paonessa, R. S.; Trogler, W. C. *Organometallics* **1982**, *1*, 768–770. (b) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647–657.

(7) The synthesis of the corresponding palladium complex has been mentioned in a footnote in ref 2b but without experimental detail.

(8) Preparation of **1**: a solution containing 62 mg (0.1 mmol) of oxalate **2** in 25 mL of dry, degassed acetonitrile was irradiated for 45 min at 254 nm using a Rayonet photoreactor. Once the solution was cooled to 0 °C, a red precipitate was formed which was separated, washed with acetonitrile, and dried under vacuum to give 45 mg (85% yield) of **1**. Characterization: mp = 112 °C; ^1H NMR (δ, C_6D_6) 1.06–2.22 (featureless, dcpe); $^{31}P\{^1H\}$ 23.43(s); MS (EI, 70 eV) *m/z* 1056 (M^+, 6); 973 ($M^+ - Cy$, 20); 422 (dcpe, 100). Anal. Calcd for $C_{52}H_{96}P_4Pd_2$: C, 59.03, H, 9.15. Found: C, 59.43, H, 9.06.

(9) Crystal data: dimensions, 0.33 × 0.26 × 0.66 mm^3; crystal system, triclinic; space group $P\bar{1}$; a = 12.785(3) Å; b = 14.057(2) Å; c = 16.399(3) Å; α = 94.74(1)°; β = 110.78(2)°; γ = 90.31(1)°; Z = 2; absorption coefficient = 7.9 cm^{-1}; Mo Kα radiation with graphite monochromator; 2θ range 1.0–50.0°; 9628 unique reflections with 5943 ≥ $3\sigma(I)$. The structure was solved by Patterson methods and refined to convergence with R = 0.032 and R_w = 0.039.

(10) Relevant torsion angles: P(1)–Pd(1)–Pd(2)–P(2), 48.98(4)°; P(3)–Pd(1)–Pd(2)–P(4), 43.13(4)°.

(11) Mednikov, E. G.; Eremenko, N. K.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1986**, *301*, C35–C37.

(12) Barnard, C. F. J.; Russell, M. J. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.: Pergamon: New York, Vol. 5, 1987; p 1099 and references therein.

(13) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074–2079.

(14) (a) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718–6719. (b) Harvey, P. D.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 2145–2147. (c) Harvey, P. D.; Adar, F.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 1312–1315. (d) Harvey, P. D.; Gray, H. B. *Polyhedron* **1990**, *9*, 1949–1953.

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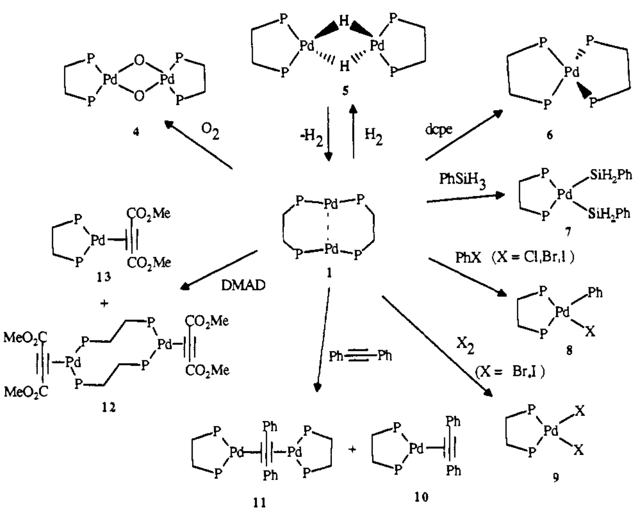
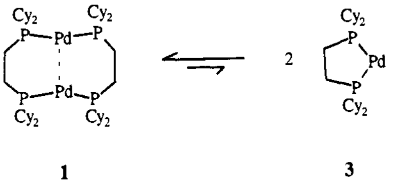
Scheme I



Some preliminary reaction chemistry of this novel dimer is summarized in Scheme I. Complex **1** is highly reactive, giving the observed products quickly at room temperature in toluene, THF, or acetonitrile solvents.[17] Surprisingly, most products are mononuclear palladium species possessing the chelating 1,2-bis(dicyclohexylphosphino)ethane ligand. These complexes are formed *as if a (dcpe)Pd(0) intermediate were the reacting species.* Thus, reactions of **1** with dcpe, bromine, iodine, phenylsilane, and PhX (X = Cl, Br, I) give products typical of coordination to or oxidative addition across a 14-e$^-$ (dcpe)Pd(0) fragment. The reaction of O_2 or H_2 with **1** gives dinuclear complexes built of two (dcpe)Pd(0) fragments which are bridged by two oxygen (**4**)[18] or two hydrogen atoms (**5**), respectively. The reaction with dihydrogen is reversible, where heating of complex **5** liberates H_2 and regenerates **1**.[19]

Although diphenylacetylene gives simple 1:1 (**10**) and 2:1 (**11**) complexes of the (dcpe)Pd(0) fragment,[20] the major product (80% yield) from the reaction of **1** with dimethylacetylene dicarboxylate (DMAD) is the bis(acetylene) π complex **12** which retains the 10-membered ring framework of the original dimer **1**. In contrast to the uncomplexed dimer, the palladium–palladium interaction in **12** is decidedly nonbonding with an intramolecular contact of 6.7 Å.[21] A minor product (**13**), the simple acetylene π complex of the (dcpe)Pd(0) fragment, is also observed. Complexes **12** and **13** do not interconvert under the conditions for their formation.

The observed reaction chemistry strongly suggests a monomer–dimer equilibrium between **1** and the (dcpe)Pd(0) intermediate **3** (eq 2).[22] Although the spectroscopic evidence (MS, NMR,



(2)

and UV–vis) indicates that **1** is the major species in solution, it is clear that **3** is the more reactive species on the basis of the preponderance of products containing the (dcpe)Pd(0) structural unit. Indeed, independent generation of **3**, via the photolysis of oxalate (**2**), in the presence of most substrates gives (dcpe)Pd(0)-based products which are identical to those obtained from solutions of **1**.[23] The dramatic difference in reactivity between **1** and **3** is attributed to both the exalted reactivity of **3**, which is isolobal with singlet carbene,[24] and to the steric protection afforded to the dimer **1** by the bulky cyclohexyl groups on the phosphine. Chemical trapping of the dimer **1** occurs only in the case of the activated and relatively unhindered acetylene, DMAD, and even in this case a small amount of the monomer is intercepted to give **13**. The formation of **13** from the monomer **3** is independently confirmed from the photolysis of the oxalate precursor **2** in the presence of excess DMAD. Complex **13** is formed quantitatively, and importantly, no evidence for the formation of the dimeric product **12** is observed.

In conclusion, the unusual palladium complex **1** is an attractive room temperature source of the reactive intermediate (dcpe)Pd(0). The high reactivity of this intermediate, for instance toward activation of the C–Cl bond of chlorobenzene, suggests that the **1** ⇌ **3** equilibrium may have important catalytic applications. Efforts in this area are currently underway.

Acknowledgment. The support of the Tulane Center for Bioenvironmental Research is gratefully acknowledged.

Supplementary Material Available: Compound characterizations; tables of crystal data, atomic coordinates and temperature factors, hydrogen coordinates, intramolecular bond distances and angles (20 pages); tables of calculated and observed structure factors for **1** (28 pages). Ordering information is given on any masthead page.

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(15) An associated strong emission at 600 nm is also observed. Wang, R.; Schmehl, R. H.; Pan, Y.; Fink, M. J., to be published (details of the photophysics).

(16) Compare with $Pd_2(dppm)_3$: λ_{max} = 440 nm, ε = 33 800 (ref 14b).

(17) Except where noted, NMR yields are greater than 90%.

(18) A peroxide structure is ruled out on the basis of vibrational spectroscopy (no ν_{O-O} in IR and Raman) and chemical evidence (does not oxidize KI in HOAc).

(19) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495–3497.

(20) Similar palladium acetylene complexes have been recently reported. Krause, J.; Bonrath, W.; Porschke, K. R. *Organometallics* **1992**, *11*, 1158.

(21) Pan, Y.; Mague, J. T.; Fink, M. J., to be published (X-ray structure).

(22) A referee proposes an alternative mechanism by which **1** reacts with substrates to form initial Pd(I) intermediates which undergo subsequent ligand and/or substituent redistribution. We have attempted unsucessfully to detect *any* intermediate in these reactions by low-temperature NMR. In addition, reactions of **1** with PhX do not give observable amounts of (dcpe)PdX_2 and (dcpe)$PdPh_2$, the expected products from substituent redistribution. Although ligand redistributions may potentially occur in some cases, we believe that the observed product distribution is best explained by the mechanistically simpler monomer–dimer equilibrium.

(23) Phenylsilane and bromine reacted thermally with the oxalate, and consequently their photochemistry was not examined. The photochemical reaction of **2** with dioxygen gave the bis(oxide) of dcpe as the only identifiable product. The same product is also obtained by the reaction of **4** with dioxygen.

(24) Hofmann, P. In *Organometallics in Organic Synthesis*; de Meijere, A., Tom Dieck, H., Eds.; Springer Verlag: Berlin, 1987; pp 1–35