

# Synthesis and Characterization of Novel Four-Membered Palladacycles

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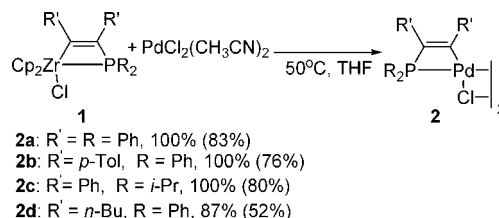
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**Summary:** Reaction of zirconophosphacyclobutenes with  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  in THF yields the air- and heat-stable four-membered palladacyclic compounds in dimeric structures, which are characterized by X-ray diffraction.

Palladacycles are one of the most popular classes of organopalladium derivatives, which are widely applied in organic synthesis, organometallic catalysis, and new molecular materials.<sup>1,2</sup> Among them, the most investigated palladacycles are five- or six-membered rings fused with an aromatic ring, and the metalated carbon is usually an aromatic  $\text{sp}^2$  carbon.<sup>3</sup> However, four-membered palladacycles with a metalated vinylic  $\text{sp}^2$  carbon are rather rare.<sup>4,5</sup> This is probably due to poor stability, which brings difficulties of preparation, isolation, and characterization of these compounds. The limitation can be overcome by changing the nature of the metalated carbon atom and the type of donor groups and their substituents. Herein we report our results describing the preparation and full characterization of novel palladaphosphacyclobutene complexes.

Scheme 1



## Results and Discussion

We recently reported that zirconophosphination of alkynes gave zirconophosphacyclobutenes, which could be transformed into  $\beta$ -functionalized alkenylphosphines through coupling reactions with various electrophiles in the presence of CuCl. In these reactions, Zr–C to Cu–C transmetalation was necessary.<sup>6</sup> With the aim of studying palladacycles, we envisioned that the transmetalation of the Zr– $\text{sp}^2$  carbon bond to the Pd– $\text{sp}^2$  carbon bond<sup>7</sup> could give palladacycles. As expected, treatment of zirconophosphacyclobutenes **1** with  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  afforded palladacycles **2** (Scheme 1). The <sup>31</sup>P NMR spectrum of **2a** showed a singlet signal at –82.6 ppm assigned to the phosphorus of a four-membered palladaphosphacycle.<sup>8</sup> Removal of the solvent and crystallization in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  at 80 °C afforded compound **2a** as a yellow solid in 83% isolated yield.

To further confirm the structure of the product, yellow crystals of **2a** suitable for X-ray analysis were obtained from its solution in  $\text{CH}_2\text{Cl}_2$  at room temperature. The structure of **2a** in Figure 1 clearly shows the formation of palladaphosphacyclobutene. The complex adopts a *transoid* conformation and exists as a chlorine-bridged dimer. The C–Pd–P angle found in complex **2a**, 67.55(1)°, is among the smallest values observed in the four-membered palladacycles, 68.7(2)–71.2(2)°.<sup>9</sup> The palladium–carbon bond length in **2a** is 2.011(4) Å, which falls between 1.989 and 2.042 Å of four-membered palladacycles.<sup>4a,9a</sup> The distance of the palladium–phosphorus bond is 2.2085(9) Å, which is noticeably shorter in comparison with other Pd–P bonds in similar complexes.<sup>5b,9a</sup> It is presumably because the electron-attracting nature of bridged chlorine leads to tighter coordination of the phosphorus atom with the palladium center. The set of Pd, P, C(1), and C(2) in compound **2a** is nearly

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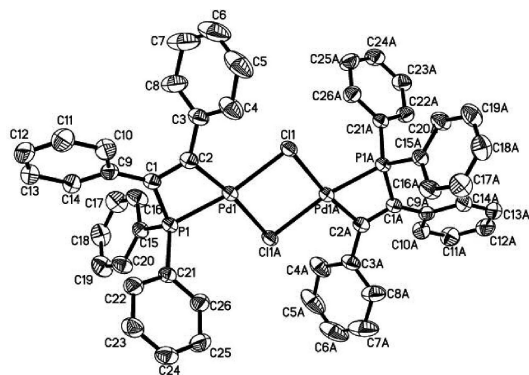
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**Figure 1.** Molecular structure of **2a**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(2), 2.011(4); Pd(1)–P(1), 2.2085(9); Pd(1)–Cl(1), 2.4209(9); Pd(1)–Cl(1)A, 2.4470(9); C(1)–C(2), 1.351(5); P(1)–C(1), 1.799(4); C(2)–Pd(1)–P(1), 67.55(1); C(2)–Pd(1)–Cl(1), 101.95(1); Pd(1)–Cl(1)–Pd(1)A, 94.34(3); C(1)–P(1)–Pd(1), 87.09(1); C(2)–C(1)–P(1), 95.6(3); C(1)–C(2)–Pd(1), 109.8(3).

**Table 1.** Crystal Data and Refinement Data for **2a** and **2c**

	<b>2a</b>	<b>2c</b>
empirical formula	C <sub>52</sub> H <sub>40</sub> Cl <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> • 0.3CH <sub>2</sub> Cl <sub>2</sub>	C <sub>40</sub> H <sub>48</sub> Cl <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub>
fw	1035.96	874.42
cryst color	yellow	yellow
temp (K)	293(2)	293(2)
cryst syst	triclinic	monoclinic
space group	P $\bar{1}$	P2(1)/n
<i>a</i> (Å)	9.30570(1)	9.2167(3)
<i>b</i> (Å)	11.1323(2)	12.9557(5)
<i>c</i> (Å)	12.2183(2)	16.6165(6)
$\alpha$ (deg)	82.9830(1)	90
$\beta$ (deg)	86.6880(1)	95.890(2)
$\gamma$ (deg)	83.4860(1)	90
volume (Å <sup>3</sup> )	1246.91(3)	1973.68(1)
<i>Z</i>	1	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.380	1.471
<i>M</i> (mm <sup>-1</sup> )	0.957	1.154
<i>F</i> (000)	521	888
cryst size (mm)	0.24 × 0.20 × 0.13	0.32 × 0.21 × 0.15
$\theta$ range (deg)	1.68–28.32	2.43–28.34
limiting indices	–10 ≤ <i>h</i> ≤ 12, –14 ≤ <i>k</i> ≤ 14, –16 ≤ <i>l</i> ≤ 16	–12 ≤ <i>h</i> ≤ 9, –17 ≤ <i>k</i> ≤ 17, –22 ≤ <i>l</i> ≤ 22
no. of reflns collected	17797	17449
no. of unique reflns	6158	4892
completeness to $\theta$ (%)	98.9( $\theta = 28.32^\circ$ )	99.1( $\theta = 28.34^\circ$ )
absorp corr	empirical	empirical
no. of params	287	208
goodness-of-fit on <i>F</i> <sup>2</sup>	1.052	0.812
final <i>R</i> indices [ <i>I</i> > 2( <i>I</i> )]	<i>R</i> 1 = 0.0328, w <i>R</i> 2 = 0.0914	<i>R</i> 1 = 0.0617, w <i>R</i> 2 = 0.1029
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0400, w <i>R</i> 2 = 0.0943	<i>R</i> 1 = 0.1468, w <i>R</i> 2 = 0.1279
largest diff peak and hole (e Å <sup>-3</sup> )	0.836 and –0.273	0.626 and –0.553

coplanar, and the mean deviation from the best plane is 0.0005 Å. The dihedral angle between the plane Pd(1), C(2), P(1) and plane C(1), P(1), C(2) is 0.1°. Despite the tension associated with a four-membered palladacycle, compound **2a** is quite stable, that is, inert to oxygen and water. The stability might be associated with the existence of geometrical rigidity around the metal center produced by a sterically congested situation due to bulky hindrance and the electronic effect of an sp<sup>2</sup> vinylic carbon with an aryl group.

Several representative examples of the transmetalation reactions are shown in Scheme 1. When aryl groups are linked to

the C=C bond, complexes **2a–c** formed exclusively. When alkyl groups are linked to the C=C bond, complex **2d** formed as the major product together with small amounts of an unknown, inseparable mixture. When alkyl groups are on the phosphorus atom, palladaphosphacyclobutene **2c** also formed in excellent yield. Yellow crystals of **2c** suitable for X-ray analysis were also obtained in a similar manner to its analogue **2a**, and the structure of **2c** is identical to **2a** except for the different substituents on the phosphorus atom. An ORTEP plot of **2c** appears in the Supporting Information.

In summary, we have successfully developed a new type of palladacycle. These novel palladacycles are air- and moisture-stable. Further scope of this class of palladacycles and applications are currently under investigation in our laboratory.

## Experimental Section

**1. General Procedures.** All manipulations were conducted in Schlenk tubes and under nitrogen with a slightly positive pressure. The reaction progress was monitored by <sup>31</sup>P NMR. The <sup>31</sup>P NMR yields were obtained in proportion to the integral area of all the <sup>31</sup>P signals determined by integration. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under nitrogen atmosphere. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a JEOL 300 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. <sup>31</sup>P NMR spectra were recorded on a Bruker AC 200 NMR spectrometer at 81 MHz under <sup>1</sup>H decoupled conditions using 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta_P = 0$  ppm) as an external standard. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. Elemental analyses were performed on a Flash EA 1112 instrument. Melting points were determined with a digital electrothermal apparatus without calibration.

**2. Representative Procedure for the Preparation of Palladaphosphacyclobutene **2a**.** (*Z*)-[2-(Dicyclopentadienylchlorozircono)-1,2-diphenylvinyl]diphenylphosphine (248 mg, 0.4 mmol), PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (104 mg, 0.4 mmol), and THF (5 mL) were added to Schlenk tube, and the mixture was stirred for 2 h at 50 °C. Palladaphosphacyclobutene **2a** was formed exclusively. <sup>31</sup>P NMR (81 MHz, THF, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –82.6. Removal of the solvent and crystallization in ClCH<sub>2</sub>CH<sub>2</sub>Cl (DCE) at 80 °C afforded 168 mg of the title compound as a yellow solid (isolated yield 83%). Mp: 270 °C (dec). IR (KBr, cm<sup>-1</sup>): 3055, 3019, 1693, 1595, 1572, 1556, 1479, 1436, 1260, 1108, 1097, 762, 744, 721, 691. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  6.88–7.86 (m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  126.8–133.7 (m, sp<sup>2</sup> carbon). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –83.4. Positive ion ESI-MS: 469.0. Anal. Calcd for C<sub>52</sub>H<sub>40</sub>Cl<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> • 1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 59.88; H, 3.92. Found: C, 59.48; H, 3.94.

**Palladaphosphacyclobutene **2b**.** Mp: 270 °C (dec). IR (KBr, cm<sup>-1</sup>): 3050, 3018, 2917, 2856, 1603, 1572, 1435, 1261, 1097, 1020, 802, 744, 690. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  2.19 (s, 6H), 2.28 (s, 6H), 6.78–7.51 (m, 28H), 7.83 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 4H), 7.88 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  21.3, 21.6, 127.0–129.4 (m, sp<sup>2</sup> carbon), 131.1, 132.7, 133.7, (d, <sup>2</sup>*J*<sub>PC</sub> = 12.2 Hz), 136.6 (d, <sup>1</sup>*J*<sub>PC</sub> = 35.8 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –84.2. Positive ion ESI-MS: 497.0. Anal. Calcd for C<sub>56</sub>H<sub>48</sub>Cl<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> • 1/2CH<sub>3</sub>CN • C<sub>6</sub>H<sub>12</sub>: C, 64.60; H, 5.29; N, 0.60. Found: C, 64.90; H, 5.16; N, 0.64.

**Palladaphosphacyclobutene **2c**.** Mp: 270 °C (dec). IR (KBr, cm<sup>-1</sup>): 3055, 2957, 2924, 2868, 1680, 1594, 1573, 1440, 1385, 1365, 1235, 1074, 1024, 811, 764, 722, 694. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  1.33 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 12H), 1.38 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 12H), 6.87–7.29 (m, 20H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  19.5, 19.8 (d, <sup>2</sup>*J*<sub>PC</sub> = 7.2 Hz), 24.5 (d, <sup>1</sup>*J*<sub>PC</sub> = 22.2 Hz), 126.4–135.6 (m, sp<sup>2</sup> carbon). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –45.6. Positive ion ESI-MS: 401.1. Anal. Calcd for

$C_{40}H_{48}Cl_2P_2Pd_2 \cdot 1/2CH_3CN \cdot CH_2Cl_2$ : C, 51.48; H, 5.30; N, 0.71. Found: C, 51.23; H, 5.28; N, 0.48.

**Palladaphosphacyclobutene 2d.** Mp: 270 °C (dec). IR (KBr,  $cm^{-1}$ ): 3055, 2955, 2926, 2857, 1710, 1587, 1564, 1457, 1435, 1377, 1120, 1096, 1069, 1018, 811, 743, 691.  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ):  $\delta$  0.64–1.42 (m, 32H), 2.20–2.28 (m, 4H), 7.38–7.77 (m, 20H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ):  $\delta$  13.7, 14.0, 22.5, 22.8, 29.9, 30.7, 31.1, 31.2, 127.9–135.2 (m,  $sp^2$  carbon);.  $^{31}P$  NMR (81 MHz,  $CDCl_3$ , 85%  $H_3PO_4$ ):  $\delta$  -88.6. Positive ion ESI-MS: 429.0.

**3. X-ray Crystallographic Studies.** Single-crystal X-ray diffraction studies for **2a** and **2c** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were

refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.<sup>10</sup> Crystal data and processing parameters for **2a** and **2c** are summarized in Table 1.

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**Supporting Information Available:** X-ray crystallography data in CIF format for complexes **2a** and **2c**, and ORTEP plot of **2c**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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