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## Synthesis and X-ray structure of new cationic allyl complexes of palladium(II) with $\alpha$ -diimine ligands

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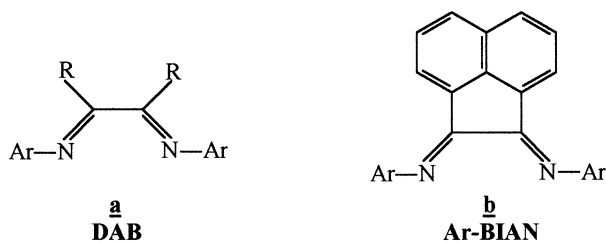
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### Abstract

The  $\alpha$ -diimine ligands Ar–N=C(R)C(R)=N–Ar react with Pd<sub>2</sub>(dba)<sub>3</sub> **1** in the presence of methylallyloxyphosphonium hexafluorophosphate [CH<sub>2</sub>=C(Me)CH<sub>2</sub>–O–P(NMe<sub>2</sub>)<sub>3</sub>]<sup>+</sup> PF<sub>6</sub><sup>–</sup> **2** to give new cationic allyl complexes of palladium with  $\alpha$ -diimine ligands **3a** and **3b**. The molecular structure for **3a** was determined by a single-crystal X-ray diffraction. © 2000 Published by Elsevier Science Ltd.

*Keywords:* palladium; cationic allyl complexes;  $\alpha$ -diimine; methylallyloxyphosphonium salt.

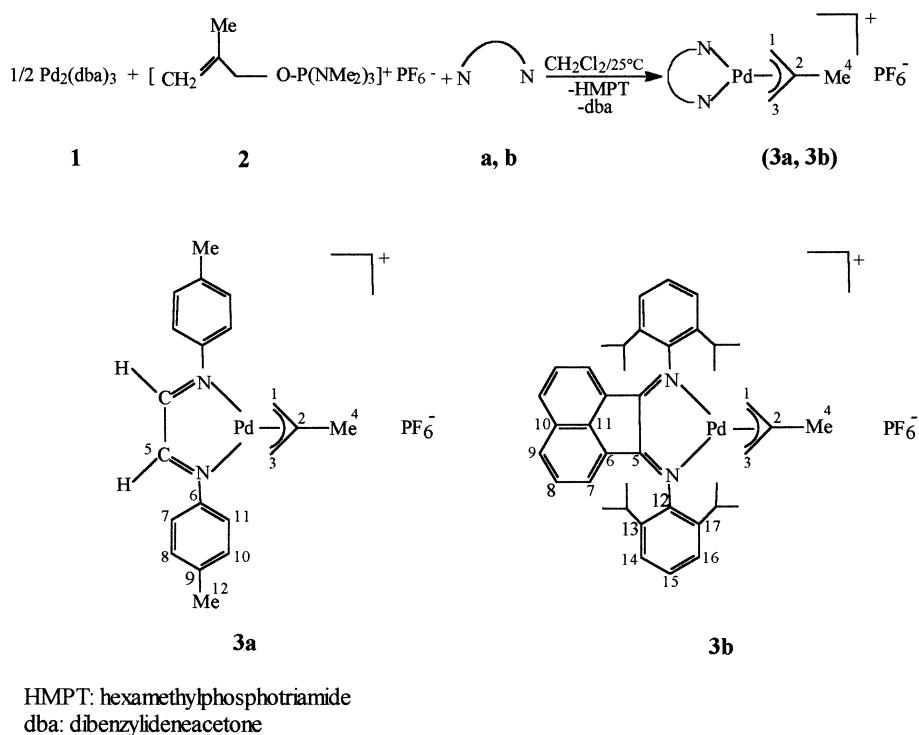
An increased interest in the chemistry of 1,4-diazabutadiene (DAB) ligands, bis(arylimino)-acenaphthene (Ar-BIAN) ligands and their complexes<sup>1–5</sup> was stimulated by the recent discovery by Brookhart and co-workers of Ni(II) and Pd(II)  $\alpha$ -olefin polymerization catalysts containing bulky  $\alpha$ -diimine ligands.<sup>6–10</sup> These catalysts show extremely high activities and allow access to high molar mass polymers whose structures vary from a highly branched, amorphous material to a linear, semicrystalline material.<sup>9</sup>



The 1,4-diazabutadiene ligands possess different possible mode of coordination as 2-, 4-, 6-, and even 8-electron donors in terminal, chelating, and bridging arrangement.<sup>11–14</sup> The variation of the steric and electronic properties of 1,4-diazabutadiene ligands is possible by changing aromatic substituent on the imine N atom.

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We report here the synthesis of new cationic allyl complexes of palladium with  $\alpha$ -diimine ligands. Indeed, the oxidative addition of methylallyloxyphosphonium hexafluorophosphate<sup>15</sup> **2** to the zerovalent compound Pd<sub>2</sub>(dba)<sub>3</sub><sup>16</sup> **1** in the presence of  $\alpha$ -diimine ligands<sup>17,18</sup> (**a,b**) led to an exclusive formation in high yields of cationic  $\eta^3$ -allyl complexes of palladium with bidentate nitrogen ligands [( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Pd(N<sup>^</sup>N)]<sup>+</sup> PF<sub>6</sub><sup>-</sup> (**3a,3b**) (Scheme 1).



Scheme 1.

The new complexes exhibit spectroscopic data in accord with the proposed structures. The <sup>1</sup>H NMR spectra of complexes **3a** and **3b** are characterized by the *syn* and *anti* allylic protons; thus, the two resonances are at 3.23 ppm (H<sub>anti</sub>); 3.67 ppm (H<sub>syn</sub>) for **3a** and at 3.23 ppm (H<sub>anti</sub>); 3.49 ppm (H<sub>syn</sub>) for **3b**. In <sup>13</sup>C NMR spectroscopy, the allylic carbons C<sub>1</sub> and C<sub>2</sub> appear at 65.4 and 63.8 ppm for **3a** and **3b**, respectively. The C=N carbon appears at 162 ppm for **3a** and 172.7 ppm for **3b**. The IR spectra of **3a** and **3b** are also instructive, since the  $\nu(\text{C}=\text{N})$  stretching frequencies (1612; 1589 cm<sup>-1</sup>) and (1654; 1625 cm<sup>-1</sup>) for **3a** and **3b**, respectively, are typical of an  $\alpha$ -diimine complex coordinated as an *s-cis* conformation.<sup>18,19</sup> The  $\nu(\text{PF}_6^-)$  value is evident (839 cm<sup>-1</sup>).

A single-crystal X-ray diffraction structure confirms the identity of complex **3a**. The ORTEP diagram of **3a** is shown in Fig. 1. The glyoxal-bis(4-methylphenyl)diimine ligand **a** was coordinated with an *s-cis* conformation as seen in Fig. 1 with Pd–N(*sp*<sup>2</sup>) bond lengths of 2.124 and 2.117 Å which are very close to those reported for other palladium–imino–nitrogen bonds.<sup>20,21</sup> The complex **3a** is a distorted square-planar complex. This distortion is illustrated by the N(1)–Pd–N(2) bond angle of 77.7(7)°. The metal–chelate ring (Pd–N1–C5–C6–N2) in complex **3a** is almost flat<sup>21</sup> as indicated by the torsion angles of –1.0(0.1), 6.0(0.1) and –4.0(0.1)° for N(1)–C(5)–C(6)–N(2), Pd–N(2)–C(6)–C(5), and Pd–N(1)–C(5)–C(6), respectively. The methyl on the allyl group is

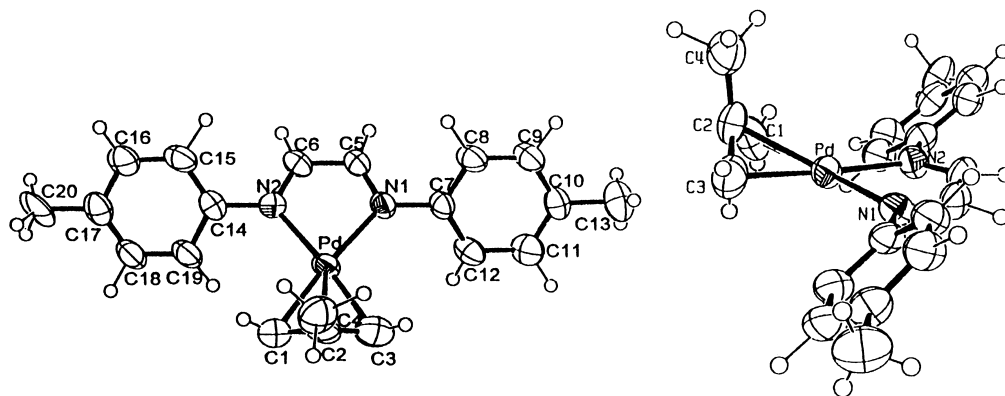


Figure 1. ORTEP diagram of **3a**. Thermal ellipsoids are at 50% probability.  $\text{PF}_6^-$  anion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd-N1 = 2.124(8), Pd-N2 = 2.117(0), Pd-C1 = 2.115(9), Pd-C2 = 2.146(7), Pd-C3 = 2.100(4), N1-C5 = 1.294(6), N1-C7 = 1.417(6), N2-C6 = 1.252(9), N2-C14 = 1.444(4), C1-C2 = 1.388(5), C2-C3 = 1.368(9), N1-Pd-N2 = 77.8(8), N1-Pd-C3 = 107.4(2), N2-Pd-C1 = 108.2(5), Pd-N1-C5 = 111.3(3), Pd-N2-C6 = 113.0(9)

slightly tilted out of the allyl plane by about  $10^\circ$  as indicated by the torsion angle of  $169.5(0.3)$  for C(4)-C(2)-C(1)-C(3). The aryl plane makes an angle of  $110.8(3)^\circ$  with the palladium coordinative plane which is normal for  $\eta^3$ -2-methylallyl complexes of palladium.<sup>21</sup> The aryl rings are tilted out of the N=C-C=N plane by about  $40^\circ$ , as indicated by torsion angles of  $41.7(0.2)$ ,  $-139.1(0.8)$ ,  $-35.3(0.1)$ , and  $145.1(0.7)^\circ$  for C(5)-N(1)-C(7)-C(8), C(5)-N(1)-C(7)-C(12), C(6)-N(2)-C(14)-C(15), C(6)-N(2)-C(14)-C(19), respectively. The  $\text{PF}_6^-$  is a regular octahedral anion.

In conclusion, the synthesis and characterization of new cationic allyl complexes of Pd with diimine ligands are described. The synthetic procedure for preparing **3a** and **3b**<sup>22–24</sup> offers great versatility for the generation of other  $\alpha$ -diimine allyl complexes of possible catalytic interest.

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22. Preparation of **3a**: To 20 ml of a CH<sub>2</sub>Cl<sub>2</sub> solution of Pd<sub>2</sub>(dba)<sub>3</sub> (113 mg, 0.12 mmol) was added 93.5 mg of salt **2** (0.24 mmol) and DAB **a** (58.3 mg, 0.24 mmol) at ambient temperature. After 24 h of stirring the mixture was filtered through a Celite filter and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (5 ml). The combined filtrates were evaporated to dryness and the product was washed with diethylether (3×10 ml) and dried in vacuo, yielding 120 mg of **3a** as an orange solid (90%). Decomposition: 230°C. IR [ $\nu$  cm<sup>-1</sup>] (KBr): 839 (PF<sub>6</sub><sup>-</sup>), 1598, 1612 (C=N). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.98 (s, 3H, H<sub>4</sub>), 2.26 (s, 6H, H<sub>12</sub>), 3.23 (s, 2H, H<sup>1</sup><sub>anti</sub>, H<sup>3</sup><sub>anti</sub>), 3.67 (s, 2H, H<sup>1</sup><sub>syn</sub>, H<sup>3</sup><sub>syn</sub>), 7.18 (s, 8H, H<sub>arom</sub>), 8.31 (s, 2H, H<sub>5</sub>). <sup>13</sup>C NMR (75.47 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  21.3 (C<sub>12</sub>), 23.5 (C<sub>4</sub>), 65.4 (C<sub>1,3</sub>), 122.7 (C<sub>7,11</sub>), 130.7 (C<sub>8,10</sub>), 136.8 (C<sub>9</sub>), 142.1 (C<sub>2</sub>), 146.9 (C<sub>6</sub>), 162.4 (C<sub>5</sub>).
23. Preparation of **3b**: The complex **3b** was obtained in 85% yield by the same procedure as a yellow-orange solid. Decomposition: 253°C. IR [ $\nu$  cm<sup>-1</sup>] (KBr): 839 (PF<sub>6</sub><sup>-</sup>), 1625, 1654 (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.06 (d, J<sub>HH</sub> = 6.66 Hz, 12H, CH<sub>3</sub>-*i*Pr), 1.44 (d, J<sub>HH</sub> = 6.93 Hz, 12H, CH<sub>3</sub>-*i*Pr), 2.16 (s, 3H, H<sub>4</sub>), 3.16 (sept, J<sub>HH</sub> = 6.66 Hz, 2H, CH-*i*Pr), 3.23 (s, 2H, H<sup>1</sup><sub>anti</sub>, H<sup>3</sup><sub>anti</sub>), 3.35 (sept, J<sub>HH</sub> = 6.93 Hz, 2H, CH-*i*Pr), 3.49 (s, 2H, H<sup>1</sup><sub>syn</sub>, H<sup>3</sup><sub>syn</sub>), 6.75 (d, J<sub>HH</sub> = 7.20 Hz, 2H, H<sub>7</sub>), 7.46 (m, 4H, H<sub>14,16</sub>), 7.53 (m, 2H, H<sub>15</sub>), 7.63 (m, 2H, H<sub>8</sub>), 8.33 (d, J = 8.19 Hz, 2H, H<sub>9</sub>). <sup>13</sup>C NMR (75.47 MHz):  $\delta$  22.9, 23.3 (CH<sub>3</sub>-*i*Pr), 23.5 (C<sub>4</sub>), 29.1, 29.4 (CH-*i*Pr), 63.8 (C<sub>1,3</sub>), 124.5 (C<sub>7</sub>), 124.7, 124.8 (C<sub>14,16</sub>), 125.6 (C<sub>15</sub>), 128.9 (C<sub>8</sub>), 129.3 (C<sub>6</sub>), 131.5 (C<sub>9</sub>), 133.7 (C<sub>10</sub>), 137.3, 137.4 (C<sub>13,17</sub>), 137.7 (C<sub>11</sub>), 143.4 (C<sub>2</sub>), 146.2 (C<sub>12</sub>), 172.7 (C<sub>5</sub>).
24. Crystallographic data for **3a**: C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>PF<sub>6</sub>Pd, *f*w = 550.8, monoclinic, *P*2<sub>1</sub>/*c* (No. 14), *Z* = 4, *a* = 8.842(3) Å, *b* = 15.157(2) Å, *c* = 16.989(3) Å,  $\beta$  = 104.80(7)°, *V* = 2201.4(0) Å<sup>3</sup>; *D*<sub>calc</sub> = 1.662 g cm<sup>-3</sup>; *R* = 0.059; *R*<sub>w</sub> = 0.063, -10 ≤ *h* ≤ 10; 0 ≤ *k* ≤ 18; 0 ≤ *l* ≤ 20; Mo ( $\lambda$  = 0.7107 Å), *T* = 296 K. Atomic coordinates and anisotropic temperature factors have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK (CCDC 141682).