

Solution and Solid-State Structures of the Binuclear Zerovalent Palladium Complex $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ (dippe = 1,2-Bis(diisopropylphosphino)ethane)

Michael D. Fryzuk,* Guy K. B. Clentsmith, and Steven J. Rettig†

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

Gerhard Hägele

Heinrich-Heine-Universität, Düsseldorf, Institut für Anorganische Chemie und Strukturchemie, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

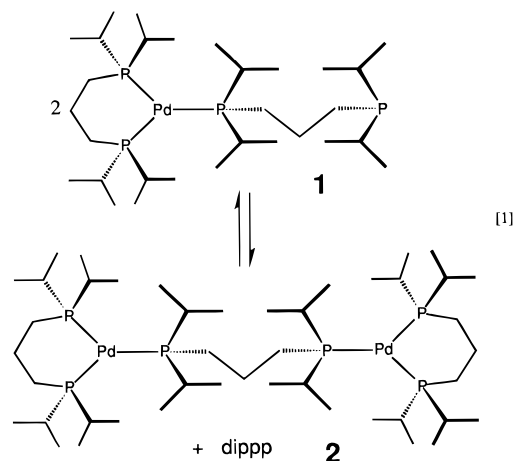
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The reaction of $\text{PdCl}_2(\text{dippe})$, where dippe = 1,2-bis(diisopropylphosphino)ethane, with 2 equiv of KBET_3H in toluene generates the binuclear palladium(0) derivative $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ (**4**) in 35% yield; alternatively, the reaction of $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}]_2(\mu\text{-Cl})_2$ with MeONa in the presence of 3 equiv of dippe generates **4** as well. Mechanistic studies on the attempted formation of mixed binuclear complexes are reported as well as the use of **4** as a catalyst for the reductive dechlorination of chloroarenes. Analysis of the second-order $[\text{AB}_2]_2$ spin system was accomplished by iteration of the 202.47 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**; the solution structure and the solid-state structures are found to be very nearly identical.

Introduction

Mononuclear zerovalent palladium phosphine complexes of the type $\text{Pd}(\text{PR}_3)_n$ ($n = 2\text{--}4$) provide one of the classic examples of ligand dissociation equilibria in coordination chemistry,^{1,2} and such equilibria are paramount to numerous catalytic processes. Normally, the use of chelating bidentate phosphines might be expected to reduce the tendency for dissociation. However, the recent study by Portnoy and Milstein clearly shows that complexes of Pd(0) incorporating bulky bidentate phosphines undergo more complicated equilibria involving mononuclear and binuclear species, with the nature of the equilibria dependent on the chelate ring size.³ For example, the solution behavior of a complex with the formula $\text{Pd}(\text{dipp})_2$ (dipp = 1,3-bis(diisopropylphosphino)propane) was shown to involve a mononuclear trigonal planar derivative in equilibrium with a binuclear complex having a bridging dipp unit and free dipp (eq 1). In contrast, the related derivative $\text{Pd}(\text{dippe})_2$ (**3**), where dippe is the two-carbon backbone ligand 1,2-bis(diisopropylphosphino)ethane, exists exclusively as the four-coordinate mononuclear complex. This difference in solution structures for these bis-(ligand) complexes **1** and **3** is further manifested in the enhanced reactivity of the former in the carbonylation of chloroarenes.^{3,4} It is interesting to note that while the binuclear species **2** in eq 1 can be isolated, no such analogous complex with dippe, i.e. $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$, has been reported.³

During our investigations on the preparation of binuclear palladium hydride complexes stabilized by bulky chelating ligands, for example, $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2$



and its corresponding adducts with Lewis acids,^{5,6} we attempted to prepare the analogous hydride dimer using the two-carbon backbone ligand, dippe. However, instead of forming $[(\text{dippe})\text{Pd}]_2(\mu\text{-H})_2$, the binuclear zerovalent complex $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$, **4**, the dippe analog of **2**, was isolated in moderate yield (eq 2).

This result gave rise to allied attempts to produce 1:1 complexes of Pd and bidentate phosphines, and in fact these rare species were directly observed and characterized.⁷ Equilibria similar to eq 1 were found to operate which has possible implications in catalysis. In addition, the single-crystal X-ray structure of **4**, which exhibits a trigonal planar coordination geometry around the Pd nuclei, was determined; furthermore its solution structure was detailed by analysis of its second-order $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which presents an interesting case of magnetic inequivalence.

† Professional officer, UBC Crystallographic Service.

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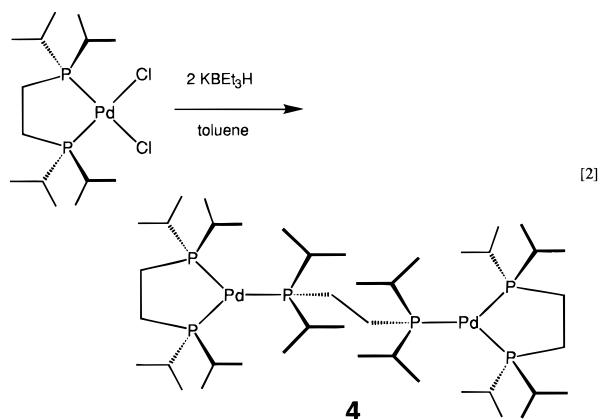
(3) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655.

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(6) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1994**, *115*, 3804.

(7) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191.



Experimental Section

General procedures are detailed elsewhere.⁶ PdCl₂(dippe) was prepared by adding 1 equiv of the chelating phosphine to a solution of PdCl₂(C₆H₅C≡N)₂ in acetone and recovered on a frit. MeOH was distilled from Mg(OMe)₂ under Ar and used to prepare MeONa solutions by addition of sodium metal. Product mixtures of the catalytic experiments were analyzed by a Hewlett Packard 5390A gas chromatograph. Solution molecular weight determinations were carried out in *d*₆-benzene by means of the isopiestic method in a Signer molecular weight apparatus;⁸ Pd(dippe)₂ was used as reference. ³¹P{¹H} and ¹H{³¹P} NMR spectroscopy were performed upon a Bruker AMX-500 instrument operating at 202.47 and 500.13 MHz, respectively; ³¹P{¹H} NMR spectra were referenced to external P(OMe)₃ (141.00 ppm with respect to 85% H₃PO₄ at 0.00 ppm); ¹H NMR spectra were referenced to internal C₆D₅-CD₂H (2.09 ppm) or C₆D₅H (7.15 ppm). ¹³C{¹H} NMR spectroscopy was performed upon a Bruker AC-200 instrument operating at 50.32 MHz; spectra were referenced to internal *d*₈-toluene (C_{ipso}, 137.5 ppm). Spectral analysis was performed upon a ³¹P{¹H} NMR spectrum (32 Kwords) ranging from 9800 to 11 450 Hz. Line broadening by exponential multiplication with LB = 1 Hz was applied to the FID prior to FT. Data were transferred to the 1D WIN-NMR⁹ program system for numerical evaluation. After subspectral analysis, starting data and the experimental spectrum were used for iteration and simulation with WIN-DAISY¹⁰ running under 1D WIN-NMR on a PC 486/33 MHz. Graphical representations were produced by 1D WIN-NMR.

[(dippe)Pd]₂(μ-dippe) (4). PdCl₂(dippe) (0.510 g; 1.16 mmol) was slurried in toluene (60 mL) and cooled to -40 °C in a dry-ice/acetone bath. A solution of 2 equiv of KBEt₃H (0.320 g; 2.32 mmol) in toluene (10 mL) was added with stirring. The temperature was maintained for 2 h during which time the PdCl₂(dippe) went up and a deep brown color developed. The reaction mixture was warmed to room temperature and passed through a frit lined with Celite. The solvent was stripped off from the filtrate, the brown residue was dissolved in toluene (2 mL), and the solution was layered with pentane (10 mL). After 24 h at -30 °C, amber crystals of **4** deposited from the solution (0.203 g, 35% yield based on Pd). Anal. Calcd for C₄₂H₉₆P₆Pd₂: C, 50.91; H, 9.68. Found: C, 50.58; H, 9.49. ¹H{³¹P} NMR (*d*₈-toluene): δ 1.99 (s, 4H, bridging CH₂), 1.95 (sept, 4H, bridging-CHMe₂, J_{H-Me} = 7.5 Hz), 1.92 (sept, 8H, chelating-CHMe₂, J_{H-Me} = 7.5 Hz), 1.42 (s, 8H, chelating-CH₂), 1.33 (d, 24H, bridging-CHMeMe', J_{Me-H} = 7.5 Hz), 1.18 and 1.05 (d, 48H, chelating-CHMeMe', J_{Me-H} = 7.5 Hz).

Alternatively **4** may be prepared by treating [(η³-C₄H₇)Pd]₂(μ-Cl)₂ (0.320 g; 0.810 mmol) with MeONa (0.100 g; 1.85 mmol)

in MeOH (50 mL), in the presence of stoichiometric dippe (0.640 g; 2.44 mmol, 1.5 equiv/Pd).¹¹ The phosphine is added directly to the yellow solution after addition of the MeONa solution. The clear solution was stirred for 12 h and then evaporated to dryness. The ochre precipitate remaining was washed repeatedly with cold hexanes (15 mL) to give pure **4** (0.500 g; 62% yield).

[(dipp)Pd]₂(dippe) (5). To a deep red solution of [(dipp)Pd]₂(μ-H)₂ (0.100 g; 0.130 mmol) in toluene (5 mL) was added a solution of dippe (0.034 g; 0.130 mmol) in toluene (10 mL). The red color rapidly discharged to give an amber solution. The solvent was removed *in vacuo* and the residue recrystallized from pentane (5 mL) to give amber crystals of **5** (0.079 g; 65% yield). Anal. Calcd for C₄₄H₁₀₀P₆Pd₂: C, 51.41; H, 9.81. Found: C, 51.44; H, 9.83. The complex is unstable in solution.

[(dippe)Pd]₂(dipp) (6). The alternative procedure for **4** was employed with [(η³-C₄H₇)Pd]₂(μ-Cl)₂ (0.312 g; 0.790 mmol), dippe (0.415 g; 1.58 mmol) and dipp (0.218 g; 0.790 mmol) in toluene (10 mL), and MeONa (0.104 g; 1.90 mmol) in MeOH (4.3 mL). Workup and recrystallization from hexanes (10 mL) gave amber crystals (0.425 g; 53% yield). Anal. Calcd for C₄₃H₉₈P₆Pd₂: C, 50.94; H, 9.74. Found: C, 51.10; H, 9.90. The complex is unstable in solution.

Pd(dippe){η²-H₂C=C(Me)CH₂OMe} (7) and [Pd(dippe)]_n (8). The same procedure was used as for **6** with [(η³-C₄H₇)Pd]₂(μ-Cl)₂ (0.201 g; 0.510 mmol), dippe (0.268 g; 1.02 mmol), and MeONa (0.055 g; 1.02 mmol) in MeOH (30 mL). Removal of the solvent gave a brown powder (0.379 g) which by ³¹P{¹H} NMR spectroscopy was a mixture of **7**, **8**, and **4** in a 7:1:2 ratio. Pd(dippe){η²-H₂C=C(Me)CH₂OMe} (**7**): ³¹P{¹H} NMR (*d*₆-benzene) δ 61.2 (d, 1P, J_{P-P'} = 66.2 Hz), 55.0 (d, 1P, J_{P-P} = 66.2 Hz); ¹H{³¹P} NMR δ 4.83 and 3.57 (d, 2H, CHHO, J_{H-H'} = 10.0 Hz), 3.46 (s, 3H, OMe), 3.18 and 3.06 (s, 2H, vinylic-CHH), 2.17 (s, 3H, vinylic-Me), isopropyl resonances obscured by those due to **4** and **8**. [Pd(dippe)]_n (**8**): ³¹P{¹H} NMR (*d*₆-benzene) δ 32.7 (s); ¹H{³¹P} NMR resonances obscured by those due to **4** and **7**. Recrystallization of the crude product from hexanes or pentane enriched the percentage composition of **4** and further characterization could not be achieved.

Pd(dipp){η²-H₂C=C(Me)CH₂OMe} (9) and [Pd(dipp)]_n (10). The same procedure was used as for **6** with [(η³-C₄H₇)Pd]₂(μ-Cl)₂ (0.215 g; 0.550 mmol), dipp (0.304 g; 1.10 mmol) in toluene (7 mL), and MeONa (0.061 g; 1.13 mmol) in MeOH (30 mL). The reaction mixture was recrystallized from pentane (2.5 mL) to give amber crystals (0.230 g) which ³¹P{¹H} NMR spectroscopy revealed to be a 9:1 mixture of **9** and **10**. A successive recrystallization and prolonged drying under vacuum gave low-melting amber crystals of **10** (0.055 g; 13% yield). Pd(dipp){η²-H₂C=C(Me)CH₂OMe} (**9**): ³¹P{¹H} NMR (*d*₆-benzene) δ 26.4 (d, 1P, J_{P-P'} = 24.9 Hz), 25.4 (d, 1P, J_{P-P} = 24.9 Hz); ¹H{³¹P} (*d*₆-benzene) δ 4.77 and 3.52 (d, 2H, CHHO, J_{H-H'} = 10.0 Hz), 3.46 (s, 3H, OMe), 2.95 and 2.85 (s, 2H, vinylic-CHH), 2.12 (s, 3H, vinylic-Me), 1.75 and 1.65 (sept, 4H, CHMeMe', J_{H-Me} = 7.0 Hz), 1.67 and 1.22 (m, 4H, CH₂-CH₂P), 1.09 and 1.05 (d, 12H, CHMeMe', J_{Me-H} = 7.0 Hz), 0.96 and 0.92 (d, 12H, CHMeMe', J_{Me-H} = 7.0 Hz); ¹³C{¹H} NMR δ 81.7 (m, CH₂O), 66.6 (d, CCH₂, J_{P-C} = 23 Hz), 56.7 (s, OMe), 49.6 (d, vinylic-CH₂, J_{P-C} = 17 Hz), 24.3 (d, vinylic-Me, J_{P-Me} = 2 Hz), ligand resonances were ambiguous. The analysis was not obtained. [Pd(dipp)]_n (**10**): Anal. Calcd for C₁₅H₃₄P₂Pd: C, 47.07; H, 8.95. Found: C, 47.35; H, 9.05. ³¹P{¹H} NMR (*d*₆-benzene): δ 34.6 (s). ¹H{³¹P} NMR (*d*₆-benzene): δ 2.44 (m, 2H, CH₂CH₂P), 1.72 (sept, 4H, CHMeMe', J_{H-Me} = 7.0 Hz), 1.46 (m, 4H, CH₂P), 1.30 and 1.20 (d, 24H, CHMeMe', J_{Me-H} = 7.0 Hz). Solution molecular weight: Calcd for [(dipp)Pd]₂, 766 g mol⁻¹; found, 750 ± 80 g mol⁻¹.

(8) (a) Signer, R. *Liebigs Ann. Chem.* **1930**, 478, 246. (b) An apparatus, similar to the one used here, is described in: Zoellner, R. W. *J. Chem. Educ.* **1990**, 67, 714.

(9) 1D WIN-NMR program system: Thiele, H.; Germanus, A.; Pape, R. Bruker Franzen Analytik, manual, 1993.

(10) WIN-DAISY program system: Weber, U.; Spiske, R.; Hoffken, H. W.; Hagele, G.; Thiele, H. Bruker Franzen Analytik, manual, 1993.

(11) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, 12, 187.

Table 1. Crystallographic Data

compd	[(dippe)Pd] ₂ (μ-dippe) (4)
formula	C ₄₂ H ₉₆ P ₆ Pd ₂
fw	999.86
cryst system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	9.152(2)
<i>b</i> , Å	29.648(3)
<i>c</i> , Å	10.553(2)
β, deg	111.11(2)
<i>V</i> , Å ³	2671.2(9)
<i>Z</i>	2
ρ _{calc} , g/cm ³	1.243
<i>T</i> , °C	21
radiation	Mo
λ, Å	0.7110 69
μ, cm ⁻¹	8.66
transm factors (relative)	0.88–1.00
<i>R</i> (<i>F</i>) ^a	0.028
<i>R</i> _w (<i>F</i>) ^a	0.027

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}.$$

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) Observed in [(dippe)Pd]₂(μ-dippe) (4)

Pd1–P1	2.2966(6)	C2–C3	1.486(4)
Pd1–P2	2.2970(6)	C1–C1*	1.529(4)
Pd1–P3	2.3019(6)		
P1–Pd1–P2	132.40(2)	P2–Pd1–P3	90.08(2)
P1–Pd1–P3	137.46(2)		

Catalyses. A bomb reactor was charged with **1** or **4** (0.1 mmol), PhCl (10 mmol), powdered NaOH (10 mmol), and MeOH (4 mL). The bomb was evacuated and heated to 90 °C in an oil bath. Periodically, a drop of solution was diluted with Et₂O and its composition analyzed by GC.

X-ray Crystallographic Analysis of [(dippe)Pd]₂(μ-dippe) (4). Selected crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 42.9–47.6°. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, showed only small random fluctuations. The data were processed¹² and corrected for Lorentz and polarization effects and for absorption (empirical, based on azimuthal scans for three reflections).

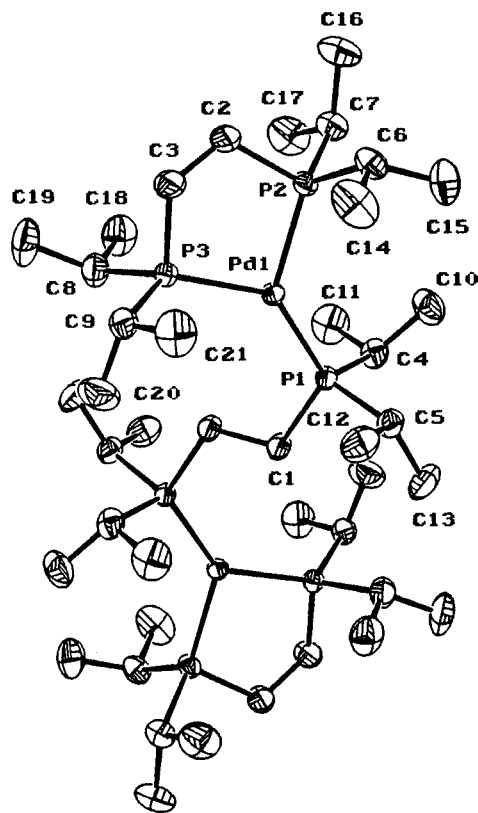
The structure was solved by conventional heavy atom methods, the coordinates of the Pd and P atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent different Fourier syntheses. The binuclear complex is situated at a crystallographic center of symmetry. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in calculated positions (methyl groups staggered, C–H = 0.98 Å and *B*_H = 1.2*B*_{bonded atom}). No correction for secondary extinction was necessary. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 13. Selected bond lengths and bond angles appear in Table 2. Complete tables of crystallographic data, atom positional and thermal parameters, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information. Structure factors are available from the authors.

Results and Discussion

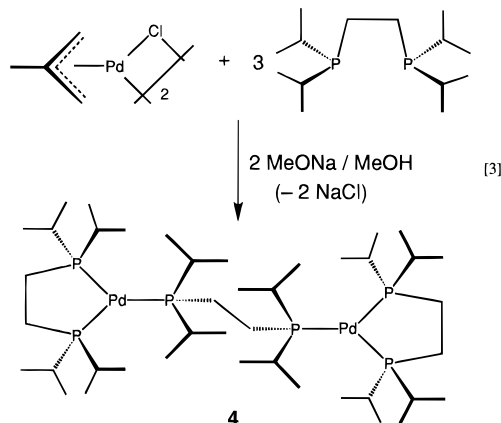
Previously, we showed that the binuclear palladium hydride complex [(dipp)Pd]₂(μ-H)₂ could be prepared

(12) TEXSAN/TEXRAY: Crystal structure analysis package (VMS Version 5.1); Molecular Structure Corp.: The Woodlands, TX, 1985.

(13) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

**Figure 1.** Molecular structure and numbering scheme of [(dippe)Pd]₂(μ-dippe) (**4**).

by reaction of the corresponding mononuclear Pd(II) precursor PdI₂(dipp) with 2 equiv of KBEt₃H in toluene.^{5,6} In an effort to extend this to the two-carbon backbone diphosphine ligand, we treated PdCl₂(dippe) with 2 equiv of KBEt₃H in toluene. From the brown solution that results, amber crystals of empirical formula Pd(dippe)_{1.5} could be reproducibly isolated in 35% yield based on Pd (53% yield based on dippe). Signals attributable to palladium hydrides were conspicuously absent from the ¹H NMR spectrum, and the ³¹P{¹H} NMR spectrum at different field strengths showed magnetically nonequivalent phosphorus nuclei; in Figure 2, the second-order ³¹P{¹H} NMR spectrum of **4** is shown. This same material could also be isolated after nucleophilic cleavage of the 2-methylallyl derivative, [(η³-C₄H₇)Pd]₂(μ-Cl)₂, in the presence of 1.5 equiv of dippe per Pd (eq 3). A binuclear structure was suggested on the basis of the ³¹P{¹H} NMR spectrum and confirmed by the solid-state X-ray crystal structure analysis (Figure 1).



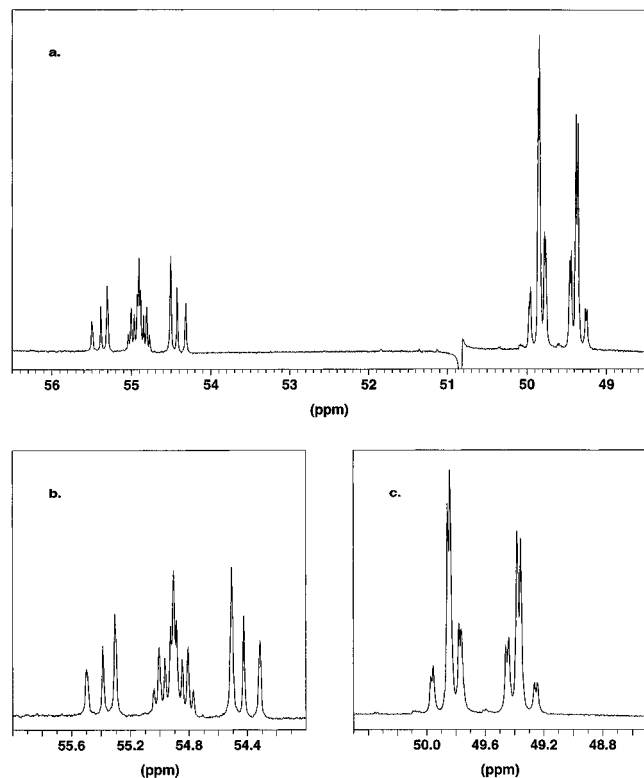


Figure 2. Experimental 202.47 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ (**4**) in d_8 -toluene: (a) total spectrum; (b) downfield region (A resonance); (c) upfield region (B_2 resonance). The absorption at 50.9 ppm results from a folded-in peak due to an impurity.

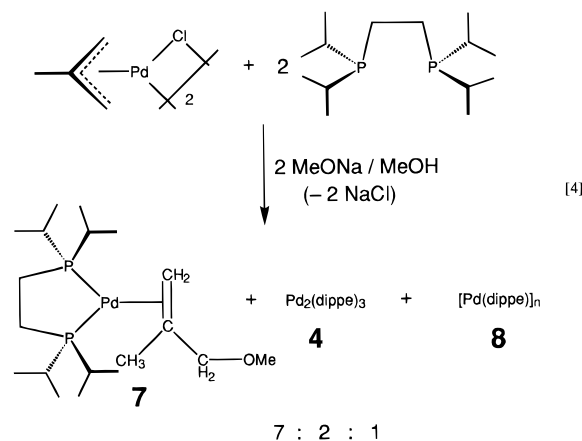
The most notable feature of the solid-state structure of **4** is the flexible coordination behavior of the bis-(diisopropylphosphino)ethane ligand (dippe). Two dippe ligands adopt a chelating mode, whereas one dippe adopts an uncharacteristic bridging mode, linking the two palladium nuclei. The center of the molecule lies on a crystallographic point of inversion, and thus each atom in one-half of the complex is equivalent to the corresponding atom on the other half. The coordination geometry around each palladium nucleus is trigonal planar with each Pd–P separation being approximately 2.30 Å, a typical value for palladium phosphine complexes in zerovalent or +I oxidation states. Unlike the homologous species $\text{Pd}_2(\text{dppm})_3$ ¹⁴ (dppm = bis(diphenylphosphino)methane), there is no suggestion of a metal–metal interaction, since each metal nucleus in **4** resides in an isolated coordination environment. The chelating P2–Pd1–P3 bond angle is 90.08(2)°, whereas the P1–Pd1–P3 and P2–Pd1–P3 angles are 132.40(2) and 137.46(2)°, respectively. The 3 donor nuclei and the palladium nucleus are all coplanar, with a mean deviation from the plane of 0.02 Å. This plane is canted to that of the bridging backbone (the plane comprising P1, C1, C1*, and P1*) by an angle of 18°.

If the solid-state structure of **4** persisted in solution, both phosphorus donors of the chelating dippe would be inequivalent and so an $[\text{ABC}]_2$ type spectrum would be observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. What is in fact observed is an $[\text{AB}_2]_2$ type system with each coordination plane providing an AB_2 component to the overall $^{31}\text{P}\{^1\text{H}\}$ spectrum (*vide infra*). Evidently, rotation of the Pd(dippe) unit around the remaining P–Pd bond must be quite facile in order to account for the

equivalence of the chelating phosphorous nuclei. The $\text{PCH}_2\text{CH}_2\text{P}$ backbone linking the palladium nuclei is not sufficiently long enough to isolate each component magnetically, and a highly second-order spectrum results. The three-carbon backbone analogue, $[(\text{dipp})\text{Pd}]_2(\mu\text{-dippe})$ (**2**) (dipp = 1,3-bis(diisopropylphosphino)propane), has been reported and characterized in solution, and this exhibits a simpler AB_2 spectrum with only marginal second-order complication.³

Since the origin of the second-order pattern observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** is due to the presence of the two-carbon backbone of the bridging dippe, we attempted to prepare the mixed-ligand system $[(\text{dipp})\text{Pd}]_2(\mu\text{-dippe})$ wherein the chelating diphosphine is the three-carbon backbone dipp ligand and the bridging unit is the dippe unit. We have previously shown⁶ that addition of ligands to the hydride dimer $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2$ results in loss of H_2 and formation of zerovalent palladium complexes; thus, addition of dippe to $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2$ resulted in the isolation of a material that reproducibly analyzed as $[(\text{dipp})\text{Pd}]_2(\mu\text{-dippe})$ (**5**). The complementary mixed-ligand complex $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ (**6**) was prepared as ochre crystals by the reaction of a 2:1 mixture of dippe and dipp with $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}]_2(\mu\text{-Cl})_2$ in the presence of MeONa.¹¹ In solution both **5** and **6** rearrange to give mixtures of the known complexes, $\text{Pd}(\text{dipp})_2$ (**1**), $[(\text{dipp})\text{Pd}]_2(\mu\text{-dippe})$ (**2**),³ and $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ (**4**) and other unidentified complexes (approximately 10%); no evidence for a second-order pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** was detected even at low temperatures. The preference of dippe to chelate rather than bridge is presumably a significant determining factor.

Given the versatility of the reaction represented in eq 3, we also ventured the addition of 2 equiv of dippe or dipp to a single equivalent of $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}]_2(\mu\text{-Cl})_2$ in the hope of isolating 14 electron complexes of the empirical formula $\text{Pd}(\text{dippe})$ or $\text{Pd}(\text{dipp})$; this latter species is the putative intermediate in the reactions catalyzed by $\text{Pd}(\text{dipp})_2$ (**1**), but it has not been directly observed.¹⁵ When dippe is used, vinylic and methoxide protons are observed in the ^1H NMR spectrum of the crude reaction mixture, and in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum three sets of resonances are observed in an approximate 7:2:1 ratio: an AB quartet at 61.2 and 55.0 ppm ($J_{\text{P-P}} = 66.2$ Hz), the familiar second-order pattern of **4**, and a singlet at 32.7 ppm (eq 4). When authentic

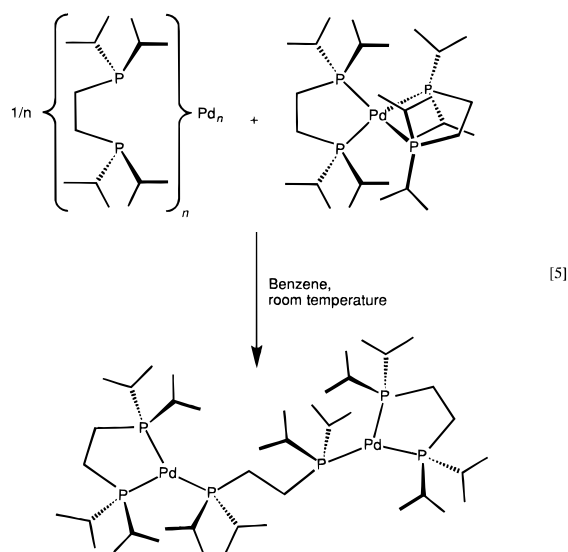


$\text{Pd}(\text{dippe})_2$ is added to this product mixture, the AB

(14) Kirss, R. U.; Eisenberg, R. *Inorg. Chem.* **1989**, *28*, 3372.

(15) The existence of the $\text{Pd}(\text{dipp})$ species was established by an inversion transfer NMR experiment. See ref 4.

quartet and the high-field singlet disappear and the concentration of **4** is enhanced. This result suggests that the AB signal arises from the olefin adduct of Pd(dippe), Pd(dippe)(η²-H₂C=C(Me)CH₂OMe) (**7**),¹⁶ and the singlet from actual [Pd(dippe)]_n (**8**), and thus the reaction may be formulated as shown in eq 5. Stoichi-



ometry requires another Pd nucleus, but the mass balance may be satisfied by precipitation of palladium metal. Neither **7** nor **8** could be isolated in a pure form from the product mixture, but when the experiment was performed with dippp in place of dippe, the analogous complexes were observed in the ³¹P{¹H} NMR spectrum: thus, the formation of Pd(dippp)(η²-H₂C=C(Me)CH₂OMe) (**9**), and [Pd(dippp)]_n (**10**) is proposed along with a trace of binuclear [(dippe)Pd]₂(μ-dippe) (**2**). Recrystallization from pentane slowly afforded an amber material which was a 9:1 mixture of **9** and **10**; drying under vacuum removed the olefin to give crystals of empirical formula Pd(dippp). As has been recently suggested with the chelating diphosphine 1,2-bis(dicyclohexylphosphino)ethane (dcype), a monomer-dimer equilibrium may be operative.¹⁷ Molecular weight determination by the Signer method gave a value of 750 ± 80 g mol⁻¹, consistent with a formulation for **10** as [Pd(dippp)]₂. [(dippe)Pd]₂(μ-dippe) (**2**) is also accessible from **10** by simple addition of mononuclear Pd(dippe)₂ (**1**).

Since **4** may be assembled from its subunits Pd(dippe)₂ and Pd(dippe) (eq 5), it is an obvious choice for inclusion in some catalytic cycle. In this sense **4** is a protected Pd(dippe) complex: the 14 electron fragment may bind to the saturated 18 electron complex Pd(dippe)₂ to give the stabilized complex **4** with 16 electrons per Pd nucleus. Our model reaction was the reductive dechlorination of PhCl by MeONa in MeOH catalyzed by Pd(0), a system developed by Milstein *et al.*¹⁸ Substrate and catalyst were mixed in a 100:1 ratio, and heating to 90 °C gave a homogeneous solution whose deep brown color and ³¹P{¹H} NMR spectrum indicated formation of Pd(dippe)PhCl. After 2 h, GC analysis indicated 70–75% conversion of PhCl to ben-

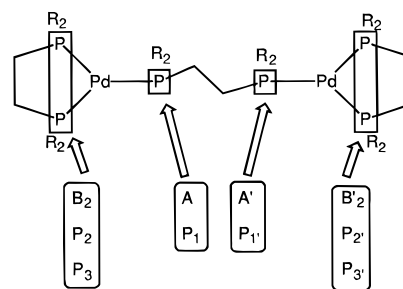


Figure 3. The ³¹P{¹H} NMR [AB₂]₂ spin system of **4** and spin labels used (R = Prⁱ).

zene whereas, under identical conditions, Pd(dippp)₂ (**1**) gave 85–90% conversion.¹⁸ Further heating of the former resulted in precipitation of metallic Pd and no improvement in conversion. As a catalyst, **4** is therefore comparable to **1** but it is not as thermally stable. These results support the idea that coordinative unsaturation is a prerequisite for reactivity.

Spectral Analysis

The 202.47 MHz ³¹P{¹H} NMR spectrum of a 2.5% solution of **4** in d₈-toluene is shown in Figure 2, which reveals the corresponding [AB₂]₂ spin system consisting of 6 phosphorus nuclei labeled according to Figure 3.

The bridging phosphorus nuclei (P₁, P₁') give rise to the A, A' multiplet centered at δ_P = 54.88 ppm. Each pair of chelating phosphorus nuclei (P₂, P₃ and P₂', P₃') is magnetically equivalent and forms the composite particle B₂ and B'₂, respectively, corresponding to a multiplet located at δ_P = 49.62 ppm. Integration confirms the intensity relation of 1:2 for the A and the B₂ regions, respectively. The spectral appearance of this [AB₂]₂ spin system is determined by the resonance frequencies, ν_A and ν_B, and three non-negligible coupling constants, J_{AB}, J_{AB'} = J_{A'B}, and J_{AA'}. The coupling constant J_{BB'} corresponds to the long-range interaction ⁷J_{P-P}, whose value approaches zero. Therefore a special situation results which leads to a more simple [AB₂]₂ spin system obeying rules similar to related or more general cases.^{19–22} For analogous [AX₂]₂ spin systems explicit expressions for transition frequencies may be derived^{23–28} leading to the direct analysis of NMR parameters from the experimental spectra.^{29–31}

Use of the [AX₂]₂ approximation for the vanishing long-range coupling constants J_{XX'} and the experimental spectrum from Figure 2 leads to starting parameters as shown in Table 3.

Iteration by WIN-DAISY¹⁰ running under 1D WIN-NMR⁹ yielded the final parameters including standard

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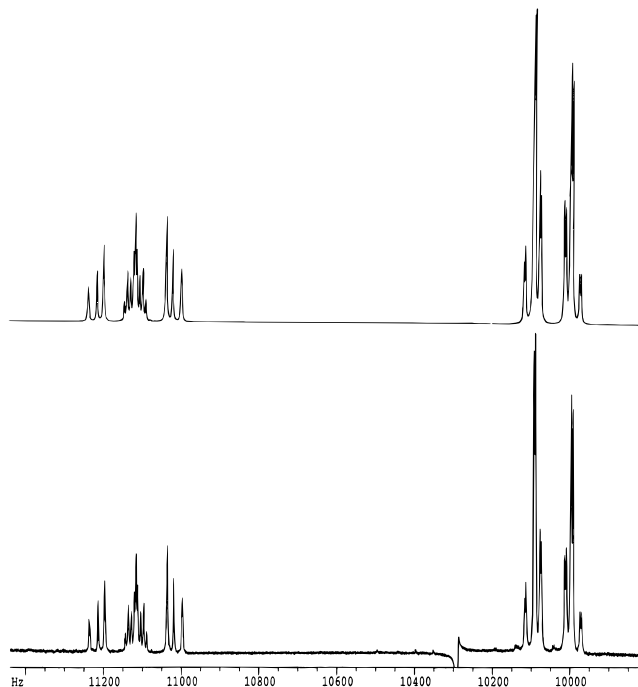


Figure 4. Simulated (top trace) and experimental (lower trace) 202.47 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ (**4**). For data see Table 3.

Table 3. Starting Parameters (Hz) Using the $[\text{AX}_2]_2$ Approximation and Final Iterated Parameters for the $[\text{AB}_2]_2$ System

general syst	P syst	start	iteration	error ^a
$\nu_A = \nu_{A'}$	$\nu_{P1} = \nu_{P1'}$	11111.8	11111.52	0.078
$\nu_B = \nu_{B'}$	$\nu_{P2/P3} = \nu_{P2'/3'}$	10041.7	10045.52	0.088
$J_{AB} = J_{AB}$	$^2J_{P1-P2/3}$	96.8	96.99	0.134
$J_{AB'} = J_{A'B}$	$^5J_{P1-P2'/3'}$	0.3	0.27	0.0029
$J_{AA'}$	$^3J_{P1-P1'}$	39.4	39.57	0.147
$J_{BB'}$	$^7J_{P2/3-P2'/3'}$	0.0	0.03	0.087
half-width (A)		2.25	2.50	
half-width (B)		2.75	2.50	
rms		0.496	0.395	

^a Quoted as a standard deviation of the iterated frequency.

deviations as shown in Table 3. The corresponding simulation is shown in Figure 4.

The phosphorus–phosphorus coupling constants are obtained as follows: phosphorus atoms of type A and B couple (across the Pd nucleus) with $J_{AB} = ^2J_{P1-P2/3} =$

97.0 Hz. This value is in accord with other palladium phosphine complexes with trigonal planar coordination.³ Both phosphorus atoms of the bridging ligand couple with $J_{AA} = ^3J_{P1-P1'} = 39.6$ Hz. A long-range coupling exists for $J_{AB'} = ^5J_{P1-P2'/3'} = 0.3$ Hz, while $J_{BB'} = ^7J_{P2/3-P2'/3'}$ is well beneath resolution or zero. The inherent coupling inside the composite particle, formed by the two phosphorus atoms of the chelating ligand, is of the $^2J_{P-P}$ type but principally not accessible by HR NMR in isotropic solutions.

Conclusion

The isolation of the zerovalent palladium complex $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$, **4**, was achieved through our attempts to prepare the binuclear palladium hydride complex $[(\text{dippe})\text{Pd}]_2(\mu\text{-H})_2$. The solid-state structure of **4** shows that one of the dippe units acts as a bridging ligand between the two trigonally coordinated palladium centers. Although the two palladium centers are electronically isolated from each other, there is magnetic exchange through the bridging dippe unit that results in the observation of a second-order $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This spectrum has been fully analyzed by means of iterative procedures. The direct observation of complexes of the formula $[\text{Pd}(\text{P}_2)]_n$ ($\text{P}_2 =$ bidentate phosphine) and the reaction that these species undergo with saturated 18 electron species have obvious implications for catalysis, and this is an area where $[(\text{dippe})\text{Pd}]_2(\mu\text{-dippe})$ exhibits potential.

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Supporting Information Available: Structural data for **4** including text describing X-ray procedures, tables of atomic coordinates and B values, crystallographic details, complete anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes, and structure diagrams (21 pages). Ordering information is given on any current masthead page.

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