

Figure 4. View of the coordination sphere of **2** showing the edge-shared bioctahedral coordination sphere.

hybridization, and the existence of C=N bonds is also evidenced from the short C-N distances. The Ru-N-Ru angle, ca. 78°, deviates considerably from the ideal sp^2 angle of 120°, and this is offset by a considerable increase in one of the other two angles

to ca. 160°. These distortions may be attributed to (i) the presence of a strong metal-metal interaction (vide infra) and (ii) the formation of a five-membered chelate ring. The difference of ca. 0.015 Å between two Ru-(μ -N) bond lengths is presumed to be due to the requirements of the chelate ring.

With the two metal atoms in oxidation state III, having t_{2g}^5 electronic configurations, the formation of a net Ru-Ru single bond may be postulated. Examples of such a bond have been previously seen in $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$ as well as in $[Ru_2(\mu-NH_2)_2(NH_3)_8]Cl_4 \cdot 4H_2O$ ³⁵ and $Ru_2(ap)_6(PMe_2Ph)_2$ ³⁶ where ap represents the anion of 2-aminopyridine.

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Registry No. **1**, 98216-98-9; **2**, 98194-59-3; $Ru_2Cl(O_2CCH_3)_4$, 38833-34-0; 3,5-(OCH₃)₂C₆H₃CONH₂, 17213-58-0; $Ru_2Cl(3,5-(OC-H_3)_2C_6H_3CONH)_4$, 98194-57-1; PPh_3 , 603-35-0; $Ru_2Cl(PhCONH)_4$, 98194-58-2; $P(p-C_6H_4CH_3)_3$, 1038-95-5; $Ru_3Cl(O_2CPh)_4$, 38832-60-9; $PhCO_2H$, 65-85-0; $RuCl(CO)(O_2CPh)(PPh_3)_2$, 50661-68-2.

Supplementary Material Available: Details of crystal structure determinations and tables of structure factors, anisotropic thermal parameters, complete bond distances and angles, and root-mean-square amplitudes of thermal vibration (75 pages). Ordering information is given on any current masthead page.

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Palladium-Palladium σ -Bonds Supported by Bis(dimethylphosphino)methane (dmpm). Synthetic, Structural, and Raman Studies of $Pd_2X_2(dmpm)_2$ (X = Cl, Br, OH)

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The reaction of bis(dimethylphosphino)methane (dmpm) with $[Pd(CO)Cl]_n$ leads to the formation of the bridged binuclear complex $Pd_2Cl_2(dmpm)_2$ (**1**). The chloride ligands of **1** are labile and may be substituted by X^- (X = Br, OH). The crystal and molecular structure of the Br derivative, $Pd_2Br_2(dmpm)_2$ (**2**), has been determined. Complex **2** crystallizes in the monoclinic space group $C2/c$ with $a = 19.623$ (5) Å, $b = 8.684$ (3) Å, $c = 16.902$ (6) Å, $\beta = 132.25$ (2)°, $V = 2132$ (3) Å³, and $Z = 4$. The structure was refined to convergence, leading to R and R_w of 0.052 and 0.057, respectively, for 1245 observations in the range $2^\circ < 2\theta < 50^\circ$ with $I \geq 2\sigma(I)$. Complex **2** possesses crystallographic 2-fold symmetry. The Pd-Pd separation is 2.603 (1) Å, consistent with a Pd-Pd bond. The molecular structure of **2** is markedly distorted from planarity of the Pd_2P_4 unit and exhibits a P(1)-Pd-Pd'-P(2) torsion angle of 50.5°. The complexes $Pd_2X_2(dmpm)_2$ are stable and soluble in H_2O . Substitution of hydroxide for the chloride ligands of **1** occurs in water to form $Pd_2(OH)_2(dmpm)_2$. Raman and IR data have been employed in the characterization of the Pd-Pd and Pd-X bonds of the $Pd_2X_2(dmpm)_2$ species. The Raman spectra of **1** and **2** in CH_2Cl_2 show $\nu(Pd-Pd)$ to be 140 and 123 cm^{-1} , respectively. Complex **1** in aqueous solution exhibits $\nu(Pd-Pd) = 140$ cm^{-1} and $\nu(Pd-OH) = 351$ cm^{-1} .

Introduction

We report studies of complexes that formally contain a Pd-Pd bond supported by the diphosphine bis(dimethylphosphino)methane (dmpm). Over the past several years, there has been considerable interest in the chemistry of binuclear complexes bridged by diphosphines. The range of structures exhibited by these complexes include (i) face-to-face bi-square-planar $M_2-(P^iP^j)_2L_4$,^{1b-f} (ii) diphosphine-supported M-M-bonded M_2-

$(P^iP^j)_2L_2$,² (iii) molecular A-frame $M_2(\mu-B)(P^iP^j)_2L_2$,³ and (iv) *endo* and *exo* A-frame adducts, $M_2(\mu-B)(P^iP^j)_2L_2L'$.⁴ An in-

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teresting chemistry of these complexes also has emerged. Insertions of small molecules into M–M^{3b-g} and M–L bonds,^{5t} additions of small molecules to one or both metals, formal oxidative additions of H₂,^{4b} and reactions of bridgehead ligands^{3c,5c} all have been observed. Most work to date has involved the diphosphine bis(diphenylphosphino)methane (dppm).⁵ An excellent review has recently appeared.⁶ A specific disadvantage of the dppm ligand is its attendant steric bulk. The phenyl rings of dppm complexes partially insulate the metal centers in a chemical sense and thus limit the ability to study the chemistry of closely interacting metal atoms. Recently, we^{7,8} and others^{9–11,14,16} initiated

studies of binuclear complexes bridged by bis(dimethylphosphino)methane. The impetus for our work was the expectation that the reactivity of M–M bonds supported by dmpm would be enhanced by its greater donor ability and lower steric requirements. Significant departures in the chemistry of dmpm relative to dppm-bridged binuclear complexes are becoming evident. Of note, a number of dmpm-bridged complexes are highly soluble and stable in water.^{7,8,22} The water solubility of dmpm complexes has made them amenable to mechanistic studies of their catalysis of the water gas shift in neutral aqueous media.⁸ The water solubility of these complexes also holds promise in facilitating the separation of products and catalysts in other homogeneously catalyzed reactions. The synthesis of the complexes Pd₂X₂(dmpm)₂ (X = Cl, Br, OH), their characterization by IR, ¹H, ¹³C, and ³¹P NMR, and Raman spectroscopy, and the crystal and molecular structure of the Br derivative, Pd₂Br₂(dmpm)₂, are described herein. The characterization of the aqueous solution species, Pd₂(OH)₂(dmpm)₂, is also described.

Experimental Section

Materials. All solvents were deoxygenated prior to use. Methanol (Aldrich Chemical Co.) and anhydrous diethyl ether (Mallinckrodt) were used without further purification. Acetonitrile and methylene chloride were freshly distilled from calcium hydride under nitrogen. Tetrahydrofuran was freshly distilled from sodium metal and benzophenone under nitrogen. [Pd(CO)Cl]_n was prepared according to the procedure published by Schnabel and Kober.²¹

Physical Measurements. Elemental analysis were performed by Dr. H. D. Lee of the Microanalytical Laboratory, Department of Chemistry, Purdue University. UV–vis spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 700 instrument, for 600–4000 cm⁻¹, and on a Digi-Lab FTS-20B instrument, for 100–400 cm⁻¹. ¹H, ³¹P{¹H} and ¹³C{¹H} NMR were recorded on a Varian XL-200 spectrophotometer. ¹H and ¹³C{¹H} NMR were measured against internal Me₄Si, and ³¹P{¹H} NMR was measured against external 85% H₃PO₄. Either CD₂Cl₂, D₂O, or CD₃CN was used for internal lock. Raman spectra were obtained by using a Coherent 52 argon ion laser source at 457.9 nm, which was focused on a spinning NMR sample cell. Backscatter was collected and focused into an entrance slit of a SPEX 1400 double monochromator equipped with an RCA 31034 photomultiplier tube.

Synthesis of Bis(dimethylphosphino)methane (dmpm). The diphosphine dmpm was prepared by methylation of PCl₂CH₂PCl₂, which was prepared by a modification of the literature procedures.^{14,20} Aluminum foil is substituted for aluminum powder in the synthesis of Cl₂-AlCH₂AlCl₂ and CH₂I₂ is used as the initiator. Addition of KCl is omitted in the conversion of Cl₂AlCH₂AlCl₂ to Cl₂PCH₂PCl₂. Conversion of Cl₂PCH₂PCl₂ to dmpm is also accomplished by a modified literature procedure.¹⁵ The Cl₂PCH₂PCl₂ is added dropwise to a solution of MeMgI in Et₂O at –10 °C. Workup of this solution involves treatment with saturated aqueous NH₄Cl followed by successive extractions with Et₂O. The Et₂O layers are combined, and the solvent is removed by evaporation under water aspiration. The dmpm is distilled at 45 °C (0.1 mmHg). Yield: 30–40%. ¹H NMR (CDCl₃): δ 1.40 (t, CH₂), 1.10 (t, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 34.9 (t, CH₂), 15.8 (t, CH₃). ³¹P{¹H} NMR (CDCl₃): δ –57.0 (s).

Synthesis of Pd₂Cl₂(dmpm)₂ (1). A slurry of 0.45 g (2.6 mmol) of [Pd(CO)Cl]_n in 20 mL of CH₂Cl₂ is prepared. The solution is degassed and cooled to –78 °C with a dry ice/2-propanol bath. To this solution is added 0.40 mL (2.6 mmol) of dmpm. The solution is allowed to warm to room temperature over a period of 2 h. The resulting orange solution is filtered and then concentrated. Diethyl ether is added to initiate precipitation, and the solution is cooled to –20 °C for ca. 10 h. A yellow orange solid is obtained and dried under vacuum, yielding 0.69 g (1.2 mmol, 95%). IR (Nujol): ν(Pd–Cl) = 260 cm⁻¹. Raman (CH₂Cl₂): ν(Pd–Pd) = 140 cm⁻¹; ν(Pd–Cl) = 257 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 2.65 (q, CH₂), 1.60 (q, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 42.0 (t, CH₂), 16.9 (q, CH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ –31 (s). Anal. Calcd for C₁₀H₂₈P₂Cl₂Pd₂: C, 21.60; H, 5.08; P, 22.29; Cl, 12.75. Found: C, 21.92; H, 5.25; P, 22.85; Cl, 12.44.

Synthesis of Pd₂Br₂(dmpm)₂ (2). A solution of 0.06 g (0.11 mmol) of Pd₂Cl₂(dmpm)₂ in 10 mL of CH₂Cl₂ is prepared. A 10-fold excess, 0.22 g (2.2 mmol) of NaBr in 10 mL of CH₃OH is added. The orange solution is stirred under N₂ for ca. 10 h. The solvent is then removed by rotary evaporation. The remaining solid is dissolved in CH₂Cl₂ and the solution filtered to remove excess NaBr. The solution is concentrated

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Pd₂Br₂(dmpm)₂^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Pd	0.56337 (5)	0.39708 (9)	0.35392 (5)	3.12 (2)
Br	0.67908 (7)	0.4391 (2)	0.55336 (8)	5.59 (4)
P(1)	0.6555 (2)	0.4983 (3)	0.3289 (2)	3.92 (8)
P(2)	0.5437 (2)	0.2751 (3)	0.1539 (2)	3.72 (7)
C(1)	0.6545 (6)	0.374 (1)	0.2414 (7)	4.1 (3)
C(2)	0.7784 (7)	0.527 (2)	0.4457 (8)	6.2 (4)
C(3)	0.6204 (8)	0.683 (2)	0.2646 (8)	6.5 (4)
C(4)	0.5180 (7)	0.247 (2)	0.0290 (8)	6.2 (4)
C(5)	0.5696 (7)	0.083 (1)	0.2055 (9)	5.4 (4)
H(1a)	0.7043	0.2994	0.2837	5*
H(1b)	0.6633	0.4321	0.2011	5*
H(2a)	0.7864	0.5944	0.4972	5*
H(2b)	0.8087	0.4331	0.4798	5*
H(2c)	0.8083	0.5769	0.4248	5*
H(3a)	0.6175	0.7599	0.3048	5*
H(3b)	0.6618	0.7233	0.2579	5*
H(3c)	0.5596	0.6805	0.1940	5*
H(4a)	0.4602	0.1945	-0.0233	5*
H(4b)	0.5157	0.3420	-0.0007	5*
H(4c)	0.5649	0.1832	0.0408	5*
H(5a)	0.5140	0.0188	0.1655	5*
H(5b)	0.6114	0.0308	0.2043	5*
H(5c)	0.5958	0.0803	0.2794	5*

^aStarred values indicate atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

under vacuum and diethyl ether added to initiate precipitation. The solution is cooled to -20 °C to obtain orange crystals, 0.042 g (0.06 mmol, 60%). X-ray quality crystals are obtained by slow solvent diffusion of CH₂Cl₂ and diethyl ether at -20 °C. IR (Nujol): $\nu(\text{Pd-Br}) = 175 \text{ cm}^{-1}$. Raman (CH₂Cl₂): $\nu(\text{Pd-Pd}) = 123 \text{ cm}^{-1}$; $\nu(\text{Pd-Br}) = 169 \text{ cm}^{-1}$. ¹H NMR (CD₃CN): δ 2.77 (q, CH₂), 1.66 (q, CH₃). ¹³C{¹H} NMR (CD₃CN): δ 42.1 (t, CH₂), 17.8 (q, CH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ -34 (s). $\Delta[0.001 \text{ M (H}_2\text{O)}] = 0.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Calcd for C₁₀H₂₈P₄Br₂Pd₂: C, 18.61; H, 4.38; Br, 24.78. Found: C, 19.09; H, 4.25; Br, 24.94.

Synthesis of Pd₂(OH)₂(dmpm)₂ (3) in H₂O. Solutions of 1 in degassed, deionized H₂O are prepared for spectroscopic characterization. Solutions of Pd₂(OH)₂(dmpm)₂ are yellow-orange; however, attempts to isolate the complex as a solid have failed. Addition of 2 equiv of AgBF₄ to solutions of 1 results in precipitation of 2 equiv of AgCl and no change in the electronic or ¹H NMR spectra. All subsequent characterizations are made on solutions of 1 in H₂O. Raman (H₂O): $\nu(\text{Pd-Pd}) = 140 \text{ cm}^{-1}$; $\nu(\text{Pd-OH}) = 351 \text{ cm}^{-1}$. ¹H NMR (D₂O): δ 2.80 (q, CH₂), 1.57 (m, CH₃). ³¹P{¹H} NMR (D₂O): δ -33 (s). $\Delta[0.001 \text{ M (H}_2\text{O)}] = 51.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Crystal Data Collection and Reduction. A yellow-orange crystal measuring 0.10 × 0.22 × 0.28 mm was used for determination of cell parameters and subsequent data collection. The crystal was mounted on a glass fiber with epoxy and transferred to the diffractometer. Crystal survey, unit cell dimension determination, and data collection were accomplished on a Enraf-Nonius CAD-4 automated single-crystal diffractometer using Zr-filtered Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) at room temperature. The observed systematic absences of *hkl* ($h + k = 2n + 1$) and *h0l* ($l = 2n + 1$) are consistent with the monoclinic space groups *Cc* and *C2/c*. Cell dimensions were determined from a least-squares refinement of 24 intense, high-angle reflections ($23^\circ < 2\theta < 37^\circ$). Lattice constants are $a = 19.623 (5) \text{ \AA}$, $b = 8.684 (3) \text{ \AA}$, $c = 16.902 (6) \text{ \AA}$, $\beta = 132.25 (2)^\circ$, $Z = 4$, $V = 2132 (3) \text{ \AA}^3$, and $\rho_{\text{calcd}} = 2.009 \text{ g cm}^{-3}$.

Data were collected from the octants *hkl* and *hkl* in the range $2^\circ \leq 2\theta \leq 50^\circ$. Three standard reflections were monitored every 100 observations, and the intensities showed no significant trends over data collection. The linear absorption coefficient for Mo K α radiation is 59.04 cm^{-1} , and an empirical absorption correction was applied to the data. The final set of data consisted of 1872 unique reflections of which 1245 had $I > 2.0\sigma(I)$.

Solution and Refinement of the Structure. The structure was solved by the MULTAN 11/82 program package and refined by full-matrix least-squares methods in the space group *C2/c*. All hydrogen atoms were included, but not refined, at calculated positions. Convergence of full-matrix least-squares refinement gave residuals of $R = 0.052$ and $R_w = 0.057$. In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. All programs used were from the SDP program

Table II. Bond Distance and Angles for Pd₂Br₂(dmpm)₂^a

(a) Bond Distances (Å)			
Pd-Pd'	2.603 (1)	P(1)-C(2)	1.835 (11)
Pd-Br	2.522 (1)	P(1)-C(3)	1.794 (12)
Pd-P(1)	2.291 (3)	P(2)-C(1)	1.823 (10)
Pd-P(2)'	2.275 (3)	P(2)-C(4)	1.828 (12)
P(1)-C(1)	1.822 (10)	P(2)-C(5)	1.793 (10)
(b) Bond Angles (deg)			
Pd'-Pd-Br	171.26 (4)	C(1)-P(1)-C(3)	104.4 (5)
Pd'-Pd-P(1)	84.70 (8)	C(2)-P(1)-C(3)	102.9 (6)
Pd'-Pd-P(2)'	85.10 (8)	Pd'-P(2)-C(1)	112.4 (4)
Br-Pd-P(1)	94.47 (8)	Pd'-P(2)-C(4)	117.9 (4)
Br-Pd-P(2)'	96.40 (8)	Pd'-P(2)-C(5)	114.3 (4)
P(1)-Pd-P(2)'	168.55 (10)	C(1)-P(2)-C(4)	104.6 (6)
Pd-P(1)-C(1)	110.0 (4)	C(1)-P(2)-C(5)	104.4 (5)
Pd-P(1)-C(2)	118.9 (4)	C(4)-P(2)-C(5)	101.9 (6)
Pd-P(1)-C(3)	115.2 (5)	P(1)-C(1)-P(2)	107.1 (5)
C(1)-P(1)-C(2)	104.0 (5)		

^aAtoms marked with a prime are related by $(1 - x, y, 0.5 - z)$.

Table III. Summary of Crystal Data and Intensity Collection for Pd₂Br₂(dmpm)₂

A. Crystal Data	
formula	Pd ₂ Br ₂ (C ₅ H ₁₄ P ₂) ₂
fw	644.8
cryst	orange blocks
cryst size	0.10 × 0.22 × 0.28 mm
cell params (errors)	
<i>a</i> , Å	19.623 (5)
<i>b</i> , Å	8.684 (3)
<i>c</i> , Å	16.902 (6)
β , deg	132.25 (2)
<i>V</i> , Å ³	2132 (3)
Laue symmetry	monoclinic
space group	<i>C2/c</i>
<i>Z</i>	4
ρ_{calcd} , g cm ⁻³	2.009
B. Data Collection and Reduction	
radiation	Zr filtered, Mo K α , ($\lambda = 0.71069 \text{ \AA}$)
diffractometer	CAD-4
temp, °C	25
scan range, deg	$2 < 2\theta < 50$
scan method	ω -2 θ
systematic absences	<i>hkl</i> , $h + k = 2n + 1$ <i>h0l</i> , $l = 2n + 1$ (045); (629); (935)
monitor reflcns	
scan angle, deg	$0.90 + 0.25 \tan \theta$
horiz aperture, mm	4.0
vert aperture, mm	$3.0 + 0.80 \tan \theta$
octants colld	<i>hkl</i> , <i>hkl</i>
no. of unique data	1872
no. of obsd data	1245 ($I > 2.0\sigma(I)$)
μ , cm ⁻¹	59.04
abs cor	empirical
<i>T</i> _{min} , <i>T</i> _{max}	0.633, 0.995
C. Solution and Refinement	
<i>R</i>	0.052
<i>R</i> _w	0.057
<i>S</i> ^a	1.346
max and mean shift/error	0.14, 0.04
max residual electron density	0.34

^aEsd of an observation of unit weight.

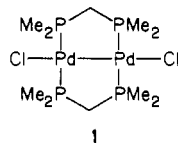
library, and all calculations were carried out on a PDP 11/34 computer.

Final positional and thermal parameters are listed in Table I. Bond distances and angles are given in Table II. The complete summary of crystal and intensity collection data can be found in Table III. Complete tables of torsion angles, refined temperature factors, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Synthesis of Binuclear Pd(I) Complexes. Complex 1 is prepared by the reaction of dmpm with [Pd(CO)Cl]_{*n*}. Yields of 1 are variable, ranging 60–90%, depending on the quality of [Pd-

(CO)Cl]_n. Typical yields for **1** of 90% are obtained when the [Pd(CO)Cl]_n is prepared and isolated in an oxygen- and moisture-free atmosphere and used promptly after preparation. The reaction with dmpm affords a dark orange solution from which orange crystals are obtained. Carbon monoxide is liberated during the reaction, and as a consequence the product is sometimes contaminated with the CO-bridged species, Pd₂Cl₂(μ-CO)(dmpm)₂.⁷ This contaminant is converted to **1** by bubbling N₂(g) through the reaction solution. Complex **1** is air stable as a solid and in nonaqueous solvents. This contrasts with the highly air-sensitive nature of dmpm and suggests that little or no dissociation of the ligand from the complex occurs in solution. Complex **1** is also soluble in EtOH, MeOH, CH₃CN, and CH₂Cl₂. The IR spectrum of **1** reveals little useful information in the 4000–400-cm⁻¹ region. In the far-IR and Raman spectra, however, bands attributed to Pd–Cl stretching are observed. For **1**, ν(Pd–Cl) is 260 and 257 cm⁻¹ by IR and Raman spectroscopy, respectively. These values compare well with ν(Pd–Cl) = 249 cm⁻¹ found for Pd₂Cl₂(dppm)₂.^{2d} In the Raman spectrum, a distinct band is seen at 140 cm⁻¹, which is assigned to ν(Pd–Pd) for **1**. The room-temperature 200-MHz ¹H NMR spectrum of **1** displays complex resonances at δ 2.65 (methylene) and δ 1.60 (methyl), both of which appear as quintets from virtual coupling to the four dmpm phosphorus nuclei in the complex. These resonances appear downfield from the free ligand values of δ 1.40 (methylene) and δ 1.10 (methyl) in CDCl₃. The complex exhibits a sharp singlet at δ -31 in the ³¹P{¹H} NMR spectrum at room temperature, suggesting a dynamic process occurs at 25 °C rendering all four phosphorus nuclei equivalent. The ³¹P{¹H} NMR signal of **1** occurs ~25 ppm downfield from the free ligand (δ -57). The ¹³C{¹H} NMR spectrum of **1** shows a triplet at δ 42.0 for the dmpm methylene with J_{P-C} = 12.9 Hz, while the methyl resonance appears as a virtual quintet at δ 16.9. These spectral data are consistent with a binuclear dmpm-bridged structure of the complex. These data together with the results of an X-ray crystallographic study of the corresponding Br-substituted complex, Pd₂Br₂(dmpm)₂ (vide infra), establish the structure of **1** as



The related Br-substituted complex, Pd₂Br₂(dmpm)₂ (**2**) is prepared by the reaction of **1** with excess NaBr in methanol/methylene chloride (eq 1). The reaction proceeds with a slight

$$\text{Pd}_2\text{Cl}_2(\text{dmpm})_2 + 2\text{NaBr} \rightarrow \text{Pd}_2\text{Br}_2(\text{dmpm})_2 + 2\text{NaCl} \quad (1)$$

darkening of the solution, and after filtration of the excess sodium salts, diethyl ether is added to produce dark orange crystals. Complex **2** exhibits ν(Pd–Br) = 175 and 169 cm⁻¹ in the IR and Raman spectra, respectively, which compares to ν(Pd–Br) for Pd₂Br₂(dppm)₂ of 186 cm⁻¹ as determined by IR spectroscopy. An additional band is observed at 123 cm⁻¹, which is assigned to ν(Pd–Pd) of **2**. The ¹H NMR spectrum of **2** displays two resonances slightly downfield from those of **1**. As with **1**, the methylene resonance (δ 2.77) is to first order a quintet with an apparent J_{P-H} = 3.83 Hz while the methyl resonance (δ 1.66) is a virtual quintet with J_{P-H} ~ 1.20 Hz. The room-temperature ³¹P{¹H} NMR spectrum of **2** is a singlet at δ -34, approximately 3 ppm upfield from that of **1**. The equivalence of all four phosphorus nuclei is again evident. The ¹³C{¹H} NMR spectrum of **2** displays a methylene triplet at δ 42.1 with J_{P-C} = 12.6 Hz and a methyl virtual quintet at δ 17.8 with J_{P-C} = 9.0 Hz. All spectroscopic data for **2** relative to **1** suggest very similar structures. Suitable crystals for X-ray analysis were obtained for **2**, and the crystal and molecular structure was determined.

Crystal Structure of Pd₂Br₂(dmpm)₂. The crystal structure is composed of discrete neutral Pd₂Br₂(dmpm)₂ molecules. There are no solvent molecules of crystallization. The molecular structure of **2** consists of two Pd atoms bridged by two mutually trans dmpm ligands. In the solid state, the molecule possesses a crystallo-

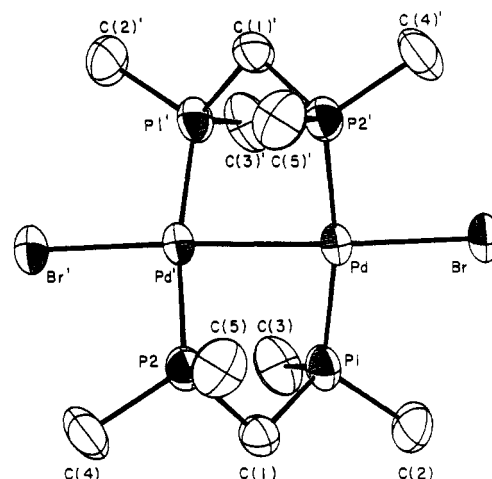


Figure 1. ORTEP drawing of the Pd₂Br₂(dmpm)₂ molecule viewed down the 2-fold rotation axis. Primed atoms are generated by the 2-fold axis.

graphically imposed 2-fold axis between the two Pd atoms. The 2-fold axis relates the primed and unprimed atoms in the ORTEP drawing of the molecule, presented in Figure 1.

The coordination geometry about each Pd atom is approximately square planar with all angles about the Pd center within ±7° of 90°. Each approximate square plane includes two transoid dmpm phosphines, a bromine atom, and a Pd–Pd interaction. The trans angles exhibited by these atoms are P(2)′–Pd–P(1)′ = 168.55 (1)° and Br–Pd–Pd′ = 171.26 (4)°. The phosphorus atoms approach tetrahedral geometry as expected. The largest deviation from idealized tetrahedral phosphorus is Pd–P(1)–C(2) = 118.9 (4)°. The P(1)–C(1)–P(2) angle through the dmpm methylene carbon is 107.1 (5)°, some 8° more acute than that of the free ligand, ~115°. The smaller methylene carbon bond angle in coordinated dmpm apparently results from the short nonbonded P(1)⋯P(2) separation of 2.931 (3) Å compared to 3.129 Å for the free ligand in the gas phase.¹⁷

The Pd–Pd separation of 2.603 (1) Å is well within the range normally reported for Pd–Pd single bonds. It falls between those observed for the unbridged complex Pd₂(CNMe)₆²⁺ (2.5310 (9) Å)¹⁹ and bridged complexes Pd₂Br₂(dppm)₂ (2.699 Å)^{2a} and Pd₂Cl(SnCl₃)(dppm)₂ (2.644 Å).^{2b} The Pd–Pd separation is significantly shorter than that of related dppm complexes and somewhat closer to that of unbridged Pd(I) complexes. This is an indication of the ability of dmpm to accommodate smaller metal–metal separations than dppm. This is accomplished by a severe twisting in the eight-membered Pd₂P₄C₂ ring (vide infra), which may not be possible with dppm because of steric requirements of the phenyl rings. The Pd–Pd internuclear separation is significantly shorter than the separation of the adjacent dmpm phosphorus atoms (P(1)⋯P(2) = 2.931 Å). The short nonbonding adjacent phosphorus distance is comparable with Pd₂Cl(SnCl₃)(dppm)₂ (P⋯P = 2.92 Å, average).^{2b}

The molecule exhibits a pronounced twisting in the solid state. The two approximately square-planar ligand arrays centered at each palladium are inclined at a torsion angle, τ = 50.5°, with respect to each other. An ORTEP drawing of **2** viewed down the Pd–Pd internuclear axis is presented in Figure 2. The degree of twisting of the eight-membered ring containing the two palladium, four phosphorus, and two methylene carbon atoms is significantly larger than that found in similar complexes, i.e. Pd₂Br₂(dppm)₂ (39°)^{2a} and Pd₂Cl(SnCl₃)(dppm)₂ (41.3°).^{2b} The Pd–Pd separation in **2** is at least 0.04 Å shorter than that in the related dppm complexes Pd₂Br₂(dppm)₂ and Pd₂Cl(SnCl₃)(dppm)₂. This apparently shortens the nonbonding distance between adjacent phosphorus atoms on dmpm. The high P(1)–Pd(1)–Pd(2)–P(2) torsion angle found in the solid-state structure of **2** is expected to lessen this relatively close P(1)⋯P(2) nonbonded interaction. An interesting comparison can be made with two related systems, which contain unsupported Pd–Pd and Pt–Pt bonds. The complexes Pd₂(CNMe)₆²⁺¹⁹ and Pt₂Cl₄(CO)₂²⁻¹⁸

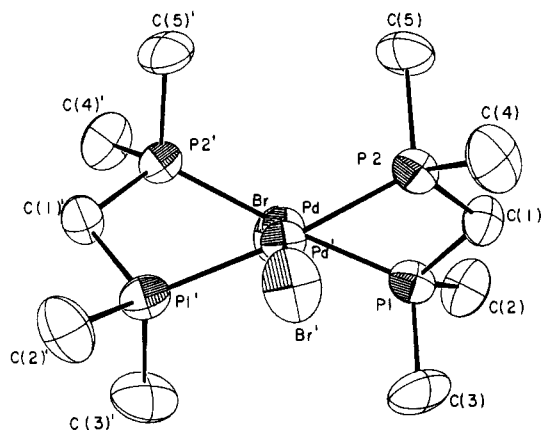


Figure 2. ORTEP drawing of the $\text{Pd}_2\text{Br}_2(\text{dmpm})_2$ molecule viewed down the Pd-Pd bond axis. The torsion angle, $\text{P}(1)\text{-Pd-Pd}'\text{-P}(2)$, between pairs of transoid phosphorus atoms is 50.5° .

exhibit dihedral angles of 89 and 60° , respectively. We note that while a dihedral angle $\tau = 90^\circ$ is ideal for minimizing ligand repulsion, an angle of $\tau = 45^\circ$ minimizes overlap of the out-of-plane metal $d\pi$ orbitals on adjacent metal centers. It appears that while nonbridged systems are free to twist to minimize ligand-ligand repulsions, the diphosphine-bridged systems are constrained by the eight-membered ring to adopt conformations characterized by torsion angles approaching 45° , minimizing electronic repulsions.

The remainder of bond distances are normal. The Pd-Br distance of $2.522(1) \text{ \AA}$ in **2** is slightly shorter than the mean Pd-Br distance in $\text{Pd}_2\text{Br}_2(\text{dppm})_2$ ($2.535(6) \text{ \AA}$). The mean Pd-P distance is $2.283(3) \text{ \AA}$, which compares favorably with that of $\text{Pd}_2\text{Br}_2(\text{dppm})_2$ ($2.288(1) \text{ \AA}$) and $\text{Pd}_2\text{Cl}(\text{SnCl}_3)(\text{dppm})_2$ ($2.310(4) \text{ \AA}$). There are no unusual intermolecular contacts.

Reaction with Water. A most unusual and interesting feature of the chemistry of the dmpm-bridged complexes is their solubility and stability in aqueous solutions. In aqueous media, complex **1** exists in equilibrium with a dihydroxy species, $\text{Pd}_2(\text{OH})_2(\text{dmpm})_2$ (**3**). Conductivity data suggest that at pH 7, **3** is a neutral complex in H_2O . When **1** is dissolved in aqueous solution, the solution conductivity increases to a value consistent with a 1:1 electrolyte and the pH decreases. These results suggest that liberation of HCl accompanies formation of **3**. Raman spectral data of **1** in H_2O show that $\nu(\text{Pd-Cl})$ is replaced by a new band at 351 cm^{-1} consistent with $\nu(\text{Pd-O})$ for **3**. Complex **3** exhibits $\nu(\text{Pd-Pd}) = 140 \text{ cm}^{-1}$, suggesting that the Pd-Pd bond remains intact in aqueous solution. The ^1H NMR spectrum of **3** in D_2O is quite similar to that of **1**. The methylene protons exhibit the typical virtual quintet at $\delta 2.80$ with $J_{\text{P-H}} = 4 \text{ Hz}$, while the methyl resonance appears as a broad singlet at $\delta 1.57$. The methylene protons resonances are also somewhat broadened compared to those of **1** and **2**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** exhibits a singlet at $\delta -33$ in D_2O , which is slightly upfield of **1** and downfield of **2**.

Complex **2** is also soluble and stable in aqueous solution; however, the degree of solubility is significantly less than that of **1**. The identity of **2** in H_2O is established by the following set of observations. Electronic spectra of **2** in CH_2Cl_2 and H_2O appear to be very similar with only small solvent shifts of the absorption bands. This observation contrasts sharply with that for **1** in CH_2Cl_2 compared to H_2O , where dramatic differences are apparent. A compilation of UV-vis electronic absorption data for **1**, **2**, and **3** in H_2O and CH_2Cl_2 solutions is given in Table IV. Addition of AgBF_4 to **2** in aqueous solution results in the precipitation of AgBr and a solution exhibiting an electronic spectrum essentially identical with that of **3** (eq 2). Addition of AgBF_4

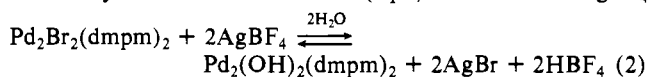
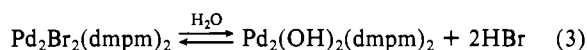


Table IV. Electronic Spectral Data of $\text{Pd}_2\text{X}_2(\text{dmpm})_2$ Complexes at 25°C

compd	solvent	λ_{max} , nm (ϵ_{max} , $\text{M}^{-1} \text{ cm}^{-1}$)
$\text{Pd}_2\text{Cl}_2(\text{dmpm})_2$	CH_2Cl_2	385 (5700), 320 (13 100), 278 (22 100), 243 (10 900)
$\text{Pd}_2(\text{OH})_2(\text{dmpm})_2$	H_2O	393 (2800), 339 (4700), 290 (9900), 261 (17 000)
$\text{Pd}_2\text{Br}_2(\text{dmpm})_2$	CH_2Cl_2	394 (9600), 333 (21 700), 279 (21 500), 245 (18 000)
$\text{Pd}_2\text{Br}_2(\text{dmpm})_2$	H_2O	400 (2900), 310 (7500), 267 (8800)

to **1** in H_2O also results in precipitation of silver halide, but no change in the UV-vis spectrum is evident, suggesting that chloride is not coordinated to palladium. The conductance of **2** is less than $1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, suggesting that **2** is a neutral species in H_2O and that essentially no HBr is liberated upon dissolution. The aqueous solution equilibrium (eq 3) apparently lies substantially toward



unsubstituted **2**. These observations collectively point to the identity of **2** in aqueous solution as the neutral species $\text{Pd}_2\text{Br}_2(\text{dmpm})_2$.

Conclusions

A structural and chemical study of dipalladium complexes bridged by dmpm has been made. The X-ray structure of **2** shows it to be quite twisted in the solid state. The Pd-Pd separation of $2.603(1) \text{ \AA}$ is unusually short for diphosphine-bridged dipalladium complexes and is consistent with a Pd-Pd single bond. The structure shows the metal-metal bond to be more exposed than those of related diphosphine-bridged complexes, which could lead to enhanced reactivity associated with the Pd-Pd bonds of these complexes. The parent complex, **1**, undergoes substitution reactions with bromide and hydroxide to produce axially substituted Pd-Pd-bonded complexes. These complexes are unusual in that they are soluble and stable in aqueous media. Complex **1** reacts with water to form the neutral dihydroxy species **3** while complex **2** dissolves in water without substantial substitution of bromide. The water solubility of these complexes presents intriguing possibilities for homogeneous catalysis in aqueous media. A major drawback of homogeneous catalysts is their difficult separation from products and reactants. In the case of water-soluble homogeneous catalysts, one can envisage straightforward phase separation of organic reactants/products and the catalyst. Further research along these lines is being conducted in our laboratories.

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Registry No. **1**, 89178-59-6; **2**, 98088-57-4; **3**, 89178-61-0; dmpm, 64065-08-3; $\text{PdCl}_2\text{CH}_2\text{PdCl}_2$, 28240-68-8; $[\text{Pd}(\text{CO})\text{Cl}]$, 43732-39-4; Pd, 7440-05-3.

Supplementary Material Available: Complete tables of general and refined temperature factors, torsion angles, and observed and calculated structure factors and a unit cell packing diagram for $\text{Pd}_2\text{Br}_2(\text{dmpm})_2$ viewed down the b axis (16 pages). Ordering information is given on any current masthead page.