

## Synthesis, X - Ray Crystal Structure and Reactions of Dimethyl(*N,N,N',N'*- tetramethylethanediamine)palladium<sup>#</sup>

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**Abstract:** The title compound has been synthesized and characterized by X-ray crystallography. Thermolysis in benzene at 80 °C affords a 3 : 1 mixture of methane and ethane, whereas reaction with benzyl bromide affords solely ethane and [Pd(CH<sub>2</sub>Ph)(Br)(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]; other preparatively useful reactions are described.

Dimethylbis(phosphine)palladium complexes have been the subject of many experimental<sup>1</sup> and theoretical<sup>2</sup> studies because of their relevance to the carbon-carbon bond formation step in palladium-catalyzed coupling reactions. Despite the fact that amines are quite good ligands for palladium(II)<sup>3</sup>, and that dimethyl(2,2'-bipyridine)palladium has been known for a long time<sup>4</sup>, simple organopalladium complexes with aliphatic amine ligands are almost unknown. The only pertinent literature concerns the preparation and various reactions of [Pd(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(tmeda)] (tmeda = *N,N,N',N'*-tetramethylethanediamine)<sup>5</sup> and some NMR evidence for [PdMe<sub>2</sub>(tmeda)] as an intermediate in the preparation of Li<sub>2</sub>PdMe<sub>4</sub> from [PdBr<sub>2</sub>(tmeda)] and excess methyllithium<sup>6</sup>. We now report the simple high yield synthesis and the single crystal X-ray diffraction structure of dimethyl(*N,N,N',N'*-tetramethylethanediamine)palladium **1**, which is thermally stable at room temperature and which has considerable potential in many fields of organopalladium(II) chemistry.

Treatment of [PdCl<sub>2</sub>(tmeda)] with two equivalents of methyllithium in diethyl ether at - 30 °C, followed by slow warming of the mixture to 0 °C, gave a grey suspension. After filtration, work-up of the filtrate afforded white crystals of [PdMe<sub>2</sub>(tmeda)] **1** (60-80%)<sup>13</sup>. This new compound is stable in nitrogen or dry air at room temperature, although it slowly turns yellow when exposed to the atmosphere. It dissolves well in benzene in which it has reasonable thermal stability. Crystals suitable for a crystal structure analysis<sup>16</sup> (data collection at 100 K) were grown from a benzene solution by addition of pentane.

A PLUTON diagram of the mononuclear structure found ( $R_F = 0.022$ ) is shown in Figure. Palladium is square planar coordinated by the two *cis* methyl groups and the two nitrogen atoms of chelating tmeda; the chelate ring is slightly puckered.

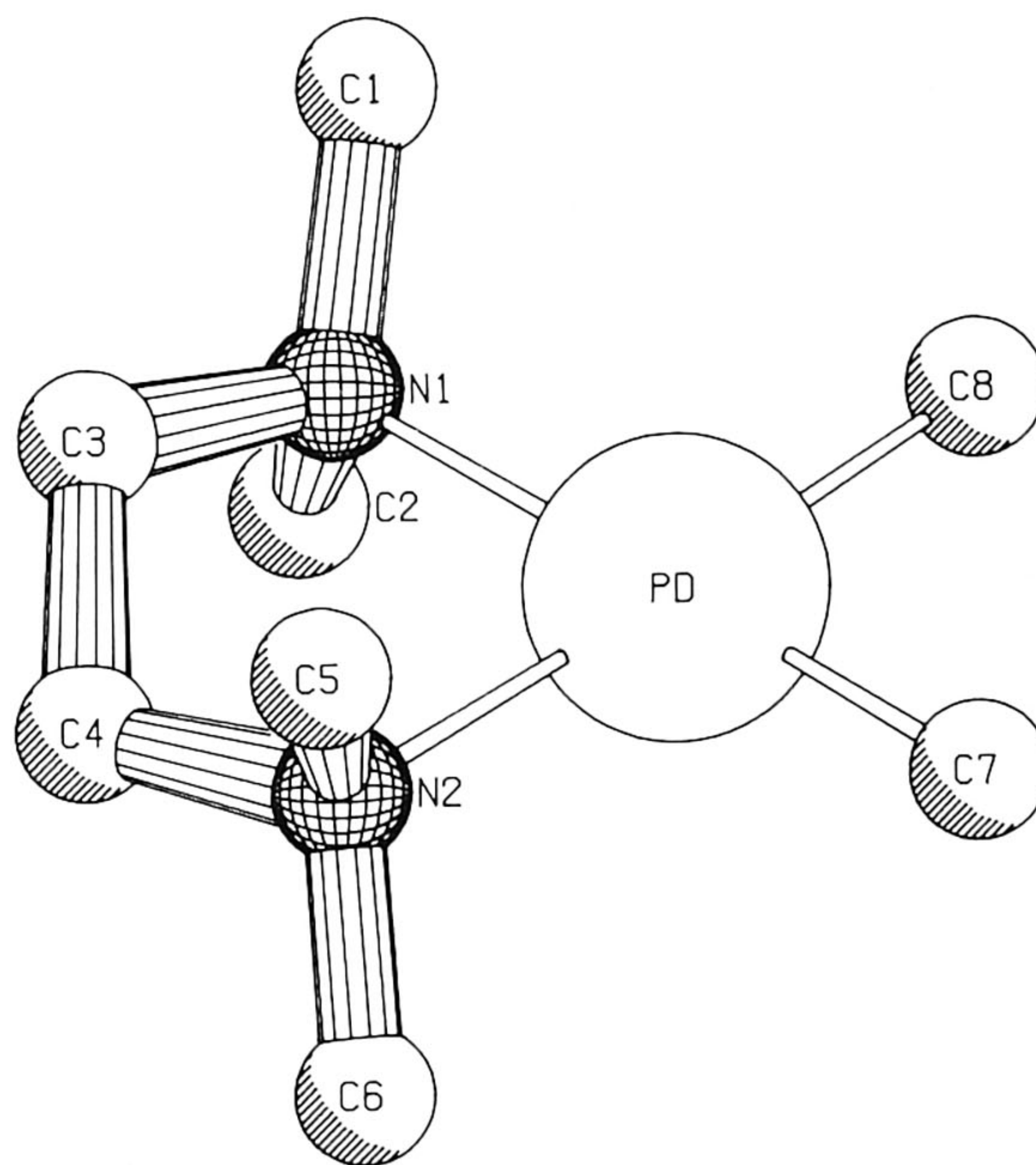


Figure : PLUTON drawing of PdMe<sub>2</sub>(tmeda) **1**. Selected bond distances (Å): Pd-N(1) 2.200(2); Pd-N(2) 2.197(2); Pd-C(7) 2.026(3); Pd-C(8) 2.029(3).

As expected, the palladium-carbon distances of 2.026(3) and 2.029(3) Å are significantly shorter than those of the related *cis*-[PdMe<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>]<sup>7</sup> (Pd-Me: 2.090(3) and 2.089(2) Å),

<sup>#</sup> Dedicated to Prof. Dr. G. J. M. van der Kerk on the occasion of his 75th birthday.



since the *trans* influence of amines is smaller than that of phosphines<sup>8</sup>. The Pd-N distances of 2.200(2) and 2.197(2) Å are very long (normal range: 1.94-2.13 Å)<sup>9</sup> and reflect the strong *trans* influence of the methyl groups.

Theoretical studies on reductive elimination reactions from PdR<sub>2</sub>L<sub>2</sub> complexes<sup>1,2</sup> suggest that the weak σ-donation from the N donor atoms in **1** should facilitate reductive elimination of R-R at lower temperatures than in the corresponding phosphine complexes. In this respect the features of the thermal decomposition of **1** are noteworthy. Heating a benzene solution of **1** at 80 °C for 5 h (70-90% conversion), did not afford the expected one equivalent of ethane<sup>1,2</sup>, but instead produced 0.85-1.0 equivalents of a 3 : 1 mixture of methane and ethane. Obviously a simple reductive elimination pathway plays but a minor role in this thermolysis. In the solid state, decomposition of **1** *in vacuo* proceeds exothermically above 120 °C, affording 1.5 to 1.6 equivalents of a 3.3 : 1 mixture of methane and ethane.

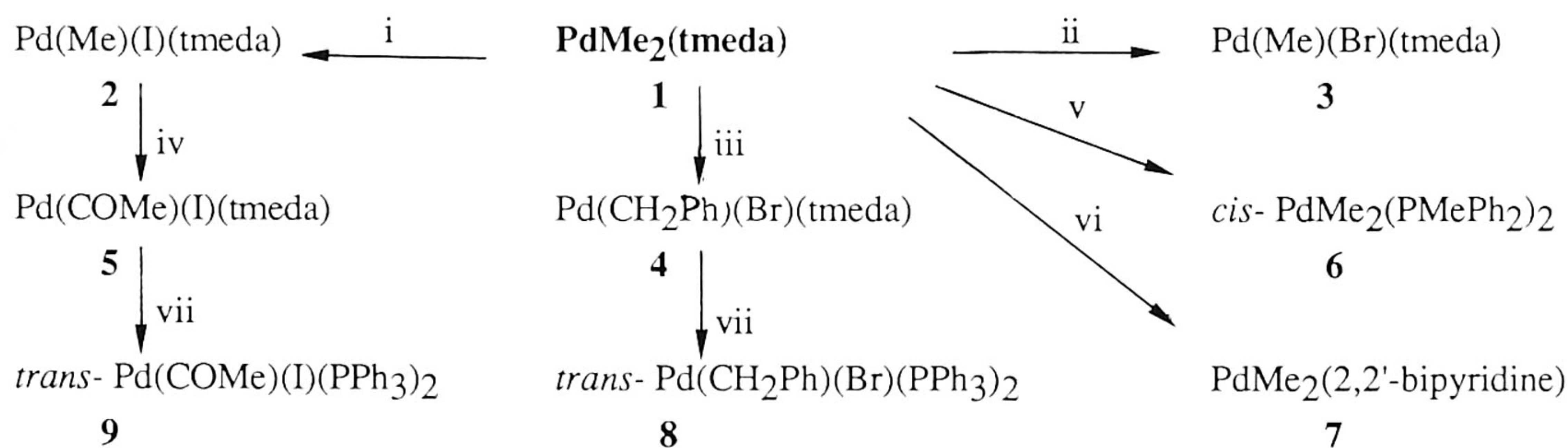
The preparative utility of [PdMe<sub>2</sub>(tmeda)] **1** in organopalladium chemistry is illustrated by the reactions shown in the Scheme. With the electrophiles MeI, MeBr, and PhCH<sub>2</sub>Br, **1** readily affords the new compounds [Pd(Me)(I)(tmeda)] **2** (90%)<sup>13</sup>, [Pd(Me)(Br)(tmeda)] **3** (85%)<sup>13</sup> and [Pd(PhCH<sub>2</sub>)(Br)(tmeda)] **4** (85%)<sup>13</sup> respectively, and, notably, one equivalent of ethane. [Pd(Me)(I)(tmeda)] reacts rapidly with CO at atmospheric pressure to give [Pd(MeCO)(I)(tmeda)] **5** (90%)<sup>13</sup>.

Moreover, a variety of other known organopalladium

complexes can be readily derived from these tmeda species since the tmeda ligand is easily replaced. For example, addition of PMePh<sub>2</sub> or 2,2'-bipyridine to PdMe<sub>2</sub>(tmeda) **1** in benzene followed by addition of pentane yielded *cis*-[PdMe<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] **6** (98%)<sup>14</sup> and [PdMe<sub>2</sub>(2,2'-bipyridine)] **7** (75%)<sup>14</sup>, respectively, and addition of PPh<sub>3</sub> to **3** and **4** in chloroform yielded *trans*-[Pd(CH<sub>2</sub>Ph)(Br)(PPh<sub>3</sub>)<sub>2</sub>] **8** (90%)<sup>14</sup> and *trans*-[Pd(COMe)(I)(PPh<sub>3</sub>)<sub>2</sub>] **9** (95%)<sup>14</sup>, respectively. These alternative high yield synthetic procedures provide products whose spectral data are in agreement with those in the literature<sup>1,10,11</sup>.

The formation of ethane and **4** from the reaction of benzyl bromide with **1** stands in contrast to the previously reported formation of ethylbenzene and *trans*-[Pd(Me)(Br)(PPh<sub>3</sub>)<sub>2</sub>] in its reaction with *cis*-[PdMe<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>12</sup>. Preliminary <sup>1</sup>H NMR results from a study of the reaction of **1** with benzyl bromide at low temperatures are consistent with the presence of a Pd(IV) species formed by *cis* oxidative addition<sup>15</sup>. This and other reactions of **1** are being studied in detail because of their relevance to the discussions concerning the role of σ-donor ligands in oxidative addition<sup>10</sup> and reductive elimination<sup>2</sup> sequences occurring at palladium centres.

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*Scheme:* i, MeI, benzene; ii, MeBr, benzene; iii, PhCH<sub>2</sub>Br, benzene; iv, CO (1 atm.), CHCl<sub>3</sub>; v, PMePh<sub>2</sub>, benzene; vi, 2,2'-bipyridine, benzene; vii, PPh<sub>3</sub>, CHCl<sub>3</sub>.

### References and footnotes

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- <sup>13</sup>Spectroscopic data for **1**: <sup>1</sup>H NMR: (200 MHz, C<sub>6</sub>H<sub>6</sub>) δ 0.46 (3H, s, PdMe), 1.70 (2H, s, NCH<sub>2</sub>), 2.05 (6H, s, NMe<sub>2</sub>). **2**: <sup>1</sup>H NMR: (80 MHz, CHCl<sub>3</sub>) δ 0.54 (s, PdMe), 2.63 (s, NMe<sub>2</sub>), 2.30-2.70 (m, NCH<sub>2</sub>). **3**: <sup>1</sup>H NMR: (80 MHz, CHCl<sub>3</sub>) δ 0.48 (s, PdMe), 2.57 (s, NMe<sub>2</sub>), 2.62 (s, N'Me<sub>2</sub>), 2.30-2.70 (m, NCH<sub>2</sub>). **4**: <sup>1</sup>H NMR: (80 MHz, CDCl<sub>3</sub>) δ 2.50 (br s, NMe<sub>2</sub> and NCH<sub>2</sub>), 3.03 (s, CH<sub>2</sub>Ph), 7.0-7.7 (m, Ph CH<sub>2</sub>). **5**: <sup>1</sup>H NMR: (80 MHz, CHCl<sub>3</sub>) δ 2.60 (s, COMe), 2.50 (s, NMe<sub>2</sub>), 2.70 (s, N'Me<sub>2</sub>).
- Analytical data: C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>Pd (252.68) **1**: calcd. C, 38.03; H, 8.78; N, 11.09; found C, 38.02; H, 8.59; N, 11.01. C<sub>7</sub>H<sub>19</sub>IN<sub>2</sub>Pd (364.55) **2**: calcd. C, 23.06; H, 5.25; N, 7.68; found C, 23.09; H, 5.14; N, 7.45. C<sub>7</sub>H<sub>19</sub>BrN<sub>2</sub>Pd (317.54) **3**: calcd. C, 26.48; H, 6.03; N, 8.82; found C, 26.40; H, 6.10; N, 8.68. C<sub>13</sub>H<sub>23</sub>BrN<sub>2</sub>Pd (393.64) **4**: calcd. C, 39.67; H, 5.89; N, 7.12; found C, 38.96; H, 5.77; N, 6.76. C<sub>8</sub>H<sub>19</sub>IN<sub>2</sub>OPd (392.67) **5**: calcd. C, 24.47; H, 4.88; N, 7.16; found C, 24.12; H, 4.83; N, 7.35.
- <sup>14</sup>Spectroscopic data: **6**: <sup>1</sup>H NMR: (80 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.90 (dd, <sup>3</sup>J(PH) 3 Hz, <sup>3</sup>J(P'H) 7 Hz; 1.36 (d, <sup>2</sup>J(PH) 5.3 Hz), 6.8-7.6 (m, Ph P). **7**: <sup>1</sup>H NMR: (200 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) δ 0.24 (s, PdMe), 7.69 (ddd, <sup>3</sup>J (4,5) 8 Hz, <sup>3</sup>J (5,6) 5 Hz, <sup>4</sup>J (3,5) 1 Hz), 8.17 (td, <sup>3</sup>J (3,4) and <sup>3</sup>J (4,5) 8 Hz, <sup>4</sup>J (4,6) 2 Hz), 8.46 (dd, <sup>3</sup>J (3,4) 8 Hz, <sup>4</sup>J (3,5) 1 Hz), 8.78 (dd, <sup>3</sup>J (5,6) 5 Hz), 8.78 (dd, <sup>4</sup>J (4,6) 1 Hz). **8**: <sup>1</sup>H NMR: (80 MHz, CDCl<sub>3</sub>) δ 2.81 (2H, s, CH<sub>2</sub>Ph), 6.5-7.3 (5H, m, Ph CH<sub>2</sub>), 7.3-7.8 (30H, m, Ph P). **9**: <sup>1</sup>H NMR: (80 MHz, CDCl<sub>3</sub>) δ 1.49 (3H, s, MeCO), 7.2-7.9 (30H, m, Ph P).
- <sup>15</sup>A 5 mm NMR tube was charged in an inert atmosphere with 25 mg of **1** dissolved in 0.5 ml of CD<sub>2</sub>Cl<sub>2</sub>. The tube was cooled to -30 °C and a fivefold excess of benzyl bromide was added. <sup>1</sup>H NMR: (200 MHz, -20 °C) δ 1.31 (3H, s, PdMe), 1.34 (3H, s, PdMe), 2.02 (3H, s, NMe), 2.21 (3H, s, NMe), 2.64 (s, NMe), 2.78 (s, NMe), 2.2-3.0 (m, -CH<sub>2</sub>N), 3.25 (1H, d, <sup>2</sup>J (AB) 6 Hz, CH HPh), 3.62 (1H, d, <sup>2</sup>J (AB) 6 Hz, CH HPh), 7.17 (3H, m, Ph CH<sub>2</sub>), 7.50 (2H, m, Ph CH<sub>2</sub>).
- <sup>16</sup>Crystal data: C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>Pd, M = 252.70, monoclinic, space group P2<sub>1</sub>/n, a = 8.518(4), b = 10.798(4), c = 12.132(5) Å, β = 99.02(4) °, U = 1102.1(8) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.523 g/cm<sup>-3</sup>, F(000) = 520. Zr-filtered MoKα radiation, λ = 0.71073 Å, μ (MoKα) = 16.2 cm<sup>-1</sup>. The structure was solved by Patterson (SHELXS86) and Fourier methods and refined by full-matrix least-squares techniques (SHELX76) to a final R<sub>F</sub> = 0.022 for 2310 reflections with I > 2.5 σ(I), (CAD4F, 100 K, ω/2θ-scan, θ < 27.5 °). Hydrogen atoms were located from a difference Fourier map and their positions and one common isotropic thermal parameter refined. The atomic co-ordinates for this work may be obtained from one of the authors (ALS).