

## Formation of Heterobicyclic Compounds through Successive Insertion of Isocyanides into a Palladium–Hydride Bond

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Reaction of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> **1** with an excess of H<sub>2</sub>SiMePh and 2,6-xylyl isocyanide gives

Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(C=NR)Cl·1/2C<sub>6</sub>H<sub>6</sub> (**3**, R = 2,6-xylyl) and heterobicyclic compound, 2,6-(2',6'-xylyl)<sub>2</sub>-3,7-(N-2',6'-xylylimino)<sub>2</sub>-4,8-(N-2',6'-xylylamino)<sub>2</sub>-2,6-diaza-bicyclo[3.3.0]octa-4,8-diene **4**; the structures of which have been determined by X-ray analysis.

The insertion of carbon monoxide into a metal–hydride bond to produce a metal–formyl moiety plays an extremely important role in the catalytic hydrogenation of CO.<sup>1</sup> In this connection, by the use of isocyanide which is isoelectronic with CO, some η<sup>1</sup>- and η<sup>2</sup>-formimidoyl complexes were prepared and characterized with the aim of elucidating the mechanistic aspects.<sup>2</sup> However, they were limited to single insertion products, e.g. PtCl(η<sup>1</sup>-HCNR)(PEt<sub>3</sub>)<sub>2</sub>,<sup>2a</sup> Ru(η<sup>1</sup>-HCNR)(MeCOO)(CO)(PPh<sub>3</sub>)<sub>2</sub>,<sup>2b</sup> (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>(μ-HCNR)(μ-PMe<sub>2</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>,<sup>2c</sup> Os<sub>3</sub>(μ-H)(μ-η<sup>2</sup>-HCNR)(CO)<sub>10</sub>,<sup>2d</sup> Re<sub>2</sub>(μ-H)(μ-η<sup>2</sup>-HCNR)(dppm)(CO)<sub>6</sub> [dppm = bis(diphenylphosphino)methane],<sup>2e</sup> (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(η<sup>2</sup>-HCNR),<sup>2f</sup> and [(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Y(μ-η<sup>2</sup>-HCNR)]<sub>2</sub>.<sup>2g</sup> Unlike the insertion of carbon monoxide, it is well known that isocyanide undergoes successive insertion into metal–carbon σ-bonds.<sup>3</sup> We have tried to apply the multiple insertion of isocyanide for useful organic synthesis reactions catalysed by organometallic compounds.<sup>4</sup> Here, we report the formation of novel heterobicyclic compounds *via* successive insertions of the steric bulky 2,6-xylyl isocyanide (XylNC) into a palladium–hydride bond.

Under a nitrogen atmosphere, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> **1** (0.3 mmol) was treated with an excess of H<sub>2</sub>SiMePh and XylNC in toluene at 110 °C. After 1 h, the dark-red solution was concentrated to 15 ml and addition of hexane gave a dark-red precipitate. Recrystallization of the precipitate from a benzene–hexane mixture gave red crystals formulated as PdCl(XylNC)<sub>6</sub>H·1/2-C<sub>6</sub>H<sub>6</sub> **3** in a 30% yield.† Chromatography of the mother liquor

on silica gel gave an orange compound formulated as {(XylNC)<sub>6</sub>H<sub>2</sub>} **4** [mass spectrum *m/z* 789 (M<sup>+</sup>)] in a 15% yield.‡

The IR spectrum of **3** showed the absorptions corresponding to N≡C (2192 cm<sup>-1</sup>) and C=N groups (1632, 1592 cm<sup>-1</sup>), and the <sup>1</sup>H NMR spectrum indicated the presence of six xylyl units (δ 1.71–2.53) and one formimidoyl moiety, HC=N (δ 7.52). An X-ray crystallographic analysis was carried out to clarify the structure of the complex **3** (Fig. 1).‡ The molecule **3** was derived from successive insertions of five isocyanide molecules into a palladium–hydride bond. The salient feature is a bidentate five-membered chelate structure, in which a pentamino ligand attaches to the Pd atom through the carbon atom C(1) of the α-imino group [Pd–C(1) 1.956(6) Å] and the

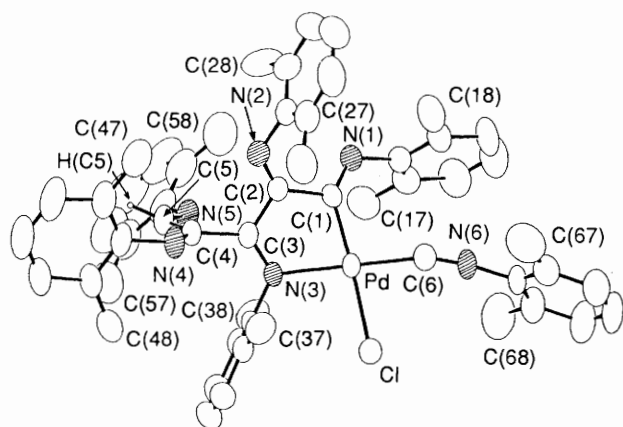


Fig. 1 A perspective drawing of the complex **3** with some selected bond distances (Å) and angles (°); Pd–Cl 2.376(2), Pd–N(3) 2.100(6), Pd–C(1) 1.956(6), Pd–C(6) 1.970(8); Cl–Pd–N(3) 96.1(1), Cl–Pd–C(1) 177.1(2), Cl–Pd–C(6) 84.1(2), N(3)–Pd–C(1) 81.3(2), N(3)–Pd–C(6) 179.7(2), C(1)–Pd–C(6) 98.6(3)

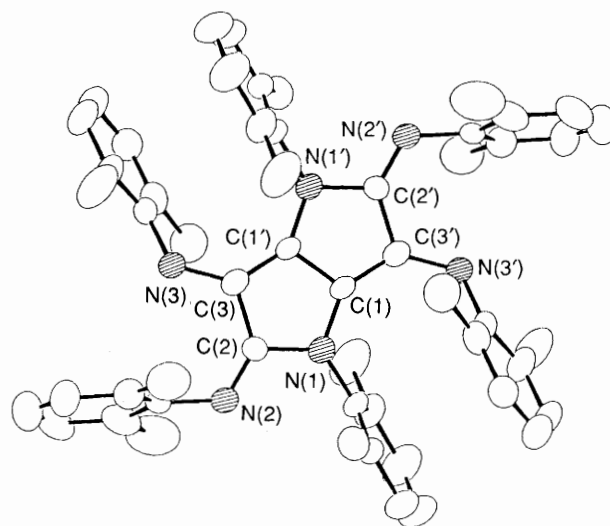
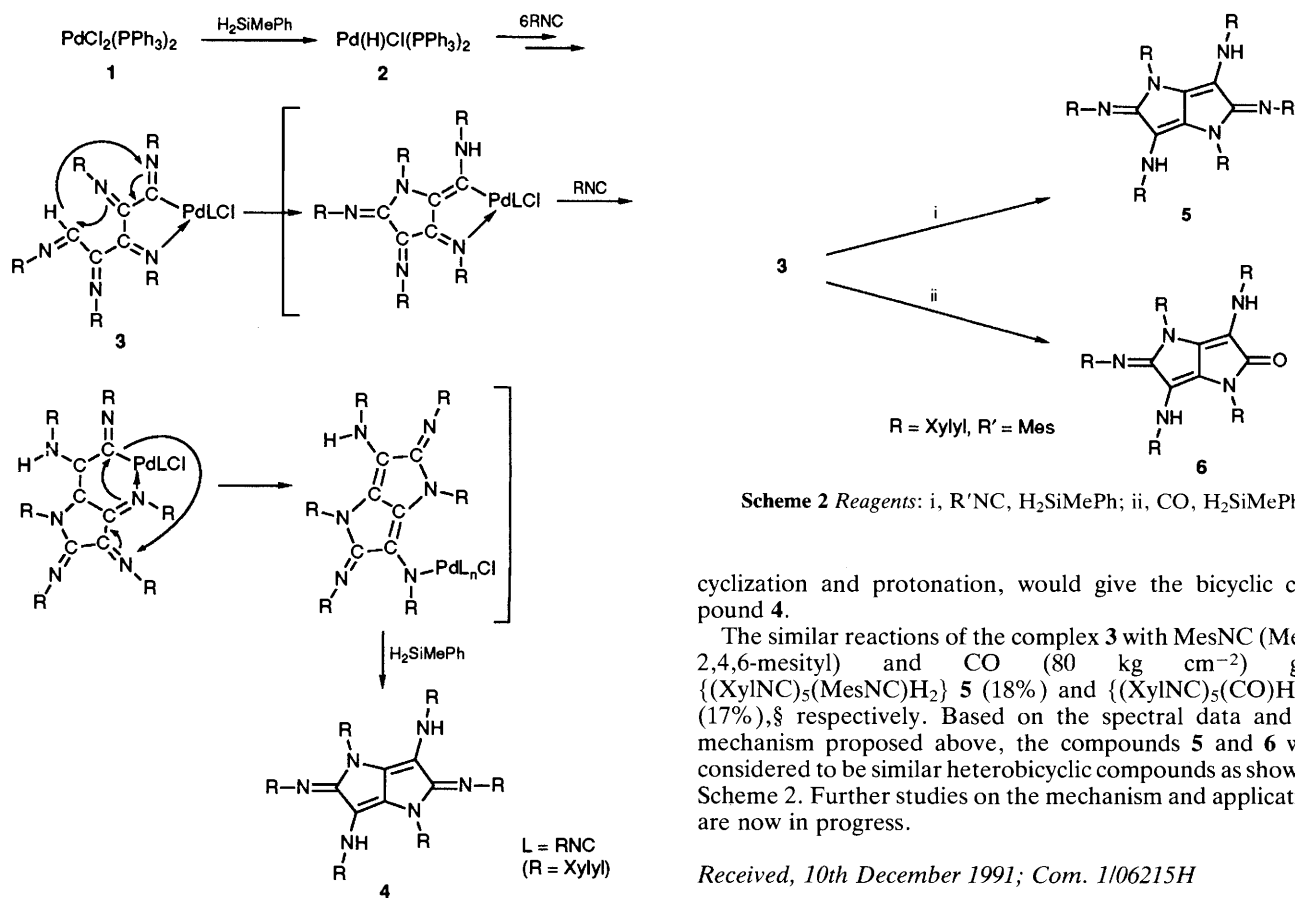


Fig. 2 A perspective drawing of the compound **4** with some selected bond distances (Å); N(1)–C(1) 1.400(7), N(1)–C(2) 1.421(7), N(2)–C(2) 1.275(8), N(3)–C(3) 1.382(8), C(1)–C(1') 1.430(7), C(2)–C(3) 1.480(8), C(1)–C(3') 1.327(8)

† Spectral data for **3**: IR(Nujol)  $\nu_{\max}$ /cm<sup>-1</sup> 2192 (N≡C), 1632, 1592 (C=N). <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 1.71 (br 12H, *o*-CH<sub>3</sub>), 1.99, 2.13, 2.17, 2.53 (s, *o*-CH<sub>3</sub>, 6H), 7.52 (s, HC=N, 1H). For **4**: IR(Nujol)  $\nu_{\max}$ /cm<sup>-1</sup> 3398 (NH) 1663, 1619, 1582 (C=C, C=N). <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 1.86, 2.15, 2.24 (s, *o*-CH<sub>3</sub>, 12H), 3.99 (s, NH, 2H). MS *m/z* 789 (M<sup>+</sup>). UV–VIS(CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ /nm 440 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 2.27 × 10<sup>5</sup>).

‡ Crystal data for **3**: C<sub>57</sub>H<sub>58</sub>N<sub>6</sub>PdCl, *M* = 969.0, triclinic, space group *P*1, *a* = 14.312(5), *b* = 15.095(7), *c* = 13.303(7) Å, α = 90.49(4), β = 97.30(3), γ = 115.59(4)°, *U* = 2565 Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.255 g cm<sup>-3</sup>, Mo-Kα radiation. The structure was solved by direct methods and refined by block-diagonal least-squares techniques to *R* = 0.067, *R<sub>w</sub>* = 0.075, using 8687 unique reflections with *F<sub>o</sub>* > 5σ(*F<sub>o</sub>*).

‡ Crystal data for **4**: C<sub>54</sub>H<sub>56</sub>N<sub>6</sub>, *M* = 789.1, monoclinic, space group *P*2<sub>1</sub>/*a*, *a* = 21.195(7), *b* = 13.237(3), *c* = 8.422(4) Å, β = 107.40(3)°, *U* = 2255 Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.163 g cm<sup>-3</sup>, Mo-Kα radiation. The structure was solved by direct methods and refined by block-diagonal least-squares techniques to *R* = 0.075, *R<sub>w</sub>* = 0.071, using 1810 unique reflections with *F<sub>o</sub>* > 3σ(*F<sub>o</sub>*). All calculations were carried out on a FACOM M-780 computer with the program system UNICS III (T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, 1979, **55**, 69). Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

Scheme 2 Reagents: i, R'NC, H<sub>2</sub>SiMePh; ii, CO, H<sub>2</sub>SiMePh

lone pair electrons of the  $\gamma$ -imino nitrogen atom [Pd-N(3) 2.100(6) Å]. The bite angle of C(1)-Pd-N(3) is 81.3(2)°. The closely related nickel complex, Ni{C(=NR)C(=NR)C(=NR)C(=NR)C(=NR)COPh}(CNR)Cl (R = Bu<sup>t</sup>), was prepared by the reaction of Ni(Bu<sup>t</sup>NC)<sub>4</sub> with PhCOCl, but was not structurally characterized.<sup>3a</sup> To our knowledge, this is the first example of the multiple insertion of isocyanide into metal-hydride bond.

By X-ray analysis, the compound **4** was confirmed to be a novel heterobicyclic compound, 2,6-di(2',6'-xylyl)-3,7-di-(N-2'-6'-xylylimino)-4,8-di(N-2',6'-xylylamino)-2,6-diaza-bicyclo[3.3.0]octa-4,8-diene, as shown in Fig. 2.† The bicyclic ring adopts a planar structure and the six xyllyl groups are nearly perpendicular to the plane so as to release the steric repulsions.

In attempts to investigate the mechanism, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> **1** was treated with H<sub>2</sub>SiMePh in the absence of XylNC to give the white powder of *trans*-Pd(H)Cl(PPh<sub>3</sub>)<sub>2</sub> **2**<sup>5</sup> in a moderate yield (54%). The hydride complex **2** underwent successive insertion of XylNC into the metal-hydride bond in refluxing benzene to give the complex **3** in a 22% yield. Further, the complex **3** reacted with XylNC in the presence of H<sub>2</sub>SiMePh at 110 °C in toluene to afford the heterobicyclic compound **4** in a 25% yield, suggesting that the complex **3** is a relatively stable intermediate in the formation of the compound **4**. In the light of these results, a plausible mechanism is depicted in Scheme 1. No intervening species between **2** and **3** was isolated, because the successive insertion of XylNC was remarkably fast. As to the steps between **3** and **4**, an initial nucleophilic attack of  $\beta$ -imino nitrogen atom to the formimidoyl carbon would lead to the first cyclization, which destabilizes the [PdCCN] five-membered chelation. Then, one more isocyanide inserted into the Pd-C bond, followed by the second

cyclization and protonation, would give the bicyclic compound **4**.

The similar reactions of the complex **3** with MesNC (Mes = 2,4,6-mesityl) and CO (80 kg cm<sup>-2</sup>) gave {(XylNC)<sub>5</sub>(MesNC)H<sub>2</sub>} **5** (18%) and {(XylNC)<sub>5</sub>(CO)H<sub>2</sub>} **6** (17%),<sup>§</sup> respectively. Based on the spectral data and the mechanism proposed above, the compounds **5** and **6** were considered to be similar heterobicyclic compounds as shown in Scheme 2. Further studies on the mechanism and applications are now in progress.

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§ Spectral data for **5**: IR (nujol)  $\nu_{\max}$ /cm<sup>-1</sup> 3405 (NH), 1677, 1628, 1610sh, 1596 (C=C, C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.85, 1.88, 2.11, 2.14, 2.23, 2.24 (s, *o*-CH<sub>3</sub>, 6H), 2.09 (s, *p*-CH<sub>3</sub>, 3H), 3.95, 4.07 (s, NH, 1H). MS *m/z* 803 (M<sup>+</sup>). UV-VIS (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ /nm 441 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 1.36 × 10<sup>5</sup>). For **6**: IR (Nujol)  $\nu_{\max}$ /cm<sup>-1</sup> 3383, 3330, (NH) 1708, 1672, 1641, 1586 (C=C, C=N, C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.88, 2.08, 2.09, 2.15, 2.21 (s, *o*-CH<sub>3</sub>, 6H), 4.43, 4.82 (s, NH, 1H). MS *m/z* 686 (M<sup>+</sup>). UV-VIS (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max}$ /nm ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 1.76 × 10<sup>5</sup>).