

Neutral Molecular Pd<sub>6</sub> Hexagons Using  $\kappa^3$ -P<sub>2</sub>O-Terdentate Ligands

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The one-step synthesis of three new P<sub>2</sub>O-terdentate carboxylic acid ditertiary phosphines 2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(X)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (X = OCH<sub>3</sub>, **L1**; X = OH, **L2**) and 2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-5-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (**L3**) by a phosphorus-based Mannich condensation reaction using Ph<sub>2</sub>PCH<sub>2</sub>OH and the appropriate amine in CH<sub>3</sub>OH is reported. Compounds **L1–L3** function as typical  $\kappa^2$ -P<sub>2</sub>-didentate ligands upon complexation to Pd(CH<sub>3</sub>)Cl(cod) (cod = cycloocta-1,5-diene), affording the neutral, mononuclear complexes Pd(CH<sub>3</sub>)Cl(**L1–L3**) (**1–3**). Metathesis of **1** with NaX (X = Br, I) gave the corresponding (methyl)bromopalladium(II) (**4**) and (methyl)iodopalladium(II) (**5**) complexes, respectively. When chloroform or chloroform/methanol solutions of **1–3** (or **5**) were allowed to stand, at ambient temperatures, yellow crystalline solids were isolated in very high yields (71–88%) and were analyzed for the novel hexameric palladium(II) compounds **6–9**. All new compounds reported have been fully characterized by a combination of spectroscopic (multinuclear NMR, Fourier transform IR, electrospray mass spectrometry, matrix-assisted laser desorption ionization time-of-flight mass spectrometry) and analytical methods. The self-assembly reactions are remarkably clean as monitored by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectroscopy. Single-crystal X-ray structures have been determined for **L1**, **4**, **7**·17CDCl<sub>3</sub>·2Et<sub>2</sub>O, **8**·6CHCl<sub>3</sub>·8CH<sub>3</sub>OH, and **9**·17CDCl<sub>3</sub>. In hexamers **7–9**, all six square-planar palladium(II) metal centers comprise a  $\kappa^2$ -P<sub>2</sub>-chelating diphosphine, a  $\kappa^1$ -O-monodentate carboxylate, and either a chloride or iodide ligand, leading to 48-membered metallomacrocycles (with outside diameters of ca. 2.5 nm). Whereas only intramolecular O–H···N hydrogen bonding between the hydroxy group and tertiary amine has been observed in **7**, strong intermolecular O–H···O hydrogen bonding of the type CO···HO(CH<sub>3</sub>)···HO, involving a methanol solvate, has been found in **8**, leading to an unprecedented three-dimensional network motif.

## Introduction

Considerable recent attention has been directed toward novel cyclic polynuclear<sup>1</sup> metal complexes, e.g., metal wheels,<sup>2</sup> metallocrowns,<sup>3</sup> cartwheels,<sup>4</sup> and catenanes,<sup>5</sup> not only for their aesthetic appeal but also for their fascinating properties and potential applications as molecular magnetic storage<sup>6</sup> or photosensitive devices and as catalysts.<sup>7</sup> Various strategies have been documented for preparing such diverse supermolecular metal-based materials.<sup>7,8</sup> Structurally characterized molecular hexagons containing either six first-row,<sup>9</sup>

late-transition,<sup>10</sup> lanthanide,<sup>11</sup> or group 14<sup>12</sup> metals have all recently been described. However, to the best of our

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knowledge, there remain very few reported<sup>13</sup> examples of hexanuclear metallomacrocycles incorporating six d<sup>8</sup> palladium centers, although smaller homotetranuclear palladium species are known.<sup>14</sup>

The assembly of highly organized architectures has commonly made use of simple ligands that incorporate group 15 or 16 donor sites. Many of these building blocks are frequently based on nitrogen (e.g., pyridyl<sup>15</sup> or pyridone<sup>16</sup> derivatives) and/or oxygen (e.g., carboxylates,<sup>17</sup> alkoxides,<sup>18</sup>

or phosphinates/phosphonates<sup>19</sup>) donor ligands as connectors between metal centers. Considerably less has been documented with tertiary phosphines, which routinely fulfill the role of spectator ligand only.<sup>20,21</sup> Recent elegant self-assembled gold(I) complexes using chelating ditertiary phosphines have been documented by Puddephatt et al.<sup>5</sup> While carboxylates have been widely used in the synthesis of metal–organic frameworks<sup>22,23</sup> and polynuclear compounds,<sup>24</sup> the use of hybrid ligands such as phosphino-carboxylic acids as building blocks for self-assembly is extremely rare.<sup>25</sup> Furthermore, the use of carboxylic acid functionalized ditertiary phosphines, bearing a “hard” oxygen and two “soft” phosphorus donors, as building blocks for the self-assembly of multimetallic cyclic structures has not been explored. In contrast, Raymond and co-workers have used hybrid tertiary phosphines with PO<sub>2</sub> donor sets for the metal-based assembly of various supramolecular clusters.<sup>26</sup>

Herein we describe a general synthetic route to three new modified ditertiary phosphines, bearing a carboxylic acid group, that can be readily prepared from inexpensive reagents. These highly functionalized compounds, in their carboxylate form, serve as excellent bridging ligands for the unprecedented syntheses of four neutral 48-membered hexanuclear Pd<sub>6</sub> metallomacrocycles. In addition, the incorporation of a predisposed hydroxy functional group on the ligand N–arene backbone can be used to construct a novel supramolecular array via strong O–H···O hydrogen bonding between CH<sub>3</sub>OH solvate and hexameric subunits.

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## Experimental Section

**Materials.** All syntheses were conducted in air with the exception of **L1**–**L3**, which were conducted under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. All solvents were distilled prior to use. The palladium(II) starting material Pd(CH<sub>3</sub>)Cl(cod) (cod = cycloocta-1,5-diene) was prepared according to a published procedure.<sup>27</sup> All other reagents were purchased from commercial suppliers and used as received.

**Instrumentation.** IR spectra were recorded as KBr pellets over the range 4000–200 cm<sup>−1</sup> using a Perkin-Elmer system 2000 FT spectrometer. <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on JEOL FX90Q, Bruker AC250, or DPX-400 FT spectrometers with chemical shifts (δ) reported relative to external tetramethylsilane or H<sub>3</sub>PO<sub>4</sub>. All NMR spectra (90, 250, or 400 MHz) were recorded in CDCl<sub>3</sub> solutions unless otherwise stated. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was recorded on a Bruker Reflex III spectrometer operated using the reflection mode [with dihydroxybenzoic acid (DHB) as the matrix]. Elemental analyses (Perkin-Elmer 2400 CHN elemental analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

**Preparation of Ligands. 2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (**L1**).** To the solids Ph<sub>2</sub>PCH<sub>2</sub>OH (1.055 g, 4.88 mmol) and 2-H<sub>2</sub>N-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (0.410 g, 2.45 mmol) was added oxygen-free CH<sub>3</sub>OH (15 mL). After the solution was stirred for ca. 16 h, the volume was reduced in vacuo and the white solid **L1** collected by suction filtration. The solid was washed with CH<sub>3</sub>OH (5 mL) and dried in vacuo (1.100 g, 80%). Selected spectroscopic data for **L1**: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) −22.3 ppm; <sup>1</sup>H NMR (400 MHz) 12.1 (s, 1H, OH), 7.88–6.47 (m, 23H, aromatic H), 4.20 (m, 4H, CH<sub>2</sub>), 3.43 (s, 3H, OCH<sub>3</sub>) ppm; IR ν<sub>CO</sub> 1699 cm<sup>−1</sup>; fast atom bombardment (FAB) MS *m/z* 564 (M). Anal. Calcd for C<sub>34</sub>H<sub>31</sub>NO<sub>3</sub>P<sub>2</sub>: C, 72.45; H, 5.56; N, 2.49. Found: C, 72.64; H, 5.35; N, 1.97.

**2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (**L2**).** To the solids Ph<sub>2</sub>PCH<sub>2</sub>OH (1.028 g, 4.75 mmol) and 2-H<sub>2</sub>N-3-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (0.364 g, 2.38 mmol) was added oxygen-free CH<sub>3</sub>OH (20 mL). After the mixture was stirred for ca. 3 days, solid **L2** was collected by suction filtration, washed with CH<sub>3</sub>OH (5 mL), and dried in vacuo (1.141 g, 87%). Selected spectroscopic data for **L2** [(CD<sub>3</sub>)<sub>2</sub>SO]: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) −18.3 ppm; <sup>1</sup>H NMR (400 MHz) 16.02 (s, 1H, CO<sub>2</sub>H), 10.25 (s, 1H, OH), 7.44–6.78 (m, 23H, aromatic H), 4.33 (s, 4H, CH<sub>2</sub>) ppm; IR ν<sub>CO</sub> 1654 cm<sup>−1</sup>; FAB MS *m/z* 550 (M). Anal. Calcd for C<sub>33</sub>H<sub>29</sub>NO<sub>3</sub>P<sub>2</sub>: C, 72.12; H, 5.33; N, 2.55. Found: C, 71.80; H, 5.26; N, 2.29.

**2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-5-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (**L3**).** To the solids Ph<sub>2</sub>PCH<sub>2</sub>OH (1.019 g, 4.71 mmol) and 2-H<sub>2</sub>N-5-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (0.365 g, 2.38 mmol) was added oxygen-free CH<sub>3</sub>OH (25 mL). Both reagents dissolved to give a yellow solution followed by the immediate formation of solid **L3**. After the mixture was stirred for ca. 1 day, **L3** was collected by suction filtration, washed with CH<sub>3</sub>OH (5 mL), and dried in vacuo (0.982 g, 76%). Selected spectroscopic data for **L3** [(CD<sub>3</sub>)<sub>2</sub>SO]: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) −20.2 ppm; <sup>1</sup>H NMR (400 MHz) 15.41 (s, 1H, CO<sub>2</sub>H), 9.81 (s, 1H, OH), 7.48–6.72 (m, 23H, aromatic H), 4.17 (s, 4H, CH<sub>2</sub>) ppm; IR ν<sub>CO</sub> 1664 cm<sup>−1</sup>; FAB MS *m/z* 550 (M). Anal. Calcd for C<sub>33</sub>H<sub>29</sub>NO<sub>3</sub>P<sub>2</sub>: C, 72.12; H, 5.33; N, 2.55. Found: C, 71.97; H, 5.24; N, 2.41.

**Synthesis of Palladium(II) Complexes. Pd(CH<sub>3</sub>)Cl{2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H} (**1**).** To a CH<sub>2</sub>Cl<sub>2</sub> (3 mL) solution of Pd(CH<sub>3</sub>)Cl(cod) (0.074 g, 0.279 mmol) was added solid

**L1** (0.156 g, 0.277 mmol). After stirring for 15 min, the solution was passed through a small Celite plug and Et<sub>2</sub>O (10 mL) and petroleum ether (bp 60–80 °C, 10 mL) were added. The solid **1** was collected by suction filtration and dried in vacuo (0.185 g, 92%). Selected spectroscopic data for **1**: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) 26.1, −7.1 ppm [<sup>2</sup>J(PP) = 50.6 Hz]; <sup>1</sup>H NMR (400 MHz) 7.87–7.01 (m, 23H, aromatic H), 4.29 (m, 2H, CH<sub>2</sub>), 3.91 (m, 2H, CH<sub>2</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 0.75 (dd, 3H, <sup>3</sup>J(PH) = 8 and 4 Hz, CH<sub>3</sub>) ppm; IR ν<sub>CO</sub> 1712, ν<sub>PdCl</sub> 296 cm<sup>−1</sup>; FAB MS *m/z* 705 (M − CH<sub>3</sub>). Anal. Calcd for C<sub>35</sub>H<sub>34</sub>NO<sub>3</sub>P<sub>2</sub>PdCl: C, 58.34; H, 4.77; N, 1.94. Found: C, 58.11; H, 4.54; N, 1.56. Compound **2** was observed, by in situ NMR, upon reaction of Pd(CH<sub>3</sub>)Cl(cod) (0.007 g, 0.0264 mmol) with 1 equiv of **L2** (0.015 g, 0.0273 mmol) in CDCl<sub>3</sub> (0.5 mL). Selected spectroscopic data for **2** (CDCl<sub>3</sub>): <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) 26.3, −7.3 ppm [<sup>2</sup>J(PP) = 48.4 Hz]; <sup>1</sup>H NMR (400 MHz) 8.00–7.01 (m, 23H, aromatic H), 4.36 (CH<sub>2</sub>), 4.15 (CH<sub>2</sub>), 0.74 (dd, 3H, <sup>3</sup>J(PH) = 7.3 and 2.6 Hz, CH<sub>3</sub>) ppm. Compound **3** was prepared in a manner similar to that of **1** (97%) using **L3**. Selected spectroscopic data for **3** [(CD<sub>3</sub>)<sub>2</sub>SO]: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) 22.8, −11.0 ppm [<sup>2</sup>J(PP) = 46.2 Hz]; <sup>1</sup>H NMR (400 MHz) 13.00 (br, 1H, CO<sub>2</sub>H), 9.66 (s, 1H, OH), 7.79–5.60 (m, 23H, aromatic H), 4.18 (s, 2H, CH<sub>2</sub>), 4.08 (s, 2H, CH<sub>2</sub>), 0.33 (dd, 3H, <sup>3</sup>J(PH) = 7.8 and 3.2 Hz, CH<sub>3</sub>) ppm; IR ν<sub>CO</sub> 1691, ν<sub>PdCl</sub> 285 cm<sup>−1</sup>. Anal. Calcd for C<sub>34</sub>H<sub>32</sub>NO<sub>3</sub>P<sub>2</sub>PdCl: C, 57.80; H, 4.57; N, 1.98. Found: C, 57.68; H, 4.36; N, 1.81.

**Pd(CH<sub>3</sub>)Br{2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H} (**4**).** To a suspension of **1** (0.078 g, 0.108 mmol) in acetone (10 mL) was added NaBr (0.111 g, 1.09 mmol) in acetone/CH<sub>3</sub>OH (1.5:1.5 mL). The mixture was stirred for 4 h and the solvent evaporated to dryness under reduced pressure. The crude solid was extracted into CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and passed through a Celite plug. The solvent was concentrated to ca. 1 mL and Et<sub>2</sub>O (15 mL) added to give **4**, which was collected by suction filtration and dried in vacuo (0.068 g, 82%). Selected spectroscopic data for **4**: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) 23.7, −7.3 ppm [<sup>2</sup>J(PP) = 50.6 Hz]; <sup>1</sup>H NMR (400 MHz) 7.97–7.07 (m, 23H, aromatic H), 4.39 (m, 2H, CH<sub>2</sub>), 4.00 (m, 2H, CH<sub>2</sub>), 3.89 (s, 3H, OCH<sub>3</sub>), 0.88 (dd, 3H, <sup>3</sup>J(PH) = 8.0 and 4.3 Hz, CH<sub>3</sub>) ppm; IR ν<sub>CO</sub> 1712 cm<sup>−1</sup>; FAB MS *m/z* 750 (M − CH<sub>3</sub>). Anal. Calcd for C<sub>35</sub>H<sub>34</sub>NO<sub>3</sub>P<sub>2</sub>PdBr·0.5H<sub>2</sub>O: C, 54.31; H, 4.57; N, 1.81. Found: C, 54.03; H, 4.33; N, 1.74.

**Pd(CH<sub>3</sub>)I{2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H} (**5**).** To a suspension of **1** (0.081 g, 0.112 mmol) in acetone (10 mL) was added NaI (0.184 g, 1.23 mmol) in acetone/CH<sub>3</sub>OH (1.5:1.5 mL). The pale-orange mixture was stirred for 2 h and the solvent evaporated to dryness under reduced pressure. The crude solid was extracted into CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and passed through a Celite plug. The solvent was concentrated to ca. 1–2 mL and Et<sub>2</sub>O (15 mL) added to give **5**, which was collected by suction filtration and dried in vacuo (0.073 g, 80%). Selected spectroscopic data for **5**: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz) 16.8, −8.8 ppm [<sup>2</sup>J(PP) = 50.6 Hz]; <sup>1</sup>H NMR (400 MHz) 7.95–6.84 (m, 23H, aromatic H), 4.34 (m, 2H, CH<sub>2</sub>), 4.00 (m, 2H, CH<sub>2</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 0.99 (dd, 3H, <sup>3</sup>J(PH) = 7.4 and 5.0 Hz, CH<sub>3</sub>) ppm; IR ν<sub>CO</sub> 1711 cm<sup>−1</sup>; FAB MS *m/z* 796 (M − CH<sub>3</sub>). Anal. Calcd for C<sub>35</sub>H<sub>34</sub>NO<sub>3</sub>P<sub>2</sub>PdI·2H<sub>2</sub>O: C, 49.62; H, 4.53; N, 1.65. Found: C, 49.66; H, 4.74; N, 1.61.

**[PdCl{2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H}]<sub>6</sub> (**6**).** Compound **1** (0.075 g, 0.104 mmol) was dissolved in CHCl<sub>3</sub> (2 mL) to afford a pale-yellow solution. After this solution was allowed to stand for ca. 20 days, a bright-yellow crystalline solid was isolated and dried in vacuo (0.057 g, 75%). Selected spectroscopic data for **6**: <sup>31</sup>P{<sup>1</sup>H} NMR 10.8, 9.5 ppm [<sup>2</sup>J(PP) = 4.9 Hz]; IR ν<sub>CO</sub> 1609, 1356, ν<sub>PdCl</sub> 305 cm<sup>−1</sup>. Anal. Calcd for C<sub>204</sub>H<sub>180</sub>N<sub>6</sub>O<sub>18</sub>P<sub>12</sub>Pd<sub>6</sub>Cl<sub>6</sub>·1.5CHCl<sub>3</sub>: C, 56.02; H, 4.16; N, 1.91. Found: C, 55.77; H, 4.17; N, 1.70.

(27) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769–5778.



**Table 1.** Details of the X-ray Data Collections and Refinements for Compounds **L1**, **4**, **7**·17CDCl<sub>3</sub>·2Et<sub>2</sub>O, **8**·6CHCl<sub>3</sub>·8CH<sub>3</sub>OH, and **9**·17CDCl<sub>3</sub>

	compound				
	<b>L1</b>	<b>4</b>	<b>7</b> ·17CDCl <sub>3</sub> ·2Et <sub>2</sub> O	<b>8</b> ·6CHCl <sub>3</sub> ·8CH <sub>3</sub> OH	<b>9</b> ·17CDCl <sub>3</sub>
formula	C <sub>34</sub> H <sub>31</sub> NO <sub>3</sub> P <sub>2</sub>	C <sub>35</sub> H <sub>34</sub> BrNO <sub>3</sub> P <sub>2</sub> Pd	C <sub>223</sub> H <sub>188</sub> Cl <sub>57</sub> D <sub>17</sub> N <sub>6</sub> - O <sub>20</sub> P <sub>12</sub> Pd <sub>6</sub>	C <sub>212</sub> H <sub>206</sub> Cl <sub>24</sub> N <sub>6</sub> - O <sub>26</sub> P <sub>12</sub> Pd <sub>6</sub>	C <sub>221</sub> H <sub>180</sub> Cl <sub>51</sub> D <sub>17</sub> I <sub>6</sub> N <sub>6</sub> - O <sub>18</sub> P <sub>12</sub> Pd <sub>6</sub>
<i>M</i>	563.54	764.88	6338.73	5114.67	6821.34
cryst dimens	0.61 × 0.26 × 0.18	0.35 × 0.26 × 0.16	0.32 × 0.23 × 0.22	0.28 × 0.23 × 0.12	0.17 × 0.17 × 0.08
cryst color	colorless	pale yellow	colorless	yellow	yellow
cryst syst	triclinic	monoclinic	trigonal	trigonal	trigonal
space group	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3
<i>a</i> /Å	10.2346(5)	12.0845(6)	50.9328(8)	34.865(9)	50.7094(13)
<i>b</i> /Å	11.5379(6)	16.9539(9)	50.9328(8)	34.865(9)	50.7094(13)
<i>c</i> /Å	13.3608(7)	16.1707(8)	27.6308(7)	16.076(6)	27.6292(10)
α/deg	108.617(2)				
β/deg	102.451(2)	97.919(2)			
γ/deg	94.244(2)				
<i>V</i> /Å <sup>3</sup>	1442.50(13)	3281.4(3)	62075(2)	16924(9)	61528(3)
<i>Z</i>	2	4	9	3	9
μ/mm <sup>-1</sup>	0.187	1.916	1.061	0.902	1.688
θ range/deg	1.66–28.84	1.75–28.84	0.80–25.00	2.19–29.00	0.80–29.15
measd rflns	12 570	27 919	148 201	40 443	182 777
indep rflns	6555	7807	24 302	8949	33 687
obsd rflns [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )]	5790	6672	17 161	5413	21 112
<i>R</i> <sub>int</sub>	0.0105	0.0273	0.0411	0.0587	0.0531
<i>R</i> 1 [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] <sup>a</sup>	0.0321	0.0480	0.0511	0.0470	0.0547
w <i>R</i> 2 (all data) <sup>b</sup>	0.0899	0.1053	0.1604	0.1477	0.1722
largest difference map features/e Å <sup>-3</sup>	0.343, −0.214	0.757, −1.173	1.534, −0.898	1.122, −0.768	1.392, −1.313

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Routinely prepared crystalline bulk samples of **6** were shown, by elemental analyses, to contain between 1 and 3 mol of CHCl<sub>3</sub>.

[PdCl<sub>2</sub>{2-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N}-3-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>}]<sub>6</sub> (**7**). The compounds **L2** (0.023 g, 0.042 mmol) and Pd(CH<sub>3</sub>)Cl(cod) (0.010 g, 0.038 mmol) were dissolved in CDCl<sub>3</sub> (1 mL) to give a pale-yellow solution. After this solution was allowed to stand for ca. 5 days, a yellow crystalline solid deposited (0.025 g, 88%). Selected spectroscopic data for **7**: <sup>31</sup>P{<sup>1</sup>H} NMR (observed in situ) 15.6, 13.9 ppm [<sup>2</sup>*J*(PP) = 6.5 Hz]; IR ν<sub>CO</sub> 1612, 1355, ν<sub>PdCl</sub> 304 cm<sup>-1</sup>. Anal. Calcd for C<sub>198</sub>H<sub>168</sub>N<sub>6</sub>O<sub>18</sub>P<sub>12</sub>Pd<sub>6</sub>Cl<sub>6</sub>·3CDCl<sub>3</sub>: C, 53.64; H, 3.84; N, 1.87. Found: C, 53.94; H, 4.07; N, 1.90. Routinely prepared crystalline bulk samples of **7** were shown, by elemental analyses, to contain between 1 and 3 mol of CHCl<sub>3</sub>. An X-ray study of **7** suggests considerably more CDCl<sub>3</sub> in the lattice per hexamer.

[PdCl<sub>2</sub>{2-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N}-5-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>}]<sub>6</sub> (**8**). The compounds **L3** (0.061 g, 0.111 mmol) and Pd(CH<sub>3</sub>)Cl(cod) (0.030 g, 0.113 mmol) were dissolved in CHCl<sub>3</sub> (15 mL) and CH<sub>3</sub>OH (1 mL) to give a colorless solution. After this solution was allowed to stand for ca. 14 days, a yellow crystalline solid deposited (0.063 g, 79%). Selected spectroscopic data for **8**: IR ν<sub>CO</sub> 1616, 1570, 1372, ν<sub>PdCl</sub> 305 cm<sup>-1</sup>. Anal. Calcd for C<sub>198</sub>H<sub>168</sub>N<sub>6</sub>O<sub>18</sub>P<sub>12</sub>Pd<sub>6</sub>Cl<sub>6</sub>·2CH<sub>3</sub>OH: C, 57.10; H, 4.23; N, 2.00. Found: C, 56.95; H, 3.88; N, 2.00.

[PdI<sub>2</sub>{2-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N}-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>}]<sub>6</sub> (**9**). Compound **5** (0.022 g, 0.0271 mmol) was dissolved in CDCl<sub>3</sub> (0.5 mL) to give an orange solution, which was allowed to stand for ca. 14 days. An orange crystalline solid was isolated and dried in vacuo (0.016 g, 71%). Selected IR data for **9**: ν<sub>CO</sub> 1607, 1362 cm<sup>-1</sup>. Anal. Calcd for C<sub>204</sub>H<sub>180</sub>N<sub>6</sub>O<sub>18</sub>P<sub>12</sub>Pd<sub>6</sub>I<sub>6</sub>·2CDCl<sub>3</sub>: C, 49.34; H, 3.67; N, 1.68. Found: C, 49.32; H, 3.53; N, 1.70. An X-ray study of **9** suggests considerably more CDCl<sub>3</sub> in the lattice per hexamer.

PdCl<sub>2</sub>{2-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N}-3-(OCH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H} (**10**). To a CH<sub>2</sub>Cl<sub>2</sub> (25 mL) solution of PdCl<sub>2</sub>(cod) (0.046 g, 0.161 mmol) was added solid **L1** (0.091 g, 0.161 mmol). After stirring for 4 h, the pale-yellow solution was concentrated under reduced pressure to ca. 10 mL and Et<sub>2</sub>O (10 mL) added to induce precipitation. Solid

**10** was collected by suction filtration and dried in vacuo (0.111 g, 93%). Selected spectroscopic data for **10**: <sup>31</sup>P{<sup>1</sup>H} NMR (36.2 MHz, CDCl<sub>3</sub>/CH<sub>3</sub>OH) 8.7 ppm; <sup>1</sup>H NMR [400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO] 13.00 (s, 1H, CO<sub>2</sub>H), 8.05–6.88 (m, 23H, aromatic H), 4.17 (m, 4H, CH<sub>2</sub>), 2.88 (s, 3H, OCH<sub>3</sub>) ppm; IR ν<sub>CO</sub> 1710, ν<sub>PdCl</sub> 309, 298 cm<sup>-1</sup>; FAB MS *m/z* 704 (M – Cl). Anal. Calcd for C<sub>34</sub>H<sub>31</sub>NO<sub>3</sub>P<sub>2</sub>·PdCl<sub>2</sub>: C, 55.11; H, 4.23; N, 1.89. Found: C, 54.33; H, 4.62; N, 1.65.

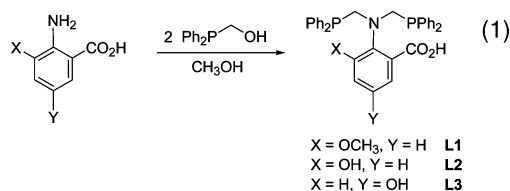
**X-ray Crystallography.** Suitable crystals of **L1** were grown by allowing a CH<sub>3</sub>OH filtrate to stand for 8 days. Crystals of **4** suitable for X-ray crystallography were obtained by allowing a CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O filtrate to stand for 7 days. For **7**–**9**, suitable crystals were obtained directly from either CDCl<sub>3</sub> (**7** and **9**) or CHCl<sub>3</sub>/CH<sub>3</sub>OH (**8**) solutions. All measurements were made on a Bruker AXS SMART 1000 CCD area detector diffractometer, at 150 K, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and narrow frame exposures (0.3°) in ω. Cell parameters were refined from the observed (ω) angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on *F*<sup>2</sup> values for all unique data by full-matrix least squares. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically. For **4**, the bromo and methyl groups exhibit positional interchange disorder, with the major component occupied 74.0(2)% of the time. For **7** and **9**, respectively 2 and 5½ molecules of CDCl<sub>3</sub> were refined as point atoms, while a further 6½ and 3 CDCl<sub>3</sub> molecules were badly disordered and were therefore modeled as diffuse regions of electron density using the Platon “Squeeze” procedure.<sup>28</sup> In **7**, there was also 1 unique molecule of Et<sub>2</sub>O that was rather diffuse and refined with poor geometry. In **8**, 1 molecule of CHCl<sub>3</sub> was disordered with two sets of Cl positions, with the major component occupied 59.3(7)% of the time. Also in **8**, a molecule of CH<sub>3</sub>OH lies close to the  $\bar{3}$  axis and was therefore refined at 1/3 occupancy. These disordered solvent molecules in **8** were refined without

(28) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

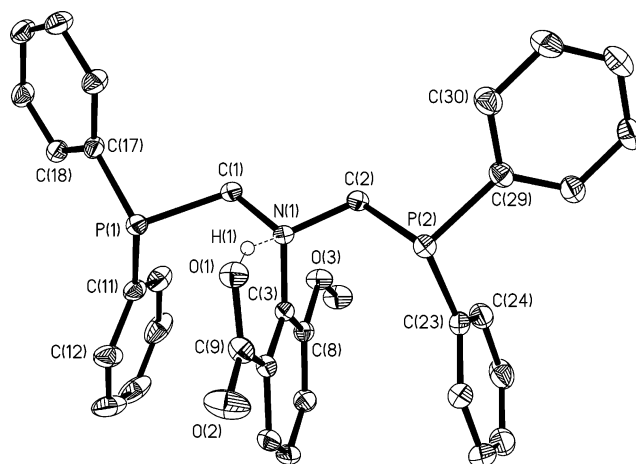
hydrogen atoms and with restraints on geometry and displacement parameters. Programs used were Bruker AXS *SMART* and *SAINT* for diffractometer control and frame integration,<sup>29</sup> Bruker *SHELXTL* for structure solution, refinement, and molecular graphics,<sup>30</sup> Mercury for molecular graphics,<sup>31</sup> and local programs.

## Results and Discussion

**Ligand Synthesis.** As part of continuing studies probing the synthetic utility of Ph<sub>2</sub>PCH<sub>2</sub>OH as an excellent synthon to functionalized tertiary phosphines,<sup>32</sup> we prepared the new P<sub>2</sub>O-terdentate ligands 2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(X)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (X = OCH<sub>3</sub>, **L1**; X = OH, **L2**) and 2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-5-(OH)-C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (**L3**) (eq 1) in high yields (typically 80%) from inexpensive, commercially available precursors. All three phosphines **L1–L3** are air-stable, colorless solids whose compositions were deduced by their characteristic <sup>31</sup>P NMR resonance [**L1**, δ(P) –22.3 ppm (CDCl<sub>3</sub>); **L2**, δ(P) –18.3 ppm {(CD<sub>3</sub>)<sub>2</sub>SO}; **L3**, δ(P) –20.2 ppm {(CD<sub>3</sub>)<sub>2</sub>SO}].<sup>33</sup> On the basis of the reagent stoichiometry used here, the <sup>1</sup>H NMR spectra further support double condensation as inferred by the absence of an NH signal that would be expected if single substitution resulted. The IR spectra (KBr disk) of **L1–L3** each showed an intense ν<sub>C=O</sub> stretch in the region 1650–1700 cm<sup>–1</sup>, while the ν<sub>OH</sub> stretching vibration was not readily discernible. Other characterizing data are given in the Experimental Section.



Suitable crystals of **L1** were grown from CH<sub>3</sub>OH over 8 days, and its X-ray structure is shown in Figure 1. Structure analysis clearly shows approximate pyramidal geometries about both phosphorus centers (Table 2).<sup>33</sup> It is noteworthy that the dihedral angle (3.9°) between the carboxylic acid and N–arene group reflects a near-planar arrangement, presumably imposed by the strong intramolecular N···H–O hydrogen bond [N(1)···O(1) 2.5597(13) Å, H(1)···N(1) 1.77 Å, and N(1)···H(1)–O(1) 155°], which also manifests itself in the mononuclear complexes **1–5** (vide infra for the X-ray structure of **4**).



**Figure 1.** Molecular structure of **L1**. All hydrogen atoms except on O(1) have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

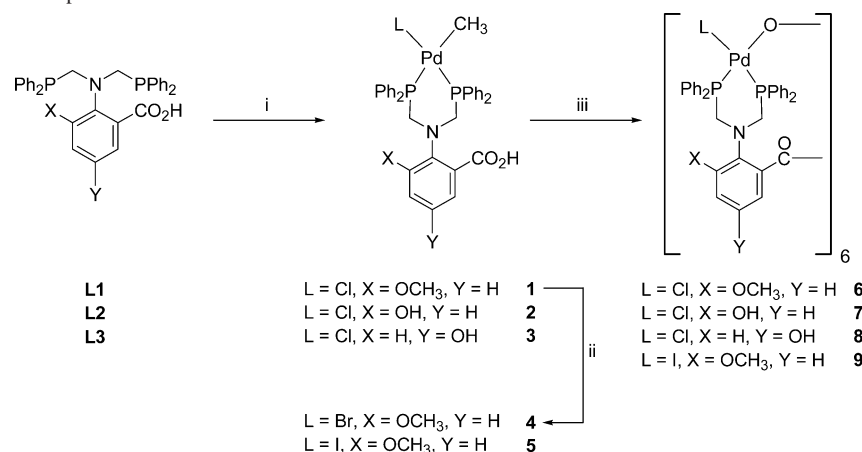
**Table 2.** Selected Bond Distances and Angles for Compounds **L1** and **4**

	<b>L1</b>	<b>4</b>
<b>Bond Length (Å)</b>		
P(1)–C(1)	1.8665(12)	1.845(4)
P(2)–C(2)	1.8679(12)	1.836(4)
C(1)–N(1)	1.4860(14)	1.493(5)
C(2)–N(1)	1.4888(15)	1.487(5)
C(9)–O(1)	1.3181(15)	1.321(5)
C(9)–O(2)	1.2133(16)	1.213(5)
Pd(1)–Br(1) <sup>a</sup>		2.4527(9)
Pd(1)–C(35) <sup>a</sup>		2.157(8)
Pd(1)–P(1)		2.3177(11)
Pd(1)–P(2)		2.2536(10)
<b>Bond Angle (deg)</b>		
P(1)–C(1)–N(1)	111.45(7)	112.2(2)
P(2)–C(2)–N(1)	111.38(7)	112.6(2)
C(1)–N(1)–C(2)	111.91(9)	111.0(3)
Br(1)–Pd(1)–P(1) <sup>a</sup>		89.79(4)
Br(1)–Pd(1)–P(2) <sup>a</sup>		173.64(4)
P(1)–Pd(1)–C(35) <sup>a</sup>		172.8(2)
P(1)–Pd(1)–P(2)		95.58(4)
Br(1)–Pd(1)–C(35) <sup>a</sup>		88.5(2)
P(2)–Pd(1)–C(35) <sup>a</sup>		86.6(2)
Pd(1)–P(1)–C(1)		117.67(12)
C(2)–P(2)–Pd(1)		113.05(12)

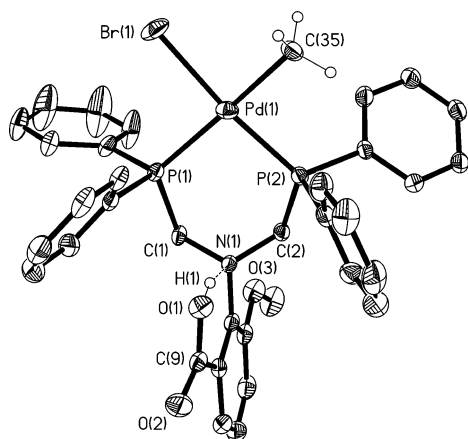
<sup>a</sup> For the major disorder components.

**Palladium(II) Chemistry.** To elucidate whether **L1–L3** could support a multinuclear array via terdentate coordination, we chose a suitable late-transition-metal precursor that would κ<sup>2</sup>-P<sub>2</sub>-chelate yet also have the propensity to form a stable M–O bond.<sup>14a</sup> Accordingly, reaction of 1 equiv of **L1–L3** with Pd(CH<sub>3</sub>)Cl(cod) in CH<sub>2</sub>Cl<sub>2</sub> (or CDCl<sub>3</sub>) gave Pd(CH<sub>3</sub>)Cl(κ<sup>2</sup>-P<sub>2</sub>-**L1–L3**) (**1–3**; Scheme 1), which displayed the usual spectroscopic and analytical data. In all three complexes, <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed the expected AX pattern for inequivalent <sup>31</sup>P nuclei in the regions 22.8–26.3 and –7.1 to –11.0 ppm [<sup>2</sup>J(PP) = 46.2–50.6 Hz]. Metathesis of **1** with NaX (X = Br, I) gave the analogous (methyl)bromo **4** and (methyl)iido **5** complexes, respectively (Scheme 1). An X-ray structure of **4** confirmed the anticipated square-planar geometry about the palladium(II) metal center (Figure 2 and Table 2) with typical Pd–P bond lengths [Pd(1)–P(1) 2.3177(11) Å and Pd(1)–P(2) 2.2536(10) Å]

- (29) *SMART and SAINT software for CCD diffractometers*; Bruker AXS Inc.: Madison, WI, 2001.
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- (33) Durran, S. E.; Elsegood, M. R. J.; Hawkins, N.; Smith, M. B.; Talib, S. *Tetrahedron Lett.* **2003**, 44, 5255–5257.

**Scheme 1.** Preparation of Compounds **1–9** from **L1–L3**<sup>a</sup>


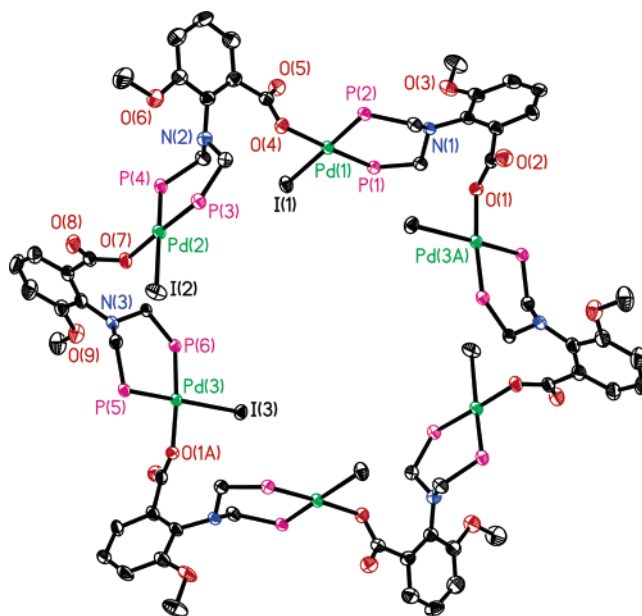
<sup>a</sup> Reagents and conditions: (i) Pd(CH<sub>3</sub>)Cl(cod); (ii) NaBr or NaI; (iii) CHCl<sub>3</sub> or CHCl<sub>3</sub>/CH<sub>3</sub>OH, room temperature.



**Figure 2.** Molecular structure of **4**. Minor disorder components and all hydrogen atoms except on O(1) and C(35) have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

and angles [P(1)–Pd(1)–P(2) 95.58(4)°]. The dihedral angle between the carboxylic acid group and the N–arene in **4** (9.4°) deviates slightly more than that in **L1**. Like **L1**, there also persists an intramolecular N···H–O hydrogen bond [N(1)···O(1) 2.644(4), H(1)···N(1) 1.86 Å, and N(1)···H(1)–O(1) 154°] with the OH group of the ortho-substituted carboxylic acid.

When CDCl<sub>3</sub> solutions of **1** were monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy over 3 days, a new species **6** with δ(P) resonances at 10.8 and 9.5 ppm [<sup>2</sup>J(PP) = 4.8 Hz] was observed accompanied by diminishment of those δ(P) signals attributed to **1**. A second minor species at δ(P) 8.3 ppm was also observed and assigned to PdCl<sub>2</sub>(κ<sup>2</sup>-P<sub>2</sub>-**L1**) (**10**) by comparison with an authentic sample prepared from PdCl<sub>2</sub>(cod) and **L1**. Preparatively, compound **6** could be obtained as a yellow, thermally stable (decomposes at >212 °C) solid<sup>34</sup> in excellent yield (75%) upon allowing a chloroform solution of **1** to stand at room temperature for ca. 20 days (Scheme 1). Using a similar approach, crystalline samples of the analogous iodo complex **9** were obtained from CDCl<sub>3</sub> solutions. By contrast, the low solubility of **L3** hampered

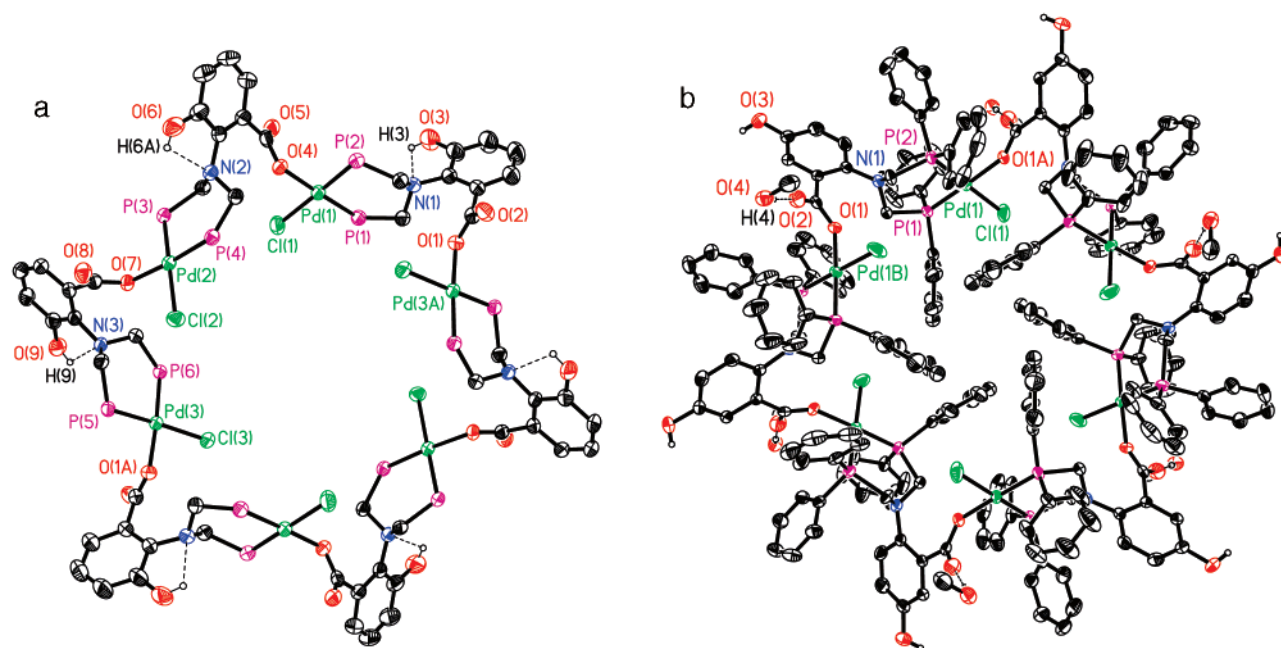


**Figure 3.** Molecular structure of a single molecule of **9**. Two phenyl groups on each phosphorus, all hydrogen atoms, and the solvent of crystallization have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

self-assembly in chloroform solution so reactions were performed in situ using Pd(CH<sub>3</sub>)Cl(cod) and **L3** in a mixed-solvent system (CDCl<sub>3</sub>/CH<sub>3</sub>OH) without prior isolation of **3**. This protocol was used for **L2** although CH<sub>3</sub>OH was not required to solubilize the ligand. After these solutions were allowed to stand for 5–14 days, the (pale)-yellow solids **7** and **8** were isolated in excellent yields (routinely ~80% in both cases). The IR spectra were particularly diagnostic and clearly indicated κ<sup>1</sup>-O-carboxylate coordination for **L1–L3** from the shift to lower wavenumbers by ca. 100 cm<sup>–1</sup> for ν<sub>C=O</sub> (with respect to **1–5**). In contrast, our attempt to observe the molecular ion of **6** by MALDI-TOF MS was unsuccessful, although a relatively abundant cluster of ions was observed at *m/z* 1410.145, which could be consistent with a dimeric species whereby both palladium(II) centers are bridged by **L1** in its deprotonated form (remaining coordination sites on both palladium centers occupied by **L1**/Cl ligands).

(34) A low-resolution X-ray diffraction data set for **6**·xCHCl<sub>3</sub> has been obtained that confirms this molecular hexagon arrangement: trigonal, *R*<sub>3</sub>, *a* = 51.668(14) Å, *c* = 27.498(7) Å, *V* = 63573(50) Å<sup>3</sup>.





**Figure 4.** (a) X-ray structure of **7**. All solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level. (b) X-ray structure of **8**. All solvents except the well-ordered CH<sub>3</sub>OH solvate have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

**Table 3.** Selected Bond Distances and Angles for the Hexamers **7**·17CDCl<sub>3</sub>·2Et<sub>2</sub>O, **8**·6CHCl<sub>3</sub>·8CH<sub>3</sub>OH, and **9**·17CDCl<sub>3</sub>

	<b>7</b> ·17CDCl <sub>3</sub> · 2Et <sub>2</sub> O	<b>8</b> ·6CHCl <sub>3</sub> · 8MeOH	<b>9</b> ·17CDCl <sub>3</sub>
Bond Length (Å)			
Pd(1)–P(1)	2.2292(12)	2.2407(12)	2.2292(13)
Pd(1)–P(2)	2.2439(12)	2.2533(12)	2.2575(13)
Pd(2)–P(3)	2.2419(11)		2.2391(14)
Pd(2)–P(4)	2.2326(11)		2.2655(15)
Pd(3)–P(5)	2.2293(11)		2.2565(13)
Pd(3)–P(6)	2.2344(11)		2.2321(14)
Pd(1)–Cl(1)	2.3311(13)	2.3332(14)	
Pd(2)–Cl(2)	2.3463(11)		
Pd(3)–Cl(3)	2.3402(11)		
Pd(1)–I(1)			2.6424(5)
Pd(2)–I(2)			2.6404(6)
Pd(3)–I(3)			2.6398(5)
Pd(1)–O(4)	2.067(3)		2.109(3)
Pd(2)–O(7)	2.059(3)		2.079(4)
Pd(1)/Pd(3)–O(1A)	2.074(3) <sup>a</sup>	2.076(3) <sup>b</sup>	2.068(3) <sup>c</sup>
Bond Angle (deg)			
P(1)–Pd–P(2)	94.06(4)	94.95(4)	93.51(5)
P(3)–Pd–P(4)	94.10(4)		94.71(5)
P(5)–Pd–P(6)	93.79(4)		92.92(5)
O(4)–Pd–Cl(1)	91.21(9)		
O(7)–Pd–Cl(2)	91.73(8)		
O(1A)–Pd–Cl(1)/Cl(3)	91.20(8) <sup>a</sup>	91.95(9)	
O(4)–Pd–I(1)			92.75(10)
O(7)–Pd–I(2)			90.16(10)
O(1A)–Pd–I(3)			90.19(9)

<sup>a</sup> Symmetry operators:  $-x + 5/3, -y + 1/3, -z + 4/3$ . <sup>b</sup> Symmetry operators:  $x - y, x - 1, -z + 1$ . <sup>c</sup> Symmetry operators:  $-x + 2/3, -y + 1/3, -z + 4/3$ .

Suitable X-ray-quality crystals of **7**·17CDCl<sub>3</sub>·2Et<sub>2</sub>O, **8**·6CHCl<sub>3</sub>·8CH<sub>3</sub>OH, and **9**·17CDCl<sub>3</sub> were obtained and all three structures determined (Figure 3 for **9**, parts a and b of Figure 4 for **7** and **8**, respectively, and Table 3). In all three cases, the hexagon core geometries are essentially identical. The X-ray structure of **9** reveals a hexamer on an inversion center with three independent palladium atoms each with a  $I/P_2/O$  coordination environment. The Pd–I, Pd–P, and

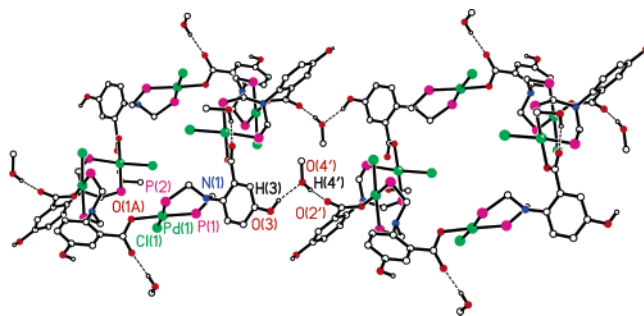
Pd–O bond lengths are all broadly as anticipated. Ligand **L1** adopts a monoanionic form ligating through both phosphorus atoms and a single oxygen-donor center from the carboxylate group. The formation of a Pd–O bond [Pd–O 2.068(3), 2.079(4), and 2.109(3) Å]<sup>14a</sup> in **9**·17CDCl<sub>3</sub> is further reflected by the change in the stretching frequency ( $\Delta\nu$  ca. 100 cm<sup>−1</sup>) of the carbonyl group of **L1** (from IR spectroscopy) in accordance with  $\kappa^1$ -O-carboxylate coordination. Each of the PdP<sub>2</sub>C<sub>2</sub>N six-membered rings has approximately the same conformation. To accommodate the hexameric ring structure, there are significant twists in the carboxylate/N–arene dihedral angles (33.5–51.0°) relative to those observed in **L1** and **4** (<10°). An insight into the internal size of the hexamer is gleaned from the nonbonding Pd···Pd separations,<sup>13a</sup> which vary from 6.63 Å (adjacent palladium centers) to 13.62 Å (internal transannular palladium centers), although the cavity is self-filling with phenyl groups (one from each ditertiary phosphine). An estimation of the maximum external transannular distance (measured between symmetry-related phenyl protons on opposite sides of the ring) gives an outside diameter of ca. 2.63 nm. Of the approximate 17 chloroform molecules of crystallization, six interact with the hexamer via Cl<sub>3</sub>C–D···O=C links to the free carboxylate oxygen (see Supporting Information). The remainder, some badly disordered, fill the voids and channels between the hexameric rings.

For **7**·17CDCl<sub>3</sub>·2Et<sub>2</sub>O, the asymmetric unit comprises three independent palladium molecules, while for **8**·6CHCl<sub>3</sub>·8CH<sub>3</sub>OH, only one palladium molecule is unique. Both **7**·17CDCl<sub>3</sub>·2Et<sub>2</sub>O and **9**·17CDCl<sub>3</sub> are close to being isomorphous (Table 1) but differ in the amount and nature of the included solvent of crystallization. The former includes diethyl ether and has the larger unit cell volume as a result, while the latter does not. The coordination environment about each metal center is composed of a chelating  $\kappa^2$ -P<sub>2</sub>-didentate

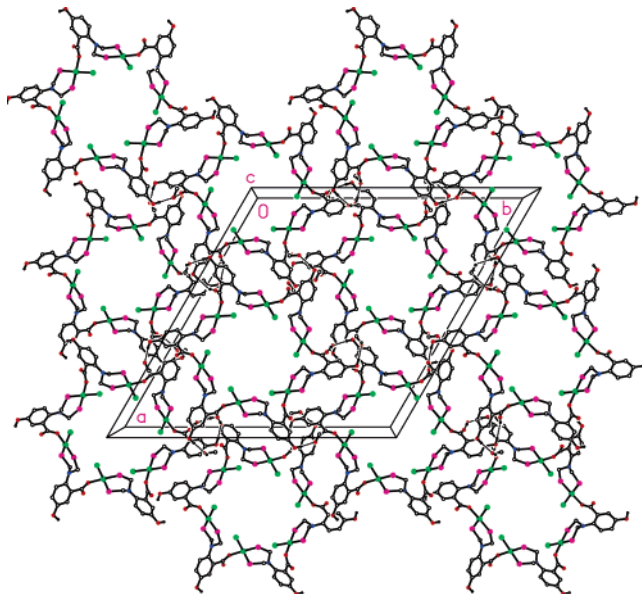
phosphine, one chloride, and a  $\kappa^1$ -O-bound carboxylate. Again isomeric **L2** and **L3** both function efficiently as  $\kappa^3$ - $P_2O$ -terdentate ligands. The Pd–O, Pd–P, and Pd–Cl lengths are all typical and in the normal ranges expected. There is little evidence for a trans influence in the Pd–P bond distances [Pd–P<sub>av</sub> 2.2383(11) Å (P trans to Cl) and Pd–P<sub>av</sub> 2.2321(11) Å (P trans to O) for **7**; Pd–P 2.2533(12) Å (P trans to Cl) and Pd–P 2.2407(12) Å (P trans to O) respectively for **8**]. Furthermore, the six-membered Pd–P–C–N–C–P ring conformations in both of these structures are best described as slightly flattened chairs in which the PdP<sub>2</sub> approaches planarity with the P<sub>2</sub>C<sub>2</sub> plane. The overall structures both comprise a hexamer containing alternate palladium metal centers and deprotonated **L2** (or **L3**) arranged to give isomeric 48-membered metallomacrocyclic rings. The closest nonbonding Pd···Pd distance in **7** is 6.659 Å (6.804 Å in **8**), while the furthest internal transannular Pd···Pd separation is 12.959 Å (12.884 Å in **8**).<sup>13a</sup> The nanoscopic size of **7** (and **8**) is 2.53 nm (and 2.59 nm) when the outside of the ring structure is examined (measured between symmetry-related phenyl protons on opposite sides of the ring). To accommodate these hexameric motifs, the carboxylate group is again likewise twisted (dihedral angles between 43 and 54° for **7** and at 39° for **8**) with respect to the N–arene group. Within the cavity, most of the available space is occupied by one phenyl ring from each phosphorus center (Figure 4b). The unprecedented ability of the flexible  $\kappa^3$ - $P_2O$ -terdentate ligand to act in this way, thus facilitating self-assembly of the hexagons shown, is clearly demonstrated, and we believe this to constitute a rare example of such a self-assembled structure.

The specific use of **L2** and **L3** allows further secondary interactions to be realized. Hence, in the case of **7**, bearing an *o*-phenolic OH group with respect to the –N(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> unit, only intramolecular hydrogen bonding [N···O 2.722(5)–2.738(5) Å, H(1)···N(1) 2.26–2.29 Å, and N(1)···H(1)–O(1) 112–117°] is observed. In contrast, **8** reveals significant intermolecular hydrogen-bonding contacts. A crystallographically well-determined CH<sub>3</sub>OH hydrogen bonds to the carbonyl group of the carboxylate [O···O 2.648(5) and 2.676(5) Å, H···O 1.81 and 1.88 Å, and O···H–O 171° and 159°]. Each hexamer makes 12 hydrogen-bonding interactions, arranged in pairs, to six adjacent hexamer rings (three above and three below the hexamer plane). Hexamers are linked through simultaneous hydrogen bonding using the phenolic O–H group on the N–phenyl ring and CH<sub>3</sub>OH solvent, affording 34-membered [R<sup>4</sup><sub>4</sub>(34) pattern]<sup>35</sup> pseudorings (Figure 5). This unique combination of interactions (symmetry-imposed) leads to the novel three-dimensional architecture shown in Figure 6, which, we believe to the best of our knowledge, has not been previously observed.

While the solubilities of **7** and **8** are extremely low in common organic (e.g., dichloromethane, acetone, and tetrahydrofuran) and polar solvents (e.g., dimethyl sulfoxide), we



**Figure 5.** X-ray structure of **8** showing the hydrogen-bonding interactions between adjacent hexamer units. Phenyl groups on phosphorus and solvent molecules except the well-ordered CH<sub>3</sub>OH solvate have been omitted for clarity.



**Figure 6.** Packing plot of **8** showing the three-dimensional network. All phenyl groups on phosphorus and solvent molecules except the well-ordered CH<sub>3</sub>OH solvate have been omitted for clarity.

have been able to monitor their in situ self-assembly in CDCl<sub>3</sub> (or CD<sub>2</sub>Cl<sub>2</sub>) by <sup>31</sup>P{<sup>1</sup>H} (Figure 7) and <sup>1</sup>H NMR spectroscopy (Figure 8). For **7**, this process can be monitored over ca. 4–5 h, whereupon under these conditions **7** crystallizes from the NMR solvent and precludes any further meaningful spectra. Upon immediate mixing, we observe mononuclear **2** along with small amounts of PdCl<sub>2</sub>(**L2**) [ $\delta$ (P) 10.5 ppm] presumably formed by protonation (trace amounts of HCl) of the Pd–CH<sub>3</sub> group. After 24 min, a new species at  $\delta$ (P) 15.6 and 13.9 ppm appears, and by 263 min, this becomes the predominant species present in solution. Similarly the <sup>1</sup>H NMR spectra reflect the same trend, namely, a gradual disappearance of the Pd–CH<sub>3</sub> signal [ $\delta$ (H) 0.7 ppm] over time and growth in the intensity of a new signal at  $\delta$ (H) 0.20 ppm corresponding to CH<sub>4</sub> formation.<sup>36</sup> No other attempts to identify CH<sub>4</sub> were pursued. Although we have not attempted to ascertain the exact integer value for *n* in [PdCl{2-[(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N]-3-(OH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>}]<sub>n</sub> and, moreover,

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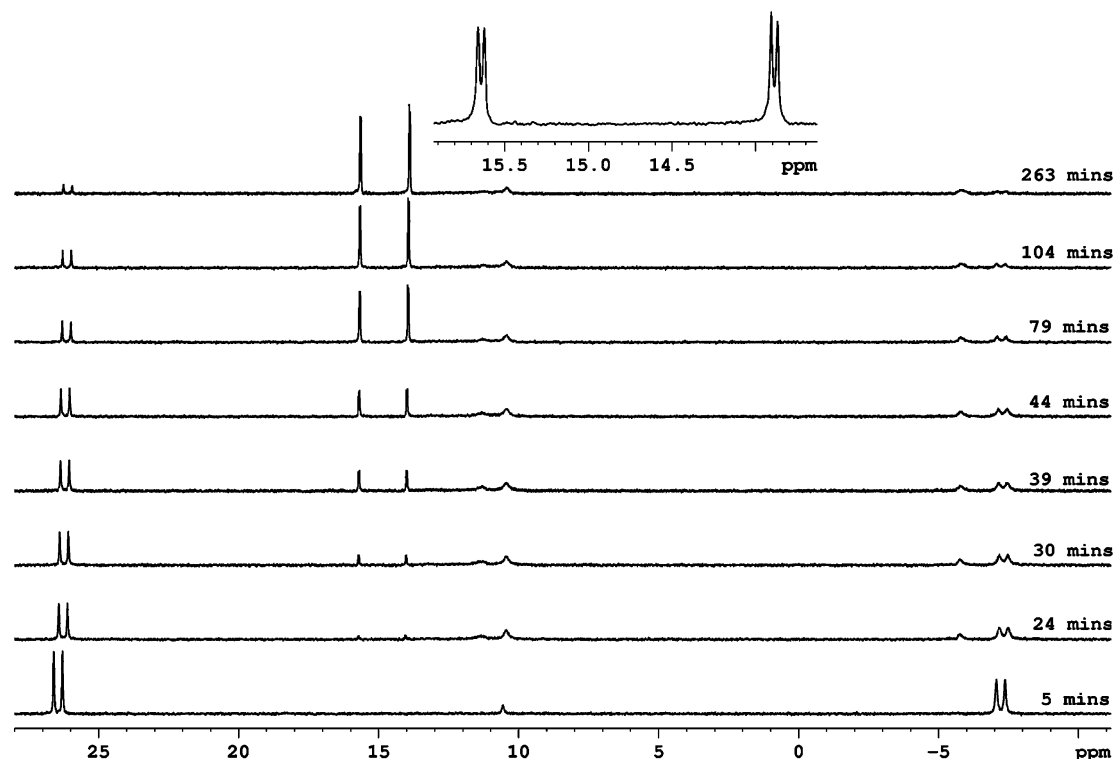


Figure 7.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **L2**/Pd(Me)Cl(cod) (1:1 ratio) recorded over time at 298 K.

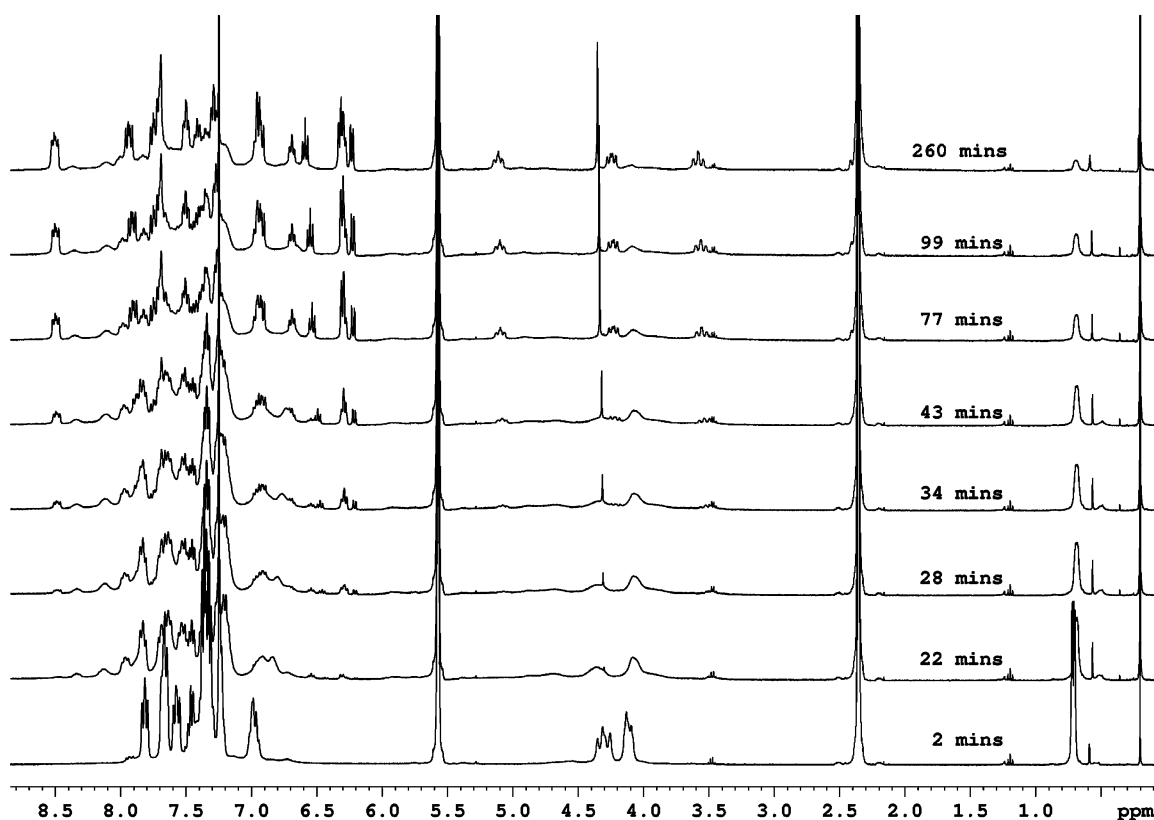


Figure 8.  $^1\text{H}$  NMR spectra of **L2**/Pd(Me)Cl(cod) (1:1 ratio) recorded over time at 298 K. The displaced cod ligand appears as two resonances at ca.  $\delta(\text{H})$  2.4 and 5.6 ppm.

whether the hexanuclear species actually predominates in solution, it is clear that this reaction proceeds very cleanly. We also find that **6**, **8**, and **9** self-assemble over longer periods than that observed for **7**, which may reflect the importance of several criteria: the predisposition of the

phenolic group, the nature of the substituent ( $-\text{OCH}_3$  vs  $-\text{OH}$ ), the terminal halide present, and the ligand solubility in the solvents used. Furthermore, while the formation of **6–9** proceeds under extremely mild conditions (i.e., ambient temperature), efforts to synthesize Pt<sub>6</sub> molecular hexagons

by a similar self-assembly process have so far proven to be unsuccessful despite using more forcing conditions ( $\text{CDCl}_3$ , 50 °C, 14 days). This observation is not too surprising given that palladium(II) complexes are generally known to be more reactive than their platinum(II) counterparts.

### Concluding Remarks

In conclusion, we have demonstrated, using simple building blocks, the synthesis of four novel nanosized molecular  $\text{Pd}_6$  hexagons using flexible carboxylic acid modified di-tertiary phosphines. The observation of discrete hexameric structures from three *different*  $\kappa^3\text{-P}_2\text{O}$ -terdentate ligands (and with two *different* halide auxiliary ligands) is evidence that the bulk samples in each case are indeed hexanuclear and are formed during the reaction. The use of suitably disposed polycarboxylated phosphines may enable new classes of porous materials<sup>22</sup> to be accessed in which the cavity size can be regulated. Moreover, manipulating the substituents

on phosphorus or by incorporating other functional polar groups on the N-arene backbone may permit other supramolecular architectures to be realized. Further ligand and coordination studies are currently in progress and will be reported in due course.

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**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates (CIF format), and ellipsoid plots for **L1**, **4**, **7**·17 $\text{CDCl}_3$ ·2 $\text{Et}_2\text{O}$ , **8**·6 $\text{CHCl}_3$ ·8 $\text{CH}_3\text{OH}$ , and **9**·17 $\text{CDCl}_3$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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