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Synthesis, X-ray crystal structure, and reactivity of $Pd_2(\mu\text{-dotpm})_2$ (dotpm = bis(di-*ortho*-tolylphosphino)methane)

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ABSTRACT

Alkylation of $PdCl_2$(dotpm) (dotpm = bis(di-*ortho*-tolylphosphino)methane) with *n*-butyllithium produces the binuclear Pd(0) complex $Pd_2(\mu\text{-dotpm})_2$ and the elimination byproducts 1-butene, *cis*-2-butene, *trans*-2-butene, butane, and octane. The dibutyl complex, Pd(dotpm)(*n*-Bu)$_2$, is presumed to be the reaction intermediate. The crystal structure of $Pd_2(\mu\text{-dotpm})_2$ reveals that the methylene groups of the bridging dotpm ligands are located on opposite sides of the Pd_2P_4 unit, forming an 8-membered ring that is in an elongated chair conformation. The four phosphorus atoms are not coplanar, and the P1–P2–P3–P4 ring has a torsion angle of 13.8°, which minimizes the spatial interactions among the *o*-tolyl rings. The Pd–Pd bond distance is 2.8560(6) Å, which indicates that there is a weak "closed-shell" bonding interaction between the d^{10}–d^{10} metal centers. Each palladium atom has a nearly linear geometry, and the eight methyl groups of the dotpm ligands shield the open coordination sites on the metal centers. Four methyl groups shield the metal atoms above and below the Pd_2P_4 ring cavity, and four methyl groups block the open metal sites outside of the Pd_2P_4 ring. The $Pd_2(\mu\text{-dotpm})_2$ complex readily undergoes oxidative addition of dichloromethane to form the rigid A-frame complex $Pd_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dotpm})_2$.

1. Introduction

Binuclear complexes $Pd_2(\mu\text{-P–P})_2$ are of interest because they contain two coordinatively unsaturated palladium(0) centers that are potential catalysts for the activation of organic halides [1–3] and hydrosilanes [1,2,4]. Another attractive feature of $Pd_2(\mu\text{-P–P})_2$ complexes is that there is a weak "closed-shell" bonding interaction between the d^{10}–d^{10} metal centers [5–11] that can potentially promote a cooperative catalytic system in which the substrate is bonded to and activated by both metal centers [5]. One consequence of this binuclear system with open coordination sites and enhanced reactivity is that $Pd_2(\mu\text{-P–P})_2$ complexes are rare, and they require sterically bulky or electron-rich substituents on the bisphosphine ligands to help stabilize them.

Bisphosphine complexes $Pd_2(\mu\text{-P–P})_2$ have been synthesized by a number of different reaction methods [1–3,12–18]. For example, $Pd_2(\mu\text{-dppm})_2$ [3,12] (dppm = bis(diphenylphosphino)methane) has not been isolated, but it is observed *in situ* from the disproportionation of $Pd_2ClMe(\mu\text{-dppm})_2$ [3], and it has been proposed as an intermediate in the electrolysis of $Pd_2(\mu\text{-dppm})_3$ [12]. Most of the other $Pd_2(\mu\text{-P–P})_2$ complexes are formed from mononuclear palladium compounds. For example, $Pd_2(\mu\text{-dippm})_2$ (dippm = bis(diisopropylphosphino)methane) is obtained as a byproduct of the catalytic reaction of 1,3-butadiene with ethyl methylacetoacetate in the presence of Pd(η^2-1,3-butadiene)(dippm); the X-ray structure of $Pd_2(\mu\text{-dippm})_2$ has been obtained [13]. The complex $Pd_2(\mu\text{-dippe})_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane) has been implicated in several reactions [14–17], but it can be isolated in high yield from the reduction of Pd(dippe)$(OAc)_2$ by hydrazine [1]. Similarly, hydrazine reduces Pd(dcpe)Cl_2 to yield $Pd_2(\mu\text{-dcpe})_2$ [1] (dcpe = 1,2-bis(dicyclohexylphosphino)ethane); this complex also forms from the photolysis of a Pd(dcpe) oxalate compound, and its X-ray structure has been determined [2]. A recent report showed that the mixed compound, $Pd_2(\mu\text{-dippe})(\mu\text{-dcpe})$, forms when $Pd_2(\mu\text{-dippe})_2$ and $Pd_2(\mu\text{-dcpe})_2$ are combined in solution; the mixed compound has not been isolated [1]. There are two examples of the reductive elimination of ethane from dimethylpalladium species to form $Pd_2(\mu\text{-P–P})_2$ complexes. Thermolysis of Pd(dcpm)Me_2 (dcpm = bis(dicyclohexylphosphino)methane) gives the dimer $Pd_2(\mu\text{-dcpm})_2$, which has been crystallographically characterized [18]. In an analogous reaction, the complex $Pd_2(\mu\text{-dtbpm})_2$ (dtbpm = bis(di-tert-butylphosphino)methane) forms in high yield from the reaction of dtbpm with Pd(tmeda)Me_2 in hot benzene; the product is believed to form from the reductive elimination of ethane via an unstable Pd(dtbpm)Me_2 intermediate [18]. We now report a new procedure for the synthesis of a $Pd_2(\mu\text{-P–P})_2$ complex that is the first example containing two substituted aryl bisphosphine bridges. Our results demonstrate that sterically bulky aryl groups stabilize the $Pd_2(\mu\text{-P–P})_2$ complex.

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2. Results and discussion

The room-temperature reaction of $PdCl_2$(dotpm) [19] (doptm = bis(di-*ortho*-tolylphosphino)methane) with 2 equivalents of *n*-BuLi in diethyl ether yields red crystals of $Pd_2(\mu$-dotpm$)_2$, **1** (Scheme 1). We believe that the reaction proceeds through the dialkylated intermediate Pd(dotpm)(*n*-Bu)$_2$, which quickly undergoes reductive elimination to yield the dimer.

The X-ray crystal structure of **1** (Fig. 1) shows that both dotpm ligands bridge the two palladium centers. The methylene groups are located on opposite sides of the Pd_2P_4 unit, forming an 8-membered ring that is in an elongated chair conformation. The four phosphorus atoms in **1** are not coplanar, and the P1–P2–P3–P4 ring has a torsion angle of 13.8°. The slight twist from planarity minimizes the spatial interactions among the *o*-tolyl rings. Notably, all eight methyl substituents of the *o*-tolyl rings are oriented toward the open sites of the coordinatively unsaturated Pd atoms. Four methyl groups shield the metal atoms above and below the Pd_2P_4 ring cavity, and four methyl groups block the open metal sites outside of the Pd_2P_4 ring.

The geometries of both Pd centers in **1** deviate slightly from linearity (P3–Pd1–P1 173.56(3)° and P4–Pd2–P2 173.99(3)°), and the two palladium atoms are drawn toward each other. The Pd1–Pd2 bond distance is 2.8560(6) Å, which is on the long end of the Pd–Pd bond range (2.7611(5)–2.8582(6) Å) found for other $Pd_2(\mu$-P–P$)_2$ complexes [2,13,18]. Although the Pd–Pd bond distance is too long for a formal Pd–Pd σ-bond (2.53–2.77 Å) [20], **1** likely possesses weak d^{10}–d^{10} Pd(0)–Pd(0) bonding interactions attributed to d–p mixing in the σ-bonding orbital that are proposed in its $Pd_2(\mu$-P–P$)_2$ analogues. The long wavelength $d\sigma^* \rightarrow p\sigma$ electronic absorption of **1** (λ_{max} = 494 nm) is slightly lower in energy than related binuclear complexes ($Pd_2(\mu$-dippe$)_2$, λ_{max} = 455 nm [1]; $Pd_2(\mu$-dcpe$)_2$, λ_{max} = 456 nm [2]; $Pd_2(\mu$-dtbpm$)_2$, λ_{max} = 462 nm [18]; $Pd_2(\mu$-dcpm$)_2$, λ_{max} = 480 nm [18]). The lower absorption energy for **1** is consistent with its relatively longer Pd–Pd bond length.

The NMR spectra for **1** are consistent with a highly symmetrical molecule. Its $^{31}P\{1H\}$ NMR spectrum in tetrahydrofuran-d_8 contains only a sharp singlet at δ −4.8. Its corresponding ^{1}H NMR spectrum contains a singlet at δ 2.48 for the eight methyl groups of the *o*-tolyl rings. The methylene signal at δ 3.33 is broad due to unresolved coupling to phosphorus. The four unique aromatic protons on each *o*-tolyl ring resonate at δ 6.87 (d), 6.94 (t), 7.09 (t), and 7.56 (broad d), where the latter resonance shows unresolved phosphorus coupling. The ^{13}C NMR spectrum of **1** contains one methyl resonance at δ 23.3, a methylene resonance at δ 32.4, and six aromatic resonances at δ 126.1, 129.2, 131.7, 133.5, 137.0, and 142.6; carbon–phosphorus coupling was not observed. Clearly, movement of the P_4 and *o*-tolyl rings in **1** is fast on the NMR time scale.

2.1. NMR study of the synthesis of complex *1*

The formation of **1** was monitored by NMR spectroscopy. When an insoluble mixture of $PdCl_2$(dotpm) in C_6D_6 is combined with solid *n*-BuLi, ^{31}P signals belonging to **1** (δ −2.8), free dotpm (δ −43.1), and an unknown species (δ −22.7) appear. Over time, the resonance for complex **1** significantly predominates (88%) in solution followed by the signal for dotpm; the singlet for the unknown species disappears completely. Similar changes were observed in the corresponding ^{1}H NMR spectra. Proton resonances for complex **1** increase in intensity while those for free dotpm gradually become minor signals in the NMR spectra. Interestingly, three proton resonances appear at δ 1.00 (t, $^3J_{HH}$ = 7.3 Hz, CH_3), 2.44 (s, $C_6H_4CH_3$), and 3.47 (t, $^2J_{PH}$ = 7.3 Hz, PCH_2P), and they decrease with the same relative magnitudes. The ratio of these three signals is approximately 6:12:2, respectively, and they are associated with another resonance at δ 1.63 (m), which is partially obscured by other reaction byproducts. Other proton signals belonging to the intermediate could not be definitively identified because of the presence of several overlapping signals in the 1–3 ppm range. In repeated studies, the four proton signals belonging to the reaction intermediate are observed only when the phosphorus signal at δ −22.7 is present in the corresponding ^{31}P NMR spectrum. The negative ^{31}P chemical shift value for the intermediate is indicative of a chelating bisphosphinomethane ligand [21,22], and the relative intensities of the proton resonances assigned to the intermediate suggest that this species has one dotpm ligand for every two methyl groups. We believe that the intermediate is the dialkylated complex Pd(dotpm)(*n*-Bu)$_2$. Other key resonances in the ^{1}H NMR

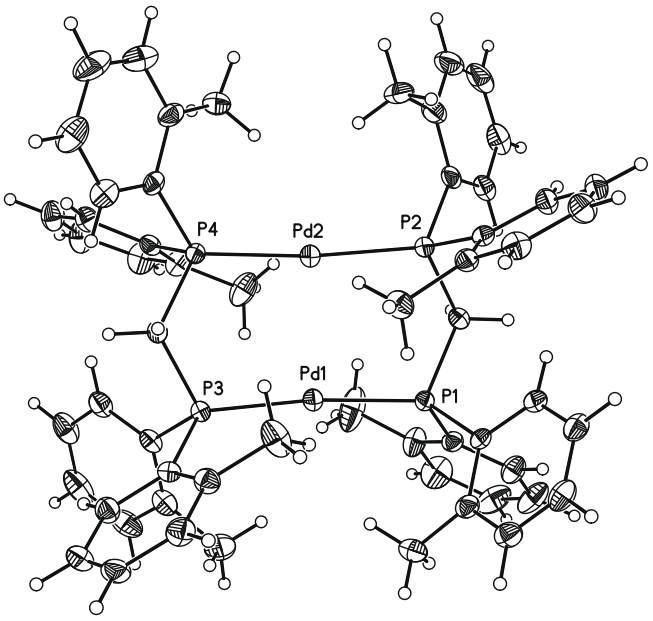
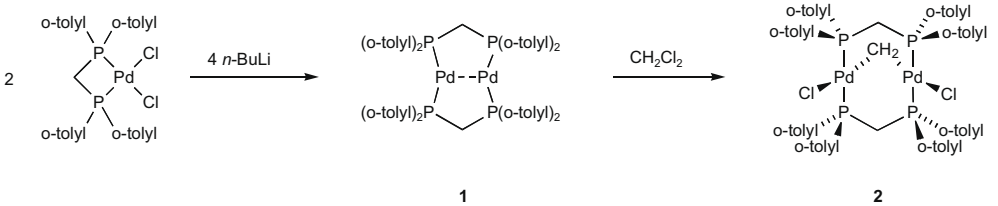


Fig. 1. Molecular structure of $Pd_2(\mu$-dotpm$)_2$ (**1**). View down the Pd_2P_4 ring cavity. Thermal ellipsoids are represented by the 35% probability surfaces. Selected bond lengths (Å) and angles (°): Pd1–Pd2 2.8560(6), Pd1–P1 2.2698(10), Pd1–P3 2.2615(10), Pd2–P2 2.2676(10), Pd2–P4 2.2643(10), P3–Pd1–P1 173.56(3), P4–Pd2–P2 173.99(3), P1–C1–P2 115.46(18), P3–C30–P4 114.81(17), P1–Pd1–Pd2–P4 170.80(3), P3–Pd1–Pd2–P2 170.14(3).



Scheme 1. Preparation and reaction of complex **1**.

spectra provide evidence for the formation of alkenes (1-butene, *cis*-2-butene, and *trans*-2-butene) and alkanes (butane and octane) during the reaction process. The NMR data suggests that 1-butene isomerizes to the more stable 2-butene compounds, and the formation of octane in the reaction solution was confirmed by GC/MS techniques. The ratio of alkenes to alkanes varies somewhat in repeated studies (1.0:1.3–1.0:1.9, respectively), however, the concentration of alkanes is always higher than the concentration of alkenes. The generation of free dihydrogen was not evident from the ^{1}H NMR spectra. Variable-temperature NMR studies conducted in toluene-d_8 show that the intermediate and free dotpm are present at −40 °C and that complex **1** is formed above 0 °C. Other phosphorus-containing species were not detected in the ^{31}P NMR spectra, and ^{1}H signals for dihydrogen and Pd hydride species were not observed. It is possible that, in the synthesis of **1**, the mononuclear dibutyl complex Pd(dotpm)(*n*-Bu)$_2$ forms initially, then rapidly undergoes β-hydride elimination of alkene and/or reductive coupling of alkane, forming the bridged dimer. Notably, the thermal decomposition of the dinuclear dibutyl complex, [$Pd_2Bu_2(\mu$-Br)(μ-dppm)$_2$]PF_6, was reported to give 1-butene and 2-butene as the only elimination products [23]. A report showed that both dimethyl complexes Pd(dcpm)Me$_2$ and Pd(dtbpm)Me$_2$ undergo reductive elimination of ethane to yield the dimers $Pd_2(\mu$-dcpm)$_2$ and $Pd_2(\mu$-dtbpm)$_2$, respectively [18]. Apparently, our synthetic route to **1** also proceeds via reductive elimination processes.

2.2. Reactivity of complex *1*

Complex **1** is stable in most organic solvents. Crystals of **1** and its pink-red powder obtained when the reaction solution is too concentrated are not very soluble in fresh diethyl ether; **1** is slightly soluble in pentane but very soluble in tetrahydrofuran, benzene, and toluene. Interestingly, complex **1** readily adds dichloromethane to form the new methylene-bridged complex $Pd_2Cl_2(\mu$-$CH_2)(\mu$-dotpm)$_2$, **2** (Scheme 1). A similar result was reported for the dppm analogue of 1; $Pd_2(\mu$-dppm)$_2$, generated *in situ*, reacts easily with dichloromethane to give $Pd_2Cl_2(\mu$-$CH_2)(\mu$-dppm)$_2$ [3]. Unlike the tri-bridged complex $Pd_2(\mu$-dppm)$_3$ [24], the dimers $Pd_2(\mu$-dppm)$_2$ and **1** are highly reactive toward C–Cl oxidative addition because their Pd(0) centers are more coordinatively unsaturated.

The room temperature ^{1}H NMR spectrum of **2** contains broad resonances throughout. The Pd–CH_2–Pd protons resonate at δ 1.64 (br s). Two resonances at δ 1.94 (br s) and 2.32 (br s) correspond to the inequivalent methyl substituents of the *o*-tolyl rings that occupy opposite sides of the Pd_2P_4 plane. The two inequivalent methylene protons of dotpm resonate at δ 3.05 (br s) and 3.78 (br s). The aromatic region of the ^{1}H NMR spectrum of **2** contains broad multiplets at δ 6.96–7.32. The room temperature ^{31}P NMR spectrum of **2** contains two very broad resonances at δ 17.7 and 23.1. Complex **2** decomposes slowly in solution even at low temperatures, therefore, meaningful ^{1}H NMR data at low temperature were not obtained. However, at −68 °C, the ^{31}P NMR spectrum of **2** contains two major signals at δ 14.9 (d of d, $^3J_{PP}$ = 54, 15 Hz) and 18.2 (d of d, $^3J_{PP}$ = 54, 15 Hz).

The A-frame complex **2** has two potential mirror planes, one along the Cl–Pd–Pd–Cl plane and another that bisects the three methylene carbon atoms. As noted previously for the crystal structure of **1**, steric crowding of the *o*-tolyl groups is minimized by a P_4 twist angle of 13.8°. We expect that complex **2** also possesses a distorted P_4 plane because steric congestion around its two Pd centers is increased significantly by the bridging methylene and terminal chlorine atoms bonded to the two metal centers. The NMR spectra of **2** at room temperature indicate that twisting of the Pd_2P_4 plane and rotation or twisting of the aromatic rings are more hindered in the A-frame structure than in its coordinatively unsaturated parent complex, **1**, or in its unsubstituted dppm analogue, $Pd_2Cl_2(\mu$-$CH_2)(\mu$-dppm)$_2$ [3,24].

2.3. Steric effects

We further examined the spatial effects of the aromatic substituents in the ligand and found that PdCl$_2$(dppm) [13,25,26] reacts with 2 equivalents of *n*-BuLi in diethyl ether to give orange-red crystals of the known binuclear complex $Pd_2(\mu$-dppm)$_3$ (Scheme 2) [27–29]. Obviously, the dipalladium(0) structure can accommodate three bridging dppm ligands but only two bridging dotpm ligands, because the *o*-tolyl groups are more sterically demanding.

The NMR study on the reaction between PdCl$_2$(dppm) and *n*-BuLi showed that after 5 min at room temperature, $Pd_2(\mu$-dppm)$_3$ is the only phosphorus-containing species present in solution. Variable-temperature NMR spectra show that $Pd_2(\mu$-dppm)$_3$ and free dppm are present at −40 °C. Dihydrogen was detected in solution (δ 4.46) however, signals for Pd hydride species were not observed. Resonances corresponding to a dibutyl reaction intermediate were not observed in any of the NMR spectra, although two similar studies reported the presence of the dimethyl complex Pd(dppm)Me$_2$ as the intermediate for the formation of $Pd_2(\mu$-dppm)$_3$ [19,30]. Apparently, the reaction involving dppm occurs faster than the dotpm reaction, and free dppm is not observed because three ligands are required to form $Pd_2(\mu$-dppm)$_3$. Proton resonances corresponding to alkene and alkane byproducts suggest that both **1** and $Pd_2(\mu$-dppm)$_3$ form through the same reaction mechanism.

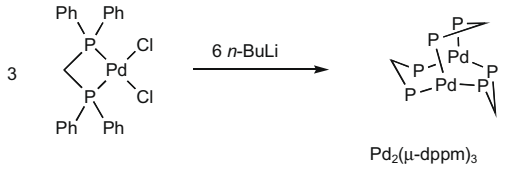
2.4. Conclusions

In summary, this study shows that PdCl$_2$(dotpm) reacts with *n*-BuLi to form $Pd_2(\mu$-dotpm)$_2$ and the elimination byproducts 1-butene, *cis*-2-butene, *trans*-2-butene, butane, and octane. Presumably, the dibutyl complex, Pd(dotpm)(*n*-Bu)$_2$, is the reaction intermediate. This reaction method is a new route for the synthesis of a zerovalent dipalladium bisphosphine complex. The complex $Pd_2(\mu$-dotpm)$_2$ quickly undergoes oxidative addition of dichloromethane to form the A-frame complex, $Pd_2Cl_2(\mu$-$CH_2)(\mu$-dotpm)$_2$. Additional studies on the reactivity of $Pd_2(\mu$-dotpm)$_2$ are underway.

3. Experimental

3.1. General methods

All operations were performed under nitrogen in a drybox or by using Schlenk and cannula methods. Diethyl ether and dichloromethane were distilled immediately before use from sodium benzophenone or calcium hydride, respectively. The compounds PdCl$_2$(dppm) [12] and dotpm [19] were prepared according to literature methods. The chemicals palladium(II) dichloride, *n*-butyllithium, and dichloromethane-d_2 were purchased from Aldrich and used as received. Benzene-d_6 (Aldrich) was distilled from sodium benzophenone. Tetrahydrofuran-d_8 (Aldrich) was dried over alumina before use. IR spectra were recorded on a Nicolet Avatar 360 Fourier transform infrared spectrometer as Nujol mulls



Scheme 2. Preparation of complex $Pd_2(\mu$-dppm)$_3$.

between KBr salt plates. The NMR data were recorded on a Bruker Avance 300 spectrometer with the following frequencies and references: 300 MHz (^{1}H, residual solvent), 75 MHz (^{13}C, residual solvent), or 121 MHz (^{31}P, external H_3PO_4). The low temperature NMR data were recorded on a Varian U400 spectrometer at 161 MHz (^{31}P) at the University of Illinois at Urbana-Champaign. Chemical shifts are reported in ppm (positive shifts to high frequency) and coupling constants in hertz. All spectra were recorded at ~20 °C except where indicated. UV–Vis data were obtained on a Varian Cary 100 UV–Visible spectrophotometer. GC/MS spectra were recorded on an HP-6890 instrument equipped with an Agilent Technologies 5975 Mass Selective Detector. Low resolution electrospray (ESI) mass spectra were obtained at the University of Illinois at Urbana-Champaign. Elemental analyses were performed by Intertek (Whitehouse, NJ).

3.2. Dichlorobis[di-(2-methylphenyl)phosphino]methane-palladium(II), $PdCl_2$(dotpm) [19]

A solid mixture of dotpm (0.655 g, 1.49 mmol) and $PdCl_2$ (0.26 g, 1.47 mmol) was suspended in 50% ethanol (25 mL) and concentrated HCl (25 mL). The mixture was refluxed for 16 h, and a yellow solid precipitated from solution. The solution was filtered. The yellow solid was washed with H_2O (2 × 25 mL) and ethanol (2 × 25 mL) then dried under vacuum. Yield: 0.804 g (89%). Anal Calc. for $C_{29}H_{30}Cl_2P_2Pd$: C, 56.38; H, 4.89; P, 10.03. Found: C, 56.50; H, 4.88; P, 9.24%. ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 12H, $C_6H_4CH_3$), 4.31 (t, $^2J_{PH}$ = 9.9 Hz, 2H, PCH_2P), 7.21–7.27 (m, 8H, $C_6H_4CH_3$), 7.44 (t, 4H, $^3J_{HH}$ = 7.4 Hz, $C_6H_4CH_3$), 8.00 (virtual quartet, J = 8.5 Hz, 7.7 Hz, 4H, $C_6H_4CH_3$). ^{31}P NMR ($CDCl_3$) δ −51.4 (s). IR (cm^{-1}) 3050 (w), 2954 (s), 2913 (s), 2838 (s), 2003 (w), 1737 (w), 1709 (w), 1634 (w), 1586 (m), 1562 (m), 1453 (s), 1374 (m), 1357 (m), 1282 (m), 1197 (m), 1166 (w), 1135 (m), 1100 (m), 1067 (m), 1032 (w), 806 (s), 762 (s), 738 (s).

3.3. Bis[μ-bis(di-(2-methylphenyl)phosphino)methane]-dipalladium(0), Pd_2(μ-dotpm)$_2$ (**1**)

To a yellow suspension of $PdCl_2$(dotpm) (0.264 g, 0.43 mmol) in diethyl ether (20 mL) was added *n*-BuLi (0.59 mL of a 1.6 M solution in hexanes, 0.94 mmol) over 30 s. The resulting bright red mixture was stirred for 2 h then filtered twice through Celite. The solution was allowed to sit at room temperature to afford red crystals of **1**. Yield: 0.091 g (39%). Mp: 150 °C (dec.). UV–Vis (toluene): λ_{max} = 494 nm. Anal Calc. for $C_{58}H_{60}P_4Pd_2$: C, 63.69; H, 5.53. Found: C, 63.71; H, 5.92%. ^{1}H NMR (thf-d_8): δ 2.48 (s, 24H, $C_6H_4CH_3$), 3.33 (br s, 4H, PCH_2P), 6.87 (d, $^3J_{HH}$ = 7.2 Hz, 8H, $C_6H_4CH_3$), 6.94 (t, $^3J_{HH}$ = 7.4 Hz, 8H, $C_6H_4CH_3$), 7.09 (t, $^3J_{HH}$ = 7.2 Hz, 8H, $C_6H_4CH_3$), 7.56 (br d, $^3J_{HH}$ = 6.8 Hz, 8H, $C_6H_4CH_3$). ^{13}C{^{1}H} NMR (thf-d_8): δ 23.3 (s, $C_6H_4CH_3$), 32.4 (s, PCH_2P), 126.1 (s, $C_6H_4CH_3$) 129.2 (s, $C_6H_4CH_3$), 131.7 (s, $C_6H_4CH_3$), 133.5 (s, $C_6H_4CH_3$), 137.0 (s, *i*-C*P* of $C_6H_4CH_3$), 142.6 (s, *i*-CCH_3 of $C_6H_4CH_3$). ^{31}P{^{1}H} NMR (thf-d_8): δ −4.8 (s).

3.4. Dichloro(μ-methylene)bis[μ-bis(di-(2-methylphenyl)phosphino)-methane] dipalladium(II), Pd_2Cl_2(μ-CH_2)(μ-dotpm)$_2$ (**2**)

Red crystals of complex **1** (15 mg, 0.014 mmol) were dissolved in CH_2Cl_2 (0.25 mL) and mixed for 45 min. The protiated solvent was removed under vacuum, and the orange-yellow residue was washed with pentane (3 × 0.5 mL) and dried under vacuum (14 mg, 87%). This compound was used without further purification. ^{1}H NMR (CD_2Cl_2): δ 1.64 (br s, 2H, $PdCH_2Pd$), 1.94 (br s, 12H, $C_6H_4CH_3$), 2.32 (br s, 12H, $C_6H_4CH_3$), 3.05 (br s, 2H, PCH_2P), 3.78 (br s, 2H, PCH_2P), 6.96–7.32 (m, 32H, $C_6H_4CH_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 17.7 (br s), 23.1 (br s). ^{31}P{^{1}H} NMR (CD_2Cl_2, −68 °C): δ 14.9 (d of d, $^2J_{PP}$ = 54, 15 Hz), 18.2 (d of d, $^2J_{PP}$ = 54, 15 Hz). mass spectrum (ESI): m/z 1143, 100% [M^+−Cl].

3.5. Tris[μ-bis(diphenylphosphino)methane]dipalladium(0), Pd_2(μ-dppm)$_3$

To a pale yellow suspension of $PdCl_2$dppm (0.30 g, 0.53 mmol) in diethyl ether (20 mL) was added *n*-BuLi (0.73 mL of a 1.6 M solution in hexanes, 1.17 mmol). The resulting dark red mixture was stirred for 2 h and filtered twice through Celite. The solution was allowed to sit at room temperature to afford orange-red crystals of Pd_2(μ-dppm)$_3$. Yield: 0.086 g (35%). Mp: 151 °C (dec.) Anal Calc. for $C_{75}H_{66}P_6Pd_2$: C, 65.94; H, 4.87. Found: C, 62.94; H, 4.62%. ^{1}H NMR (thf-d_8): δ 3.04 (br s, 6H, PCH_2P), 6.79 (t, $^3J_{HH}$ = 7.5 Hz, 24H, *m*-C_6H_5), 6.96 (t, $^3J_{HH}$ = 7.2 Hz, 12H, *p*-C_6H_5), 7.24 (d, $^3J_{HH}$ = 6.9 Hz, 24H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (thf-d_8): δ 29.6 (s, PCH_2P), 127.0 (s, *p*-C_6H_5), 127.2 (s, *m*-C_6H_5), 132.3 (s, *o*-C_6H_5), 142.5 (m, *i*-C_6H_5). ^{31}P{^{1}H} NMR (thf-d_8): δ 13.0 (s).

3.6. NMR experiments on the formation of **1** and Pd_2(μ-dppm)$_3$

Room temperature: For the synthesis of **1**, *n*-BuLi (0.038 mL of a 1.6 M solution in hexanes, 0.06 mmol) was added to an NMR tube in the glovebox, and the solvent was removed under vacuum leaving a white residue. The dichloride complex, $PdCl_2$(dotpm), (17 mg, 0.028 mmol) was mixed with C_6D_6 (0.3 mL) in a vial, and the yellow slurry was transferred to the NMR tube. The NMR tube was placed in the NMR probe and the progression of the reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After the reaction was complete, the mixture was opened to air and octane was eluted from silica gel using hexanes. The same procedure was used for the synthesis of Pd_2(μ-dppm)$_3$, with *n*-BuLi (0.037 mL of a 1.6 M solution in hexanes, 0.06 mmol) and $PdCl_2$(dppm), (15 mg, 0.027 mmol). Variable temperature: *n*-BuLi was added to an NMR tube in the glovebox, and the solvent was removed under vacuum. The dichloride complex, $PdCl_2$(P–P) was added to the NMR tube, which was cooled to −78 °C before toluene-d_8 (0.6 mL) was injected. The NMR sample was vigorously shaken immediately before it was inserted into the NMR probe, which was pre-cooled to −40 °C. The progression of the reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and the NMR probe was warmed in 10 °C increments. Data were collected approximately 5 min after the desired temperature had been reached.

Complex 1: ^{1}H NMR (C_6D_6): δ 2.68 (s, 24H, $C_6H_4CH_3$), 3.30 (t, $^2J_{PH}$ = 3.4 Hz, 4H, PCH_2P), 6.80–6.98 (m, $C_6H_4CH_3$), 7.53 (d, $^3J_{HH}$ = 5.8 Hz, 8H, $C_6H_4CH_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ −2.8 (s).

Pd(dotpm)(n-Bu)$_2$: ^{1}H NMR (C_6D_6): δ 1.00 (t, $^3J_{HH}$ = 7.3 Hz, 6H, CH_3), 1.63 (m), 2.44 (s, 12H, $C_6H_4CH_3$), 3.47 (t, $^2J_{PH}$ = 7.3 Hz, 2H, PCH_2P). ^{31}P{^{1}H} NMR (C_6D_6): δ −22.7 (s).

dotpm: ^{1}H NMR (C_6D_6): δ 2.30 (s, 12H, $C_6H_4CH_3$), 7.35 (d, $^3J_{HH}$ = 5.9 Hz, 4H, $C_6H_4CH_3$). Other signals were hidden by signals due to **1**. ^{31}P{^{1}H} NMR (C_6D_6): δ −43.1 (s).

1-Butene: ^{1}H NMR (C_6D_6): δ 1.92 (m, 2H, CH_2), 4.94 (d, $^3J_{HH}$ = 10.2 Hz, 1H, CH=CH_2), 4.99 (d, $^3J_{HH}$ = 17.2 Hz, 1H, CH=CH_2), 5.79 (m, 1H, CH=CH_2). Its methyl signal was obscured by those due to other byproducts.

cis-2-Butene: ^{1}H NMR (C_6D_6): δ 1.50 (d, $^3J_{HH}$ = 4.9 Hz, 6H, CH_3), 5.47 (m, 2H, =C*H*).

trans-2-Butene: ^{1}H NMR (C_6D_6): δ 1.56 (d, $^3J_{HH}$ = 4.7 Hz, 6H, CH_3), 5.38 (m, 2H, =C*H*).

Butane: ^{1}H NMR (C_6D_6): δ 0.85 (t, CH_3), 1.23 (m, CH_2).

Octane: ^{1}H NMR (C_6D_6): δ 0.88 (t, CH_3), 1.25 (br s, CH_2). GC/MS: m/z 114 (M^+).

Pd_2(μ-dppm)$_3$: ^{1}H NMR (C_6D_6): δ 3.17 (s, 6H, PCH_2P), 6.77–7.11 (m, 36H, C_6H_5), 7.44 (d, $^3J_{HH}$ = 7.1 Hz, 24H, *o*-C_6H_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 15.6 (s).

Table 1
Crystal data and structural parameters for $Pd_2(\mu\text{-dotpm})_2$ (**1**).

Empirical formula	$C_{58}H_{60}P_4Pd_2$
Formula weight	1093.74
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	12.750(3)
b (Å)	13.354(3)
c (Å)	16.634(4)
α (°)	70.673(4)
β (°)	82.640(4)
γ (°)	67.249(4)
Volume (Å^3)	2464.6(10)
Z	2
ρ_{calc} (g cm^{-3})	1.474
Absorption coefficient (mm^{-1})	0.898
F(0 0 0)	1120
Crystal size (mm)	0.100 × 0.180 × 0.190
θ Range for data collection (°)	1.73–25.39
Index ranges	−15 h 15, −15 k 16, −20 l 20
Reflections collected, unique	25218, 9009 [R_{int} = 0.0391]
Refinement method	Full-matrix least-squares on F^2
Completeness to θ (°)	25.39, 99.4
Data, restraints, parameters	9009, 38, 585
Goodness-of-fit on F^2	0.960
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0362, wR_2 = 0.0905
R indices (all data)	R_1 = 0.0597, wR_2 = 0.0980
Largest difference in peak and hole (e Å^{-3})	1.444 and −0.530

3.7. Crystal structure of **1**

A single crystal of $Pd_2(\mu\text{-dotpm})_2$ (**1**) grown from a diethy ether solution was mounted using Parantone-N oil (Exxon), and data were collected with a Siemens Platform/CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 193 K. The measurement parameters are listed in Table 1. The structure was solved using direct methods and refined with SHELXTL. A structural model consisting of the host molecule was developed. The phenyl groups on P1 were idealized with each other. The distance between C3 and H1B was restrained to prevent close interactions between atoms. The positions of hydrogen atoms in the methyl groups were optimized by rotation about R–C bonds with idealized C–H, R–H and H–H distances. The remaining hydrogen atoms were included as riding idealized contributors. Crystallographic data may be obtained as a CIF file (see Appendix A).

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Appendix A. Supplementary data

CCDC 749906 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.010.

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