[(dppp)Pd]$_2$(SO$_3$CF$_3$)$_2$: A Palladium(I) Dimer with "Side-on" Phosphine Coordination

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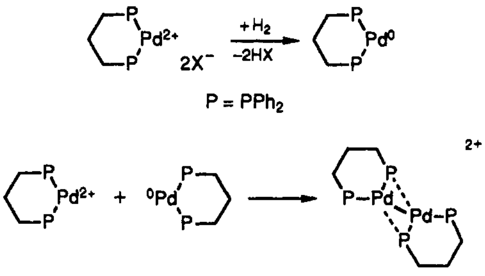
Summary: (dppp)Pd(CF$_3$SO$_3$)$_2$ (dppp = 1,3-bis(diphenylphosphino)propane) reacts with H$_2$ to give the dimeric title complex 1. The crystal structure shows that the complex is a Pd(I) dimer with a metal–metal bond length of 2.701 (3) Å. Each metal is coordinated by only one dppp ligand, of which, peculiarly, one phosphorus atom occupies an (asymmetrically) bridging position. There is an interaction between each palladium and an aryl group of an adjacent dppp ligand, but ab initio calculations indicate that the bridged dimeric structure is preferred *even in the absence* of such interactions. Reaction with donor ligands (CO, CH$_3$CN) destroys the "side-on" Pd–P interaction and results in the formation of normal square-planar palladium(I) dimers.

Complexes of Pd(I) are relatively rare, and those that are known are most often dimeric or cluster species. The dimeric Pd$_2^{2+}$ unit, in particular, occurs in a variety of complexes.[1-3] It usually contains three strong donor ligands per palladium atom and is best described as consisting of two normal square-planar Pd(L)$_3$(Pd) units. We here report on the synthesis and the molecular structure determination of a coordinatively unsaturated Pd(I) dimer, [(dppp)Pd]$_2^{2+}$(CF$_3$SO$_3$)$^-_2$ (1), together with a preliminary account of ab initio calculations on a model complex with PH$_3$ ligands.

Complex 1 can be synthesized from (dppp)Pd(CF$_3$SO$_3$)$_2$ under reducing conditions in various ways. The reaction with H$_2$ (20 bar, dichloromethane, methanol, methylorthoformate) gave the best results,[4] with yields exceeding 60%. The originally yellow solution turned deep red, and the brown complex 1 precipitated from the solution. The elemental analysis agreed with the composition [(dppp)-Pd(CF$_3$SO$_3$)]$_n$.[5] The ^{31}P NMR spectrum[4] showed an AA′XX′ pattern, indicating a dimeric structure. The P–P coupling constants suggested the presence of a palladium–palladium bond, which was confirmed by the X-ray diffraction study (below). Scheme I illustrates how the dimers may be formed. An alternative mechanism involves heterolytic splitting of a H$_2$ molecule to give a hydride which subsequently dimerizes with reductive elimination of $^1/_2$ mol of H$_2$/mol of Pd; the overall reaction remains the same. A single-crystal X-ray determination[4] showed that the compound is indeed a palladium dimer with a metal–metal bond (Figure 1). The coordination of the Pd$_2^{2+}$ unit involves only the two diphosphine ligands; the dications [(dppp)Pd]$_2^{2+}$ are separated from the anions by normal van der Waals distances. Table I contains relevant bond lengths and angles. Two phosphorus atoms occupy positions forming the more or less linear arrangement P–Pd–Pd–P (∠P–Pd–Pd = 161.1 (1)°, P–Pd = 2.329 (4) Å). The two other phosphorus atoms occupy bridging positions, with P–Pd distances of 2.235 (4) and 2.690 (4) Å and a Pd–P–Pd angle of 65.2 (1)°. The X-ray structure suggests an interaction between the ipso carbon of a phenyl group at the bridging phosphine and a palladium atom. The Pd–C interaction persists in solution: the ^{13}C NMR spectrum shows a broad resonance for this carbon atom at 104 ppm.[4]

Scheme I



cation of 1

Recently, the related complex [(Ph$_2$PCH=CH$_2$)$_2$Pd]$_2^{2+}$ (2) has been reported.[6] This compound also contains a

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(1) Allegra, G.; Tettamanti Casagrande, G.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289. Werner, H.; Tune, D.; Parker, G.; Krüger, C.; Brown, D. J. *Angew. Chem.* **1975**, *87*, 205.

(2) For reviews, see: Balch, A. L. *Comments Inorg. Chem.* **1984**, *3*, 51. Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155.

(3) Lindsay, C. H.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1980**, *19*, 3503 and references therein.

(4) Preparation of 1: A solution of (dppp)Pd(SO$_3$CF$_3$)$_2$ (2.5 g), 20 mL of methanol and dichloromethane (1/1, v/v), and 2 mL of methyl orthoformate was transferred to an autoclave with a Teflon liner and was magnetically stirred under 20 bar of H$_2$ for 1.5 h at 25 °C. After the pressure was released, the brownish red powder of 1 was filtered off, washed with ether and dichloromethane, and dried in vacuo for 48 h at 80 °C (yield 1.6 g). Anal. Calcd for C$_{56}$H$_{52}$F$_6$P$_4$Pd$_2$O$_6$S$_2$: C, 50.35; H, 3.92. Found: C, 49.64; H, 4.03; Cl, 0.15. A portion of this powder (0.25 g) was redissolved in 25 mL of dichloromethane under 15 bar of carbon monoxide. The pressure was released, and under atmospheric CO pressure crystals of 1 slowly appeared; these turned out to be suitable for X-ray analysis. ^{31}P NMR (CD$_2$Cl$_2$, 200 MHz): δ_A 13.2 ppm, δ_X −5.9 ppm, $J_{AA'}$ = 197 Hz, $J_{XX'}$ = 3 Hz, J_{AX} = −60 Hz, $J_{AX'}$ = 114 Hz. ^{13}C NMR (C$_2$D$_2$Cl$_4$, 25 °C, 300 MHz; δ, ppm (J_{PC}, Hz)): 134.8 and 131.5 (p_A and p_X), 2 × 133.7 (12) (o_A and o_X), 130.6 (10) (m_X), 129.0 (10) (m_A), 127.8 (39) (i_A), 104 (60) (i_X), 29.2 (~32) (CH$_2$P$_X$), 28.5 (~28) (CH$_2$P$_A$), 18.7 (~−5 and −9) (CH$_2$$CH_2CH_2$). The ^{13}C spectrum shows only one type of phenyl group attached to each phosphorus atom, which implies that dissociation of the Pd–C$_{ipso}$ bond must be rapid on the NMR time scale. Consequently, the coordination shift $\Delta\delta$ for this carbon atom is approximately 2(104–128) = −48 ppm. Crystallographic data for 1 (C$_{56}$H$_{52}$F$_6$P$_4$Pd$_2$O$_6$S$_2$): M_r = 1335.8; space group $P2_1/n$ (No. 14); a = 12.857 (3) Å; b = 15.464 (3) Å; c = 13.938 (3) Å; β = 90.65 (2)°; V = 2771 (1) Å^3; Z = 2; d_{calc} = 1.60 g/cm^3; Nicolet R3m diffractometer, room temperature; μ(Mo Kα) = 8.9 cm^{-1}; scan method ω (Wyckoff); data collection $4 < 2\vartheta < 50°$; number of unique data 4886; total number of data used 2035 ($I < 2.5\sigma(I)$); solution by heavy-atom methods (Patterson and Fourier) with full-matrix least-squares refinement to convergence (refined parameters 214); R = 0.078, R_w = 0.084, S = 1.53; final residual peaks 1.3 and 1.5 e/Å^3 near the palladium atoms, others <1 e/Å^3.

(5) The similar red dimer [(dppe)Pd]$_2$(ClO$_4$)$_2$ has been reported, but structural data are lacking: Davies, J. A.; Hartley, F. R.; Murray, S. G.; Marshall, G. *J. Mol. Catal.* **1981**, *10*, 171.

(6) Wilson, W. L.; Nelson, J. H.; Alcock, N. W. *Organometallics* **1990**, *9*, 1699.

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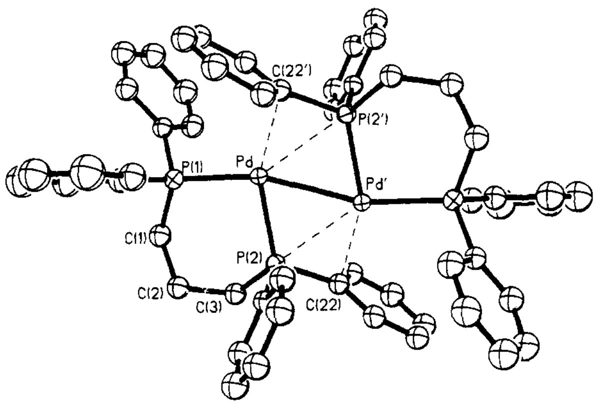


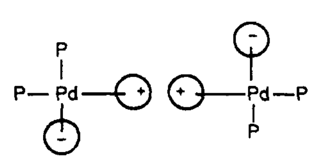
Figure 1. Molecular structure of the dication of 1, $[(dppp)Pd]_2^{2+}$.

Table I. Selected Crystallographic Data for 1

	Bond Lengths (Å)		
Pd–P(1)	2.329 (4)	Pd–P(2)	2.235 (4)
Pd–Pd'	2.701 (3)	Pd–P(2')	2.690 (4)
Pd–C(22')	2.385 (16)	P(1)–C(1)	1.822 (17)
P(1)–C(4)	1.819 (17)	P(1)–C(10)	1.815 (18)
P(2)–C(3)	1.819 (17)	P(2)–C(16)	1.804 (16)
P(2)–C(22)	1.812 (16)	C(1)–C(2)	1.568 (24)
C(2)–C(3)	1.543 (23)		
	Bond Angles (deg)		
P(1)–Pd–P(2)	97.9 (2)	P(1)–Pd–Pd'	161.1 (1)
P(2)–Pd–Pd'	65.2 (1)	P(1)–Pd–P(2')	146.7 (2)
P(2)–Pd–P(2')	114.2 (1)	Pd'–Pd–P(2')	49.0 (1)
P(1)–Pd–C(22')	111.5 (4)	P(2)–Pd–C(22')	147.4 (4)
Pd'–Pd–C(22')	87.1 (4)	P(2')–Pd–C(22')	41.3 (4)
Pd–P(1)–C(1)	115.2 (6)	Pd–P(1)–C(4)	112.7 (6)

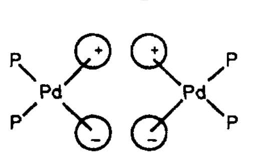
Pd–Pd bond, four phosphorus ligands, and monovalent palladium, but in addition it has two coordinating *vinyl* groups. In both complexes the coordination planes of the two palladium atoms are nearly coplanar. The Pd coordination environments differ from regular 4-coordination by having a Pd–Pd–P angle much smaller than 90° (71° for 2, 65° for 1). One might argue that in 2 this angle is constrained by the *vinyl*-Pd interaction. In view of the much weaker *phenyl*-Pd interaction in 1, one would then expect a *larger* Pd–Pd–P angle in 1, in contrast to our observations. This led us to suspect that Pd–C interactions, though undoubtedly present in both 1 and 2,[7] are not the sole *cause* of the bridged structure.

To clarify this point, we have carried out a series of ab initio calculations[8] on $[(PH_3)_2Pd]_2^{2+}$ model systems. The monomer $Pd(PH_3)_2^+$ (formally a d^9 radical) prefers a linear structure, but bending is necessary to form a metal–metal bond. With the x axis along the P–Pd–P bisector and the ligands in the xy plane, the SOMO of the bent monomer is an in-plane d_{xy} orbital, and this monomer can dimerize in two ways (structures 3 and 4), corresponding to σ- and π-bonds between the metal atoms. Our calculations indicate that the two structures are comparable in energy.



3

σ-bond formation



4

π-bond formation

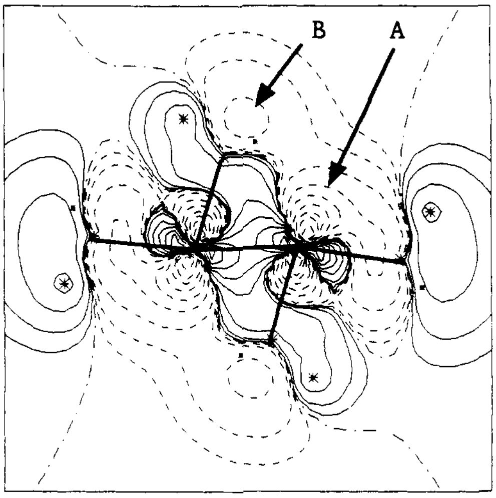


Figure 2. Orbital plot of the metal–metal bonding HOMO of 3, showing the overlap between the "unused" Pd lobe (A) and the backside of the phosphine lone pair (B) in the "semibridging" Pd–P interaction.

Table II contains the calculated geometries of the σ-bonded dimers 3 and the corresponding X-ray data for complexes 1 and 2. Most features of the experimental structures are nicely reproduced at the closed-shell RHF level. The metal–ligand distances are systematically too large, due to the small basis set employed, but the differences in bond length between the terminal and bridging phosphines are predicted correctly. What is more, the semibridging or side-on coordination is obtained in the absence of any supporting Pd–alkene interaction! The tilting of the perpendicular Pd–P bonds toward the neighboring Pd atoms creates an overlap between the "unused" Pd d_{xy} lobes and the backsides of the phosphine lone pairs, as illustrated in Figure 2.[14] The side-on Pd–P interaction is only weakly bonding: less than 10 kcal/mol is required to open up the Pd–Pd–P angle to 90°. Therefore, the side-on approach should be considered as only one of the means by which the unsaturated palladium atoms can relieve their coordinative unsaturation without losing the energy of the dative bonds.

Calculations indicated that the addition of two molecules of CO would lead to an adduct with structure 5, comparable to the well-known $[Pd_2Cl_4(\mu\text{-}CO)_2]_2^{2-}$ ion.[9] Indeed,

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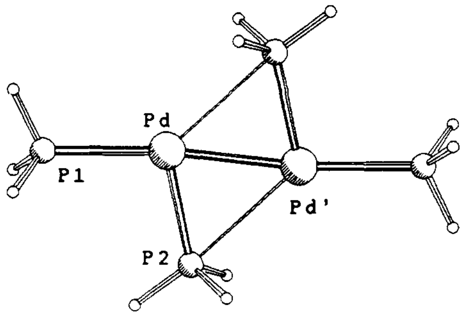
[7] An unambiguous example of an interaction between palladium and a phenyl ipso carbon atom in a *monomeric* complex has recently been observed: Falvello, L. R.; Forniés, J.; Navarro, R.; Sicilia, V.; Tomás, M. *Angew. Chem.* **1990**, *102*, 952. For further examples of metal–C_{ipso} interactions, see: Chen, H.; Bartlett, R. A.; Olmstead, M. M.; Power, R. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1990**, *1112*, 1048. Taube, R. *Comments Inorg. Chem.* **1984**, *3*, 69.

[8] The GAMESS program was used[8a,b] using a minimal basis set (STO-3G)[8c] for the ligand atoms and a nearly minimal basis set for the palladium atom.[8d] Most calculations were done at the restricted Hartree–Fock level,[8e] but we have also repeated some of the calculations at the generalized valence bond level,[8f] using 1 GVB pair for the metal–metal bond. Geometries were either completely optimized (structures Fopt in Table II) or optimized with a fixed P_1PdP_2 angle and the PH_3 cones pointing toward the metal atoms (to simulate the constraints of the dppp ligand; structures Popt in Table II); we have assumed C_{2h} symmetry for 3 and D_{2h} symmetry for 4. In calculations for 3, the PH_3 model ligands in the "bridging" positions were rotated by 180° with respect to the "real" PR_3 ligands in 1 and 2 to prevent any spurious direct (agostic) Pd···H interactions. (a) Guest, M. F.; Kendrick, J. *GAMESS Users Manual*; SERC Daresbury Laboratory: Daresbury, U.K., 1986; CCP1/86. (b) Guest, M. F.; Harrison, R. J.; van Lenthe, J. H.; Corler, L. C. H. *Theor. Chim. Acta* **1987**, *71*, 117. (c) Pietro, W. J.; Hehre, W. J. *J. Comput. Chem.* **1983**, *4*, 241 and references therein. (d) Postma, J. R. To be submitted for publication. Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984. (e) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69. (f) Goddard, W. A., III; Dunning, T. H.; Hay, W. J.; Dunning, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

[9] Loggin, P. L.; Goodfellow, R. J.; Herbert, I. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, 1077.

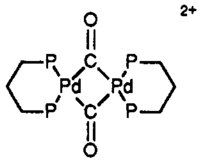
Table II. Experimental and Calculated Geometries of $[PdL_2]_2^{2+}$ Dimers[a]



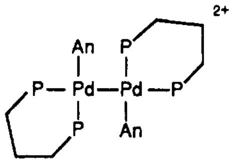
molecule	Pd-Pd'	Pd-P1	Pd-P2	Pd'-P2	∠Pd'PdP2	∠P1PdP2
1 (X-ray)	2.70	2.33	2.24	2.69	65	98
2[b] (X-ray)	2.75	2.33	2.26	2.94	71	98
3 RHF/Fopt	2.66	2.48	2.37	2.96	72	102
RHF/Popt	2.63	2.48	2.38	3.04	75	(98)
GVB/Popt	2.89	2.52	2.55	3.08	69	(98)

[a] Distances in Å and angles in degrees. [b] Reference 6; averages over two crystallographically independent values.

dimer **1** reacts reversibly with 15 bar of CO to give a carbonyl complex with a ^{31}P NMR spectrum[10] consistent with that of **5**. However, a fluxional unbridged structure cannot be ruled out at this point. Dissolution of **1** in acetonitrile gave a new complex having an AA'XX'-type ^{31}P NMR spectrum,[10] to which we assigned structure **6** similar to known isonitrile complexes of monovalent palladium.[11] Ab initio calculations gave an energy minimum for **6** with two perpendicular coordination planes.



5



6

In conclusion, both experiments and calculations indicate that delicate interactions determine the structures of the Pd_2^{2+} dimers. However, the preference for bridging[12] or rather side-on phosphine bonding appears to be an intrinsic feature of $[PdL_2]_2^{2+}$ complexes; phenyl or vinyl coordination—though certainly present in **1** and **2**—plays a less prominent role in determining the structure of the dimers.[13]

Supplementary Material Available: Details of the structure determination and listings of crystal data, positional and thermal parameters, and bond distances and angles for 1 (6 pages); a listing of observed and calculated structure factors for 1 (18 pages). Ordering information is given on any current masthead page.

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[10] Complex **5**: ^{31}P NMR δ 9.0 ppm, singlet. Complex **6**: ^{31}P NMR (CD_2Cl_2, 200 MHz) δ_A 13.5 ppm, δ_X −14.7 ppm, $J_{AA'}$ = 303 Hz, $J_{XX'}$ = 5 Hz, J_{AX} = −77 Hz, $J_{AX'}$ = 82 Hz.

[11] Goldberg, S. Z.; Eisenberg, R. *Inorg. Chem.* **1976**, *15*, 535.

[12] Recently a triply bridging trifluorophosphine has been discovered, $[(\mu_3\text{-}PF_3)Pd_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu\text{-}Cl)]^+$: Balch, A. L.; Davis, B. J.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8592.

[13] There are several other examples of Pd^I or Pt^I dimers with acute M–M–P angles: Messbauer, B.; Meyer, H.; Walther, B.; Heeg, M. J.; Maqsudur Rahman, A. F. M.; Oliver, J. P. *Inorg. Chem.* **1983**, *22*, 272. Wagner, K. P.; Hess, R. W.; Treichel, P. M.; Calabrese, J. C. *Inorg. Chem.* **1975**, *14*, 1121. Anderson, G. K.; Lin, M.; Rath, N. P. *Organometallics* **1990**, *9*, 2880. Arnold, D. P.; Bennett, M. A.; Bilton, M. S.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1982**, 115. Bennett, M. A.; Berry, D. E.; Bhargava, S. K.; Ditzel, E. J.; Robertson, G. B.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1613. In these cases, however the "extra" metal–ligand interactions are much stronger than the Pd–Ph interaction in **1** and they are probably dominant in determining the molecular structure.

[14] Because of its p-orbital contribution, the phosphine lone-pair donor orbital has a considerable amount of electron density pointing *away* from the metal (as shown in Figure 2), which overlaps with the "unused" lobe of the PdL_2^+ SOMO. This is not a direct agostic Pd–H interaction (or Pd–C in complex **3**): a direct interaction would result in a specific elongation of the P–H or P–C bonds involved, but we do not see such an elongation either in the X-ray structure of **1** or in the calculated structure of **3**.