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Spontaneous Multiple Insertion of a Bulky Aromatic Isocyanide into the Palladium−Hydride Bond of *trans*-[Pd(H)Cl(PPh$_3$)$_2$], Leading to Formation of Heterobicyclic and Pyrrole Compounds

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The reaction of [PdCl$_2$(PPh$_3$)$_2$] (**1**) with an excess of 2,6-xylyl isocyanide (XylNC) and H$_2$SiMePh in refluxing toluene gave a mononuclear palladium complex of a polyimino ligand, [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(C≡NR)Cl]·$^1/_2$C$_6$H$_6$ (**3**·$^1/_2$C$_6$H$_6$: R = Xyl, 30%), and a novel heterobicyclic compound, 2,6-(2′,6′-xylyl)$_2$-3,7-(*N*-2′,6′-xylylimino)$_2$-4,8-(*N*-2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (**4a**, 15%), structures of which were determined by X-ray analyses. When the reaction was carried out in the presence of triethylamine, the yield of **4a** increased up to 44%. The complex **3** involves a pentaimino moiety [−C(=NR){C(=NR)}$_3$CH(=NR)] derived from a successive insertion of isocyanide into the palladium−hydride bond of *trans*-[Pd(H)Cl(PPh$_3$)$_2$] (**2**), which was generated from the reaction of **1** and H$_2$SiMePh in *situ*. The pentaimino ligand attaches to the metal through the carbon atom of the α-imino group and the lone pair electron of the γ-imino nitrogen atom, resulting in a five-membered chelate ring. The reaction of **3** with XylNC in the presence of H$_2$SiMePh afforded the heterobicyclic compound **4a**. Similar treatments of **3** with 2,4,6-mesityl isocyanide (MesNC) and carbon monoxide (~80 kg cm^{-2}) in the presence of H$_2$SiMePh gave 2,6-(2′,6′-xylyl)$_2$-3-(2′,4′,6′-mesitylimino)-7-(2′,6′-xylylimino)-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (**5**) and 2,6-(2′,6′-xylyl)$_2$-7-(2′,6′-xylylimino)-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-dien-3-one (**6**), respectively. The structure of **6** was confirmed by X-ray crystallography. When complex **3** was treated with HC≡CPh, a pyrrole compound, 1-(2′,6′-xylylamino)-2-phenyl-4-R′-pyrrole (R′ = C(=NR){C(=NR)}$_2$CH(=NR), R = Xyl) (**7**), was obtained. The structure of **7**·C$_6$H$_6$ was confirmed by X-ray crystallography. Possible mechanisms for **4**−**7** were proposed.

Introduction

Insertion reactions of carbon monoxide are of fundamental importance in organometallic chemistry and play a key role in many homogeneous catalytic reactions promoted by transition metal complexes.[1−3] Since isocyanide has an isoelectronic structure with carbon monoxide, its insertion reaction into metal−carbon bonds has been extensively studied.[4−7] Unlike carbon monoxide, isocyanide readily undergoes multiple insertion into various metal−carbon σ-bonds, providing useful synthetic routes to nitrogen-containing organic compounds.[4−6] Recently, the insertion reactions of isocyanide into metal−hydride bonds to produce η^1- and η^2-formimidoyl complexes have also been reported, with the aim of elucidating the mechanistic aspects of the catalytic hydrogenation of CO.[3] Isolated examples were, however, limited to single insertion products such as [PtCl(η^1-HCNR)(PEt$_3$)$_2$],[8−10] [Ru(η^1-HCNR)(CH$_3$COO)(CO)(PPh$_3$)$_2$],[11] [(η-C$_5$H$_5$)$_2$Co$_2$(μ-HCNR)(μ-PMe$_2$)$_2$](PF$_6$) (C$_5$H$_5$ = cyclopentadienyl),[12] [Os$_3$(μ-H)(μ-η^2-HCNR)(CO)$_{10}$],[13] [Re$_2$(μ-H)(μ-η^2-HCNR)(dppm)(CO)$_6$] (dppm = 1,2-bis(diphenylphosphino)methane),[14] [(η-C$_5$Me$_5$)$_2$Zr(H)(η^2-HCNR)] (C$_5$Me$_5$ = pentamethylcyclopentadienyl),[15] and [(η-C$_5$H$_5$)$_2$Y(μ-η^2-HCNR)]$_2$.[16] Notably, the multiple insertion reaction of isocyanide into a metal−hydride bond has not been reported thus far.

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We have studied insertion reactions of isocyanides into various transition metal−carbon bonds, where the metals are Pt,[17] Pd,[18] Ni,[19] Co,[20] Fe,[21] and Mo,[22] with a hope of establishing efficient synthetic routes to polyimino and/or nitrogen-containing compounds. Treatments of Pd complexes of azobenzene with isocyanides led to formation of 3-imino-2-phenylindazolines,[18c] and those of [$PdCl_2$(isocyanide)$_2$] with phenyl-substituted cyclopentadienyl groups, ketenimine compounds.[23] The reactions of Co_2(isocyanide)$_8$ with aromatic azo compounds, malonic esters, and cyanoacetate gave the corresponding indazoline and indazole derivatives[20d] and cyclic polyimino compounds,[20f] and those with carbon polyhalides, benzyl bromide, and 2-bromo acetophenone afforded indolenine, tetraiminohexane, and diiminofuran derivatives, respectively.[20c,g−i] The reaction of diphenylacetylene complex, [CpCo(PhC_2Ph)PPh_3], with RNC gave triiminodiphenylcyclopentene.[20b] Recently, we have reported a spontaneous multiple insertion of bulky aromatic isocyanides, 2,6-xylyl (Xyl) and 2,4,6-mesityl (Mes) isocyanides, into the palladium−carbon σ-bond of [Pd(CH_3)I(PPh_3)$_2$], leading to a triple insertion product of [Pd{C(=NR)C(=NR)C(=NR)CH_3}(RNC)I] (R = Xyl or Mes).[18e] The spontaneous feature of bulky aromatic isocyanides is interestingly contrasted with aliphatic, *tert*-butyl, and cyclohexyl isocyanides which underwent stepwise insertion.[18b] We wish to describe, in this report, the formation of novel heterobicyclic and pyrrole compounds *via* spontaneous multiple insertion of the sterically bulky isocyanides into a palladium−hydride bond. A preliminary account of this work has already appeared.[24]

Experimental Section

Toluene, benzene, and hexane were distilled over calcium hydride and tetrahydrofuran and diethyl ether over lithium aluminum hydride prior to use. Other reagents were of the best commercial grade and were used as received. Isocyanides,[25] [$PdCl_2(PPh_3)_2$] (**1**),[26] and *trans*-[Pd(H)Cl(PPh_3)$_2$] (**2**)[27] were prepared by the known methods. Complex **2** could also be prepared by the procedure described below. All reactions were carried out under a nitrogen atmosphere with standard Schlenk and vacuum line techniques.

Measurements. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GX-400 instrument at 400 and 100 MHz, respectively. Chemical shifts were calibrated to tetramethylsilane as an external reference. Infrared and electronic absorption spectra were recorded with Jasco A-100 and Ubest-30 spectrometers, respectively. Mass spectra were measured on a Hitachi M-80 spectrometer. High-resolution mass spectroscopy was carried out on a JEOL DX300 spectrometer. HPLC analysis was performed with a TSK-CCPM system (TOSO Co. Ltd.) using an ODS-80TM reversed phase column (5 mm i.d. × 100 mm) and a Model UV-8011 UV−vis detector. Methanol was used as an eluent. Fractionation of organic compounds was carried out on the same HPLC system using a large ODS column (20 mm i.d. × 300 mm).

Preparation of *trans*-[Pd(H)Cl(PPh_3)$_2$] (2). A 50 mL benzene suspension containing [$PdCl_2(PPh_3)_2$] (**1**) (200 mg, 0.285 mmol) and $H_2SiMePh$ (350 mg, 2.86 mmol) was incubated at 70−80 °C for 1 h. The resultant red solution was concentrated to ca. 10 mL, and an addition of hexane afforded the off-white powder of *trans*-[Pd(H)Cl(PPh_3)$_2$] (**2**) in 54% yield (103 mg). The spectroscopic data [IR (Nujol): ν(Pd−H) 2060^{sh}, 2055 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −13.2 (br, Pd−H)] were in accord with reported ones.[27]

Preparation of [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(C≡NR)Cl]·$^1/_2C_6H_6$ (3·$^1/_2C_6H_6$) (R = Xyl). A mixture of [$PdCl_2(PPh_3)_2$] (**1**) (500 mg, 0.712 mmol), XylNC (930 mg, 7.12 mmol), and $H_2SiMePh$ (870 mg, 7.12 mmol) was refluxed in 50 mL of toluene for 1 h. The dark red reaction mixture was concentrated to ca. 10 mL. Hexane (5 mL) was added to the solution to give a dark red precipitate. Recrystallization of the precipitate from a benzene/hexane mixed solvent afforded red prismatic crystals of [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(C≡NR)Cl]·$^1/_2C_6H_6$ (**3**·$^1/_2C_6H_6$) (R = Xyl) (210 mg, 30% based on Pd). The mother liquor was used to isolate an organic compound. Anal. Calcd for $C_{57}H_{58}N_6PdCl$: C, 70.65; H, 6.03; N, 8.67. Found: C, 70.42; H, 5.91; N, 8.65. ^{1}H NMR ($CDCl_3$): δ 1.71 (br, 12H, *o*-Me), 1.99, 2.13, 2.17, 2.53 (s, 4 × 6H, *o*-Me), 6.3−7.1 (m, 18H, Ar), 7.52 (s, 1H, HC=N). ^{13}C NMR ($CDCl_3$): δ 18.03, 18.52, 18.68, 18.72, 19.52 (q, *o*-Me), 153.87 (d, CH=NR), 160.40, 168.44, 172.36, 173.60 (s, N≡C, C=N). IR (Nujol): ν(N≡C) 2192 s, ν(C=N) 1632, 1592 cm^{-1}. UV−vis (in benzene): λ_{max} (ϵ) 319 nm (1.2 × 10^4 M^{-1} cm^{-1}).

Preparation of 2,6-(2′,6′-Xylyl)$_2$-3,7-(2′,6′-xylylimino)$_2$-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (4a). Method A. The mother liquor described above was chromatographed on a silica gel column (10 mm i.d. × 120 mm) eluted with a benzene/hexane (1:4) mixed solvent. The yellow fraction was collected, concentrated to ca. 1 mL, and kept at −25 °C. Yellow crystals of 2,6-(2′,6′-xylyl)$_2$-3,7-(2′,6′-xylylimino)$_2$-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (**4a**) were obtained in 15% yield *versus* Pd (84 mg). ^{1}H NMR ($CDCl_3$): δ 1.86, 2.15, 2.24 (s, 3 × 12H, *o*-Me), 3.99 (s, 2H, NH), 6.6−6.9 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$): δ 18.58, 18.91 (q, *o*-Me), 127.20, 129.39 (s, C=C), 135.10 (s, C=N). IR (Nujol): ν(NH) 3398, ν(C=N, C=C) 1663, 1619, 1582 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (ϵ) 440 nm (2.27 × 10^5 M^{-1} cm^{-1}). MS: *m/z* 789 (M$^+$). High-resolution MS: Found 788.4530 (M$^+$), calcd 788.4494.

Method B. Complex **3** (100 mg, 0.103 mmol), XylNC (95 mg, 0.721 mmol), and $H_2SiMePh$ (164 mg, 1.34 mmol) were dissolved in 20 mL of toluene, and the solution was incubated at 110 °C for 2 h. The resultant solution was concentrated and passed through a short silica gel column (10 mm i.d. × 30 mm). The organic components were analyzed by HPLC. The yield of **4a** was 25% based on Pd.

Method C. A mixture of [$PdCl_2(PPh_3)_2$] (**1**) (27 mg, 0.038 mmol), XylNC (50 mg, 0.38 mmol), $H_2SiMePh$ (46 mg, 0.28 mmol), and triethylamine (193 mg, 1.91 mmol) was heated at 110 °C in toluene for 1 h. The reaction mixture was concen-

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trated and passed through a short silica gel column (10 mm i.d. × 30 mm). The organic components were analyzed by HPLC. The yield of **4a** was 44% based on Pd. Some other Pd complexes, amines, and silane derivatives were examined instead of complex **1**, triethylamine, and $H_2SiMePh$, respectively.

Reaction of *trans*-[Pd(H)Cl(PPh$_3$)$_2$] (2) with XylNC. A 20 mL benzene solution containing XylNC (394 mg, 3.00 mmol) was added dropwise to a benzene solution of *trans*-[Pd(H)Cl(PPh$_3$)$_2$] (**2**) (200 mg, 0.300 mmol) at −10 °C. The mixture was slowly warmed to room temperature and then refluxed in benzene for 1 h. The resultant dark red solution was concentrated to ca. 10 mL, and addition of hexane gave a pale yellow powder of [PdCl$_2$(XylNC)(PPh$_3$)] (79 mg, 46%), which was filtered off. Hexane (5 mL) was added to the filtrate to yield red crystals of **3** (64 mg, 22%). The mother liquor was chromatographed on silica gel as described in method A to give a small amount of **4a** (5 mg, 2%).

Preparation of 2,6-(2′,6′-Mesityl)$_2$-3,7-(2′,6′-mesitylimino)$_2$-4,8-(2′,6′-mesitylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (4b). A mixture of [PdCl$_2$(PPh$_3$)$_2$] (**1**) (250 mg, 0.356 mmol), MesNC (515 mg, 3.56 mmol), and $H_2SiMePh$ (435 mg, 7.12 mmol) was refluxed in toluene for 1 h. The resultant solution was chromatographed on a silica gel column (10 mm i.d. × 120 mm) eluted with a benzene/hexane (1:4) mixed solvent. The yellow fraction was collected, concentrated to ca. 1 mL, and kept at −25 °C. Yellow crystals of 2,6-(2′,6′-mesityl)$_2$-3,7-(2′,6′-mesitylimino)$_2$-4,8-(2′,6′-mesitylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (**4b**) were obtained in 22% yield *vs* Pd (68 mg). ^{1}H NMR (CDCl$_3$): δ 1.82, 2.09, 2.12, 2.17 (s, 4 × 12H, *o*,*p*-Me), 2.07 (s, 6H, *p*-Me), 4.01 (s, 2H, NH), 6.39, 6.48, 6.64 (s, 3 × 4H, Ar). IR (Nujol): ν(NH) 3380, ν(C=N, C=C) 1658, 1609, 1575 cm^{-1}. UV−vis (CH$_2$Cl$_2$): λ_{max} (ϵ) 439 nm (1.33 × 10^5 M^{-1} cm^{-1}). MS: *m*/*z* 873 (M$^+$). High-resolution MS: Found 872.5589 (M$^+$), calcd 872.5505.

Preparation of 2,6-(2′,6′-Xylyl)$_2$-3-(2′,4′,6′-mesitylimino)-7-(2′,6′-xylylimino)-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (5). Complex **3** (100 mg, 0.103 mmol), MesNC (105 mg, 0.721 mmol), and $H_2SiMePh$ (164 mg, 1.34 mmol) were dissolved in 20 mL of toluene, and the solution was heated at 110 °C for 2 h. The reaction mixture was passed through a silica gel short column (10 mm i.d. × 30 mm), and compound **5** contained in the benzene eluate was purified by HPLC. The fraction of **5** was collected and recrystallized from hexane to afford yellow crystals (15 mg, 18% vs Pd). ^{1}H NMR (CDCl$_3$): δ 1.85, 1.86, 2.11, 2.14, 2.23, 2.24 (s, 6 × 6H, *o*-Me), 2.09 (s, 3H, *p*-Me), 3.95, 4.07 (s, 2 × 1H, NH), 6.6−6.9 (m, 17H, Ar). IR (Nujol): ν(NH) 3405, ν(C=N, C=C) 1677, 1628, 1610^{sh}, 1596 cm^{-1}. UV−vis (CH$_2$Cl$_2$): λ_{max} (ϵ) 441 nm (1.36 × 10^5 M^{-1} cm^{-1}). MS: *m*/*z* 803 (M$^+$). High-resolution MS: Found 802.4632 (M$^+$), calcd 802.4723.

Preparation of 2,6-(2′,6′-Xylyl)$_2$-7-(2′,6′-xylylimino)-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-dien-3-one (6). Complex **3** (100 mg, 0.103 mmol) and $H_2SiMePh$ (183 mg, 1.34 mmol) were heated in toluene at 130 °C for 24 h under a pressure of carbon monoxide (~80 kg cm^{-2}). The reaction mixture was passed through a silica gel short column (10 mm i.d. × 30 mm), and compound **6** contained in the benzene eluate was purified by HPLC. The fraction of **6** was collected and recrystallized from hexane to afford yellow crystals (12 mg, 17% vs Pd). ^{1}H NMR (CDCl$_3$): δ 1.88, 2.08, 2.09, 2.15, 2.21 (s, 5 × 6H, *o*-Me), 4.43, 4.82 (s, 2 × 1H, NH), 6.6−6.9 (m, 15H, Ar). IR (Nujol): ν(NH) 3383, 3330, ν(C=N, C=C, C=O) 1708, 1672, 1641, 1586 cm^{-1}. UV−vis (CH$_2$Cl$_2$): λ_{max} (ϵ) 421 nm (1.76 × 10^5 M^{-1} cm^{-1}). MS: *m*/*z* 686 (M$^+$). High-resolution MS: Found 685.3749 (M$^+$), calcd 685.3717.

Preparation of 1-(2′,6′-Xylylamino)-2-phenyl-4-R′-*N*′-xylylpyrole (R′ = −C(=NXyl){C(=NXyl)}$_2$CH(=NXyl)) (7). Complex **3** (100 mg, 0.103 mmol) and phenylacetylene (105 mg, 1.03 mmol) were dissolved in 20 mL of toluene, and the solution was incubated at 110 °C for 2 h. The reaction mixture was passed through a silica gel short column (10 mm i.d. × 30 mm), and the benzene eluate was concentrated to dryness. The residue was crystallized from hexane to afford orange crystals of **7** (20 mg, 22% vs Pd). Anal. Calcd for $C_{62}H_{62}N_8$: C, 83.56; H, 7.01; N, 9.43. Found: C, 83.19; H, 7.00; N, 9.33. ^{1}H NMR (CDCl$_3$): δ 1.42, 1.64, 1.89, 1.99, 2.05, 2.30 (s, 6 × 6H, *o*-Me), 4.91 (s, 1H, NH), 6.7−7.2 (m, 23H, Ar). IR (Nujol): ν(NH) 3348, ν(C=N, C=C) 1609, 1591, 1505 cm^{-1}. UV−vis (CH$_2$Cl$_2$): λ_{max} (ϵ) 360 (1.67 × 10^4), 320 nm (1.47 × 10^4 M^{-1} cm^{-1}). MS: *m*/*z* 891 (M$^+$).

Crystal Data and Intensity Measurements for 3·$^1/_2$C$_6$H$_6$, 4a, 6, and 7·C$_6$H$_6$. X-ray-quality crystals of **3**·$^1/_2$C$_6$H$_6$, **4a**, **6**, and **7**·C$_6$H$_6$ were obtained by recrystallizations from benzene/hexane mixed solvents. Crystal data and experimental conditions are summarized in Table 1.

Structure Solution and Refinement. The structure of **3** was solved by direct methods with MULTAN78.[28] The coordinates of all hydrogen atoms were determined by difference Fourier syntheses. The structure was refined with the block-diagonal least-square techniques minimizing $\sum w(|F_o| - |F_c|)^2$. Final refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms converged to $R = 0.067$ and $R_w = 0.078$ ($w = 1$). The structure of **4a** was solved and refined by methods similar to those described above to $R = 0.075$ and $R_w = 0.071$ ($w = 1$). The structures of **6** and **7**·C$_6$H$_6$ were solved by direct methods with MITHRIL.[29] The coordinates of all hydrogen atoms were calculated at the ideal positions, taking the C−H distance as being 0.95 Å, and were not refined. Final full-matrix least-squares refinement with isotropic thermal parameters for non-hydrogen atoms converged to $R = 0.093$ and $R_w = 0.066$ ($w = 1/\sigma^2(F_o)$) for **6**, and that with anisotropic temperature factors for the N(1)−N(6) and C(1)−C(8) atoms and isotropic ones for the other non-hydrogen atoms, to $R = 0.077$ and $R_w = 0.083$ ($w = 1/\sigma^2(F_o)$) for **7**·C$_6$H$_6$.

Atomic scattering factors and values of f' and f'' for Pd, Cl, O, N, and C were taken from the literatures.[30] All calculations for **3** and **4a** were carried out on a FACOM M-780 computer with the program system UNICS III,[31] and those for **6** and **7**, on a Digital VAX Station 3100 with the TEXSAN Program System.[32] The perspective views were drawn by using the programs ORTEP[33] and PLUTO.[34] Compilation of final atomic parameters for all non-hydrogen atoms is supplied as Supporting Information.

Results and Discussion

Preparations of [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(CNR)Cl]·$^1/_2$C$_6$H$_6$ (3·$^1/_2$C$_6$H$_6$) and 2,6-(1-Xylyl)$_2$-3,7-(1-xylylimino)$_2$-4,8-(*N*-1-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (4a). Complex [PdCl$_2$(PPh$_3$)$_2$] (**1**) was treated with excess amounts of $H_2SiMePh$ and XylNC in toluene at 110 °C for 1 h. The resultant dark red solution was concentrated, and an addition of hexane gave a dark red precipitate. Recrystallization of the precipitate from a benzene−hexane mixed solvent gave red crystals formulated as [PdCl(XylNC)$_6$H]·$^1/_2$C$_6$H$_6$ (**3**·$^1/_2$C$_6$H$_6$) in 30% yield. By chromatography of the filtrate on silica gel, a yellow organic compound formulated as [(XylNC)$_6$H$_2$] (**4a**) was obtained in 15% yield based on Pd. Both compounds **3** and **4a** were not obtained in the absence of $H_2SiMePh$,

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Table 1. Crystallographic and Experimental Data for $3\cdot{}^1/_2C_6H_6$, 4a, 6, and $7\cdot C_6H_6$

	compound			
	3$\cdot{}^1/_2C_6H_6$	**4a**	**6**	**7**$\cdot C_6H_6$
formula	$C_{57}H_{58}N_6PdCl$	$C_{54}H_{56}N_6$	$C_{46}H_{47}N_5$	$C_{68}H_{68}N_6$
fw	969.00	789.08	685.91	969.33
cryst size, mm	0.48 × 0.38 × 0.20	0.40 × 0.20 × 0.14	0.45 × 0.23 × 0.13	0.60 × 0.40 × 0.50
cryst system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	14.312(5)	21.195(7)	12.804(3)	11.688(2)
b, Å	15.095(7)	13.237(3)	18.214(6)	21.611(4)
c, Å	13.303(7)	8.422(4)	8.301(2)	11.222(3)
α, deg	90.49(4)		91.67(3)	94.39(2)
β, deg	97.30(3)	107.40(3)	98.36(2)	94.83(2)
γ, deg	115.59(4)		94.08(2)	97.12(2)
V, Å^3	2565	2255	1909	2792
Z	2	2	2	2
T, °C	23	23	23	23
machine	CAD4	AFC4	AFC5S	AFC5S
D_{calcd}, g cm^{-1}	1.255	1.163	1.193	1.153
abs coeff, cm^{-1}	4.49	0.64	0.67	1.07
abs corr	analytical method	none	none	ψ-scan method
scan method	ω ($2\theta < 30°$), $\omega-2\theta$ ($30 < 2\theta < 55°$)	ω ($2\theta < 30°$), $\omega-2\theta$ ($30 < 2\theta < 50°$)	$\omega-2\theta$	$\omega-2\theta$
2θ max, deg	55	50	45	45
no. of unique data	9739	2203	3598	4872
no. of obsd data	8687 ($I > 2.5\sigma(I)$)	1810 ($I > 1.5\sigma(I)$)	849 ($I > 3\sigma(I)$)	2005 ($I > 3\sigma(I)$)
solution	direct methods, MULTAN78	direct methods, MULTAN78	direct methods, MITHRIL	direct methods, MITHRIL
no. of variables	807	384	209	367
data/param ratio	10.76	4.71	4.06	5.46
R^a	0.067	0.075	0.093	0.077
$R_w{}^a$	0.075	0.071	0.066	0.083
ρ_{max}, e Å^{-3}	1.45 (around Pd)	0.31	0.35	0.29

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

nor by using $SiMe_2Ph_2$ instead of $H_2SiMePh$. The IR spectrum of **3** showed the absorptions corresponding to N≡C (2192 cm^{-1}) and C═N groups (1632, 1592 cm^{-1}). The IR spectral pattern was comparable to that of [Pd{C(═NR)C(═NR)C(═NR)CH$_3$}(RNC)I] (**8**) (R = Xyl), which involves a terminal isocyanide and a triimino moiety derived from the multiple insertion of isocyanide into a Pd−C σ-bond.[18e] The ^{1}H NMR spectrum indicated the presence of six xylyl units at δ 1.71, 1.99, 2.13, 2.17, and 2.53 with a 2:1:1:1:1 intensity ratio and one formimidoyl residue (HC═N) at δ 7.52. The resonance at δ 1.99 was assigned to a terminal isocyanide because it showed a ligand exchange with free XylNC. The ^{13}C NMR spectrum of **3** also exhibited six methyl signals at δ 18.03−19.52 and one doublet peak for the formimidoyl carbon at δ 153.87. A mononuclear palladium with a terminal isocyanide, a chloride anion, and a polyimino ligand, formed by multiple insertion of five isocyanide molecules into a Pd−H bond, was inferred for a structure of **3** in the light of spectroscopic and analytical data. An X-ray analysis of **3** confirmed the proposed structure (*vide infra*).

When [PdCl$_2$(PPh$_3$)$_2$] (**1**) was treated with an excess amount of $H_2SiMePh$ in the absence of XylNC, the palladium hydride complex, *trans*-[Pd(H)Cl(PPh$_3$)$_2$] (**2**), was obtained in 54% yield. This procedure is more convenient compared with the known method by using the reaction of zerovalent palladium complex, [Pd(PPh$_3$)$_4$] or [Pd(PPh$_3$)$_2$(CO)], with HCl (32%).[27] The hydride complex **2** was transformed to **3** in 22% yield by treatment with an excess of XylNC in refluxing toluene.

The mass spectrum indicated that the organic compound **4a** was a co-oligomerization product of six isocyanide molecules and two hydrogen atoms which were seemingly derived from $H_2SiMePh$. In the ^{1}H NMR spectrum of **4a**, only three singlets assignable to the *o*-methyl groups of xylyl units were observed at δ 1.86, 2.15, and 2.24 together with that to the amino protons at δ 3.99, suggesting that the molecule **4a** has a symmetrical structure. The IR spectrum showed the presence of amino groups at 3398 cm^{-1} (NH) and C═C and C═N groups at 1663, 1619, and 1582 cm^{-1}. By an X-ray analysis, compound **4a** was revealed to be a novel heterobicyclic compound, 2,6-(1-xylyl)$_2$-3,7-(1-xylylimino)$_2$-4,8-(*N*-1-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (*vide infra*). Compound **4a** was also prepared by the reaction of complex **3** with excess XylNC and $H_2SiMePh$ in 25% yield. The yield of the bicyclic compound **4a** increased up to 44% (vs Pd) by an addition of Et_3N (Table 2, no. 1), though complex **3** was not obtained at all. Other tertiary amines (nPr$_3$N, nBu$_3$N, and Me$_2$PhN) and pyridine were also effective (18−39%), but secondary and primary amines, Et$_2$NH and nPr$_2$NH, suppressed the formation of **4a** (0−5%) due to complicated side reactions. $H_2SiMePh$ could be replaced by HSiMe$_2$Ph and H$_2$SiPh$_2$ in 31−34% yields, whereas H$_3$SiPh, SiMe$_2$Ph$_2$, and (SiMe$_2$Ph)$_2$ were not effective. The palladium complexes containing aliphatic tertiary phosphines, [PdCl$_2$(PCy$_3$)$_2$], [PdCl$_2$(PMe$_3$)$_2$], and [PdCl$_2$(PnBu$_3$)$_2$], showed almost no activity for the formation of **4a**, and the use of [PdCl$_2$(PMe$_2$Ph)$_2$] and [PdCl$_2$(PMePh$_2$)$_2$] resulted in low yields. These results tentatively suggested that dissociation of phosphine ligands is an important step for the formation of **4a**. The chelating diphosphine complex, [PdCl$_2$(dppe)], did not have the activity, because it does not accommodate the *trans*-[Pd(H)Cl**P**$_2$] geometry. The analogous heterobicyclic compound, 2,6-(1-mesityl)$_2$-3,7-(1-mesitylimino)$_2$-4,8-(*N*-1-mesitylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (**4b**), was prepared by the reaction of [PdCl$_2$(PPh$_3$)$_2$] with MesNC and $H_2SiMePh$ in 22% yield.

Table 2. Formation of 4a from the Reaction of [PdCl$_2$P$_2$] with XylNC and Silanes in the Presence of Amines[a]

no.	**P** ligand	silane	amine	yield of **4a**, %[b]
1	PPh$_3$	H$_2$SiMePh	Et$_3$N	44
2	PPh$_3$	H$_2$SiMePh	pyridine	39
3	PPh$_3$	H$_2$SiMePh	Me$_2$PhN	29
4	PPh$_3$	H$_2$SiMePh	*n*Pr$_3$N	22
5	PPh$_3$	H$_2$SiMePh	*i*Bu$_3$N	18
6	PPh$_3$	H$_2$SiMePh	Et$_2$NH	5
7	PPh$_3$	H$_2$SiMePh	*n*Pr$_2$NH	5
8	PPh$_3$	H$_2$SiMePh	Ph$_3$N	trace
9	PPh$_3$	H$_2$SiMePh	none	15
10	PMe$_3$	H$_2$SiMePh	Et$_3$N	3
11	PMe$_2$Ph	H$_2$SiMePh	Et$_3$N	7
12	PMePh$_2$	H$_2$SiMePh	Et$_3$N	20
13	P*n*Bu$_3$	H$_2$SiMePh	Et$_3$N	trace
14	PCy$_3$	H$_2$SiMePh	Et$_3$N	trace
15	dppe[c]	H$_2$SiMePh	Et$_3$N	0
16	no complex	H$_2$SiMePh	Et$_3$N	0
17	PPh$_3$	H$_2$SiPh$_2$	Et$_3$N	34
18	PPh$_3$	HSiMe$_2$Ph	Et$_3$N	31
19	PPh$_3$	H$_3$SiPh	Et$_3$N	trace
20	PPh$_3$	SiMe$_2$Ph$_2$	Et$_3$N	0
21	PPh$_3$	(SiMe$_2$Ph)$_2$	Et$_3$N	0
22	PPh$_3$	none	Et$_3$N	0

[a] A mixture of [PdCl$_2$**P**$_2$] (0.038 mmol) and XylNC (0.38 mmol) was incubated at 110 °C in toluene for 1 h in the presence of silane (0.28 mmol) and amine (1.9 mmol). [b] Determined by HPLC. [c] **P**$_2$ = dppe (1,2-bis(diphenylphosphino)ethane).

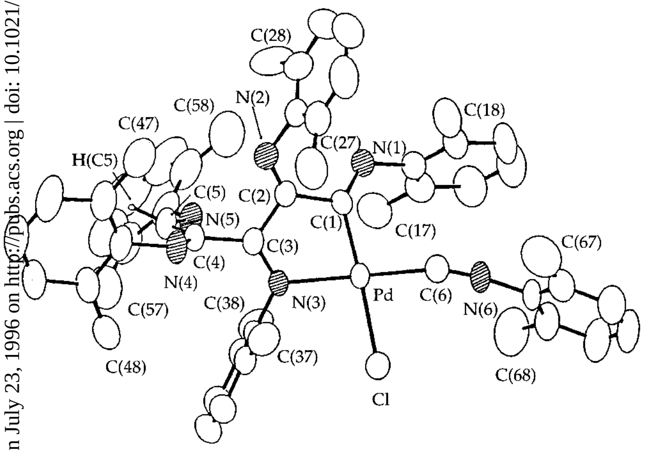
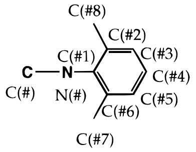


Figure 1. ORTEP plot of [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(C≡NR)Cl] (**3**, R = Xyl). Thermal ellipsoids are drawn at the 40% probability level, and aromatic hydrogen atoms are omitted for clarity.

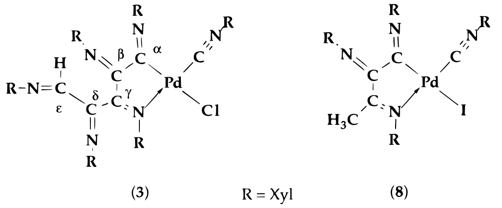
Table 3. Selected Bond Distances (Å) and Angles (deg) for 3[a]

	Distances		
Pd−Cl	2.376(2)	Pd−N(3)	2.100(6)
Pd−C(1)	1.956(6)	Pd−C(6)	1.970(8)
N(1)−C(1)	1.271(8)	N(1)−C(11)	1.437(11)
N(2)−C(2)	1.252(9)	N(2)−C(21)	1.438(7)
N(3)−C(3)	1.260(9)	N(3)−C(31)	1.435(7)
N(4)−C(4)	1.274(9)	N(4)−C(41)	1.452(12)
N(5)−C(5)	1.272(9)	N(5)−C(51)	1.417(9)
N(6)−C(6)	1.133(12)	N(6)−C(61)	1.409(12)
C(1)−C(2)	1.547(11)	C(2)−C(3)	1.482(8)
C(3)−C(4)	1.522(11)	C(4)−C(5)	1.455(9)
C(5)−H(C5)	0.97(8)		
	Angles		
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)
C(1)−N(1)−C(11)	122.0(6)	C(2)−N(2)−C(21)	124.3(7)
Pd−N(3)−C(3)	115.3(4)	Pd−N(3)−C(31)	121.2(5)
C(3)−N(3)−C(31)	123.4(6)	C(4)−N(4)−C(41)	120.7(6)
C(5)−N(5)−C(51)	122.2(8)	C(6)−N(6)−C(61)	171.8(6)
Pd−C(1)−N(1)	134.9(6)	Pd−C(1)−C(2)	109.3(4)
N(1)−C(1)−C(2)	115.3(6)	N(2)−C(2)−C(1)	129.8(5)
N(2)−C(2)−C(3)	118.9(7)	C(1)−C(2)−C(3)	110.9(5)
N(3)−C(3)−C(2)	116.2(7)	N(3)−C(3)−C(4)	124.6(5)
C(2)−C(3)−C(4)	118.9(6)	N(4)−C(4)−C(3)	116.6(6)
N(4)−C(4)−C(5)	128.1(7)	C(3)−C(4)−C(5)	115.4(6)
N(5)−C(5)−C(4)	118.2(7)	N(5)−C(5)−H(C5)	120(4)
C(4)−C(5)−H(C5)	119(3)	Pd−C(6)−N(6)	163.8(6)

[a] Estimated standard deviations are given in parentheses. See Figure 1 for atom labels. In this report, a systematic atomic numbering is used for xylyl units shown as follows:



Structure of [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(CNR)Cl]·$^1/_2$C$_6$H$_6$ (3·$^1/_2$C$_6$H$_6$). An X-ray crystallographic analysis was carried out to clarify the structure of complex **3**. The unit cell contains two discrete molecules of complex **3** and one lattice benzene without the unusual contacts between them. A perspective drawing of complex **3** with the atomic numbering scheme is given in Figure 1, and some selected bond distances and angles are listed in Table 3. The palladium atom is coordinated by a chlorine atom (Pd(1)−Cl(1) = 2.376(2) Å), a terminal XylNC (Pd(1)−C(6) = 1.970(8) Å), and a bidentate polyimino ligand in a square planar geometry. The polyimino moiety consists of four xylylimino groups and a terminal formimidoyl unit (C(5)−H(1) = 0.97(8) Å) and coordinates to the Pd atom through the carbon atom of α-imino group (Pd−C(1) = 1.956(6) Å) and the lone pair electrons of the γ-imino nitrogen atom (Pd−N(3) = 2.100(6) Å), forming a five-membered chelate ring (C(1)−Pd−N(3) = 81.3(2)°). The chelate ring is no longer planar, taking a gauche conformation with the C(1) and C(2) atoms significantly deviated from the best plane. The C(1) and N(3) atoms occupy the coordination sites *trans* to the chlorine and the terminal carbon atom of isocyanide, respectively. The α- and β-imino groups are twisted with a torsional angle of 43° (N(1)−C(1)−C(2)−N(2)). A similar coordination geometry with five-membered chelation of a polyimino moiety was also found in complex **8**[18e] and [Ni{C(=NR)C(=NR)C(=NR)CH$_3$}(RNC)Cl] (**9**, R = *t*Bu).[35] The σ-bond distance between the palladium and the imino carbon atoms in **3** is shorter than the corresponding value (2.03(2) Å) of **8**, ascribable to the smaller *trans* effect of Cl$^-$ compared to I$^-$. The γ-imino and ε-formimidoyl units are coplanar to each other (torsion angle N(4)−C(4)−C(5)−N(5) = 175°) and are nearly perpendicular to the five-membered chelate ring (torsion angle N(3)−C(3)−C(4)−N(4) = 81°), probably to avoid steric repulsions. The closely related nickel complex involving a pentaimino moiety, [Ni{C(=NR)C(=NR)C(=NR)C(=NR)C(=NR)COPh}-



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[35] Carmona, E.; Marin, J. M.; Palma, P.; Poveda, M. L. *J. Organomet. Chem.* **1989**, *377*, 157.

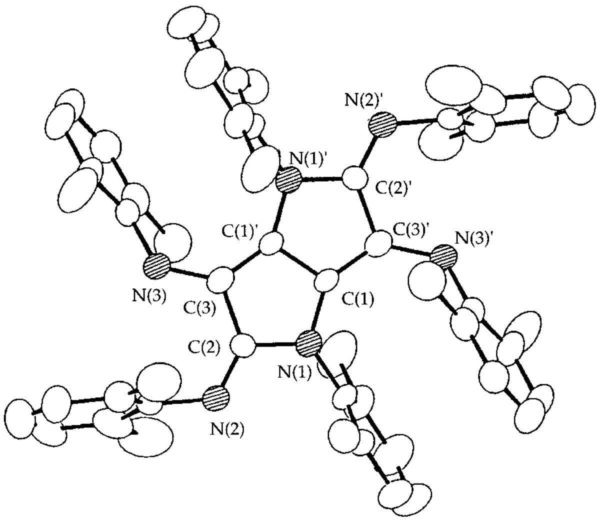
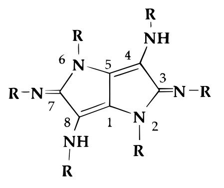


Figure 2. ORTEP view of 2,6-(2′,6′-xylyl)$_2$-3,7-(N-2′,6′-xylylimino)$_2$-4,8-(N-2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]-octa-4,8-diene (**4a**). Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

(CNR)Cl] (R= tBu), has been prepared by the reaction of Ni(^{t}BuNC)$_4$ with PhCOCl but has not been structurally characterized.[36,37] The molecular structure indicated that complex **3** was derived from insertion of an isocyanide molecule into a metal−hydride bond followed by successive insertion of four isocyanides into a Pd−C bond. To our knowledge, this is the first example of the multiple insertion of isocyanide into metal−hydride bonds.

Structure of 2,6-(1-xylyl)$_2$-3,7-(1-xylylimino)$_2$-4,8-(N-1-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]octa-4,8-diene (4a). A perspective drawing of compound **4a** with the atomic numbering scheme is given in Figure 2, and some selected bond lengths and angles are listed in Table 4. The molecule has a crystallographically imposed inversion center at the middle of the C(1)−C(1)′ bond. The molecule comprises a planar [3.3.0] bicyclic ring with two five-membered rings, each involving a cyclic amino nitrogen atom (N(1)), an ene−amine unit (C(1)′−C(3) = 1.327(8) Å, C(3)−N(3) = 1.382(8) Å), and an imino group (C(2)−N(2) = 1.275(8) Å). The bond length between the two ring-junction carbons (C(1) and C(1)′) is 1.430(7) Å. While the C(1)′−C(3) and C(2)−N(2) bond distances correspond to typical values for C=C and C=N double bonds, the other in-ring C−C and C−N bonds show somewhat shorter values than those for typical single bonds. These indicated that the π-electrons in the rings are delocalized to some extent, which is consistent with the upfield shift of C=N carbon resonance (δ 135.10) in the ^{13}C NMR spectrum. The six xylyl groups are nearly perpendicular to the ring plane so as to release the steric repulsions.



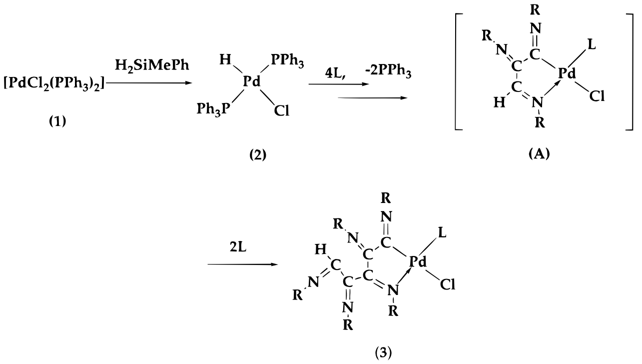
(**4a**) R = Xyl

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for 4a[a]

Distances			
N(1)−C(1)	1.400(7)	N(1)−C(2)	1.421(7)
N(1)−C(11)	1.443(6)	N(2)−C(2)	1.275(8)
N(2)−C(21)	1.416(8)	N(3)−C(3)	1.382(8)
N(3)−C(31)	1.418(9)	C(2)−C(3)	1.480(8)
C(1)−C(1)′	1.430(7)	C(1)−C(3)′	1.327(8)
N(3)−H(N3)	0.98(7)		
Angles			
C(1)−N(1)−C(2)	107.6(4)	C(1)−N(1)−C(11)	126.4(5)
C(2)−N(1)−C(11)	121.7(5)	C(2)−N(2)−C(21)	122.2(5)
C(3)−N(3)−C(31)	125.0(6)	N(1)−C(2)−N(2)	119.0(5)
N(2)−C(2)−C(3)	107.6(5)	N(3)−C(3)−C(2)	121.6(5)

[a] Estimated standard deviations are given in parentheses. See Figure 2 for atom labels.

Scheme 1[a]



[a] L = RNC, R = Xyl.

Reactions of Complex 3 with Mesityl Isocyanide and Carbon Monoxide. The reaction of complex **3** with excess MesNC in the presence of H$_2$SiMePh gave a compound formulated as {(XylNC)$_5$(MesNC)H$_2$} (**5**, 18%) from a mass spectrum, with trace amounts of **4a**,**b** (2−3%). The formation of **4a**,**b** implied decomposition reactions of **3** including de-iminoacylation, and regeneration of Pd−H species took place as side reactions, which may be responsible for the low yield of desired compound. The IR spectrum of **5** showed the presence of amino groups at 3405 cm^{-1} (NH) and C=C and C=N groups at 1677, 1628, 1610^{sh}, and 1596 cm^{-1}. In the ^{1}H NMR spectrum, seven methyl signals were observed at δ 1.85, 1.86, 2.09, 2.11, 2.14, 2.23, and 2.24 with an intensity ratio of 2:2:1:2:2:2:2 and two resonances for amino protons at δ 3.95 and 4.07, consistent with the asymmetric heterobicyclic structure as shown in Scheme 2. A similar reaction of **3** with CO (~80 kg cm^{-2}) also afforded compound **6** formulated as {(XylNC)$_5$(CO)H$_2$} in 17% yield. The IR spectrum showed absorptions due to amino (3383, 3330 cm^{-1}) and C=C, C=N (1672, 1641, 1586 cm^{-1}), and C=O (1708 cm^{-1}) groups. The ^{1}H NMR spectrum exhibited five resonances for methyl groups of xylyl units at δ 1.88, 2.08, 2.09, 2.15, and 2.21 and two peaks for amino groups at δ 4.43 and 4.82. The UV−vis spectrum is similar to those of **4a**,**b**. The structure of **6** was confirmed by X-ray crystallography to have a heterobicyclic structure similar to **4a**. A perspective drawing is illustrated in Figure 3, and some selected bond angles and distances are listed in Table 5. One of the imino groups in **4a** is replaced by a carbonyl group in **6**. The C(6)−O(1) bond distance of 1.20(1) Å is in the normal range for C=O double bonds.

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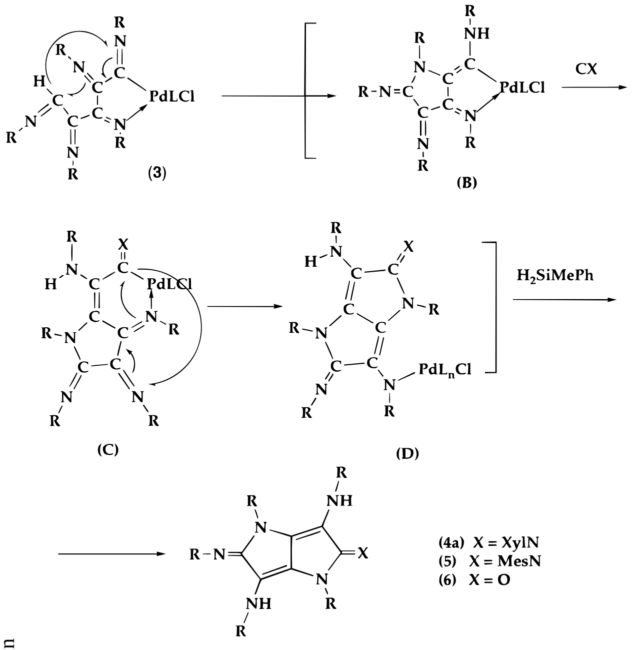
(37) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180.

Scheme 2[a]



[a] L = RNC, R = Xyl.

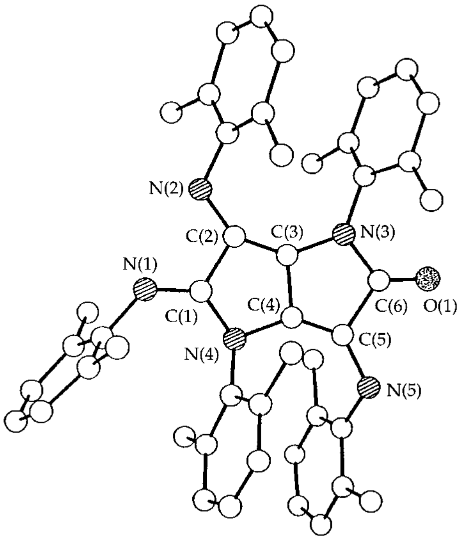


Figure 3. PLUTO diagram of 2,6-(2′,6′-xylyl)$_2$-7-(2′,6′-xylylimino)-4,8-(2′,6′-xylylamino)$_2$-2,6-diazabicyclo[3.3.0]-octa-4,8-dien-3-one (**6**). Hydrogen atoms are omitted for clarity.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for 6[a]

Distances			
O(1)−C(6)	1.20(3)	N(1)−C(1)	1.29(3)
N(1)−C(11)	1.44(2)	N(2)−C(2)	1.35(2)
N(2)−C(21)	1.44(3)	N(3)−C(3)	1.43(3)
N(3)−C(6)	1.39(3)	N(3)−C(31)	1.48(2)
N(4)−C(1)	1.41(2)	N(4)−C(4)	1.41(2)
N(4)−C(41)	1.44(2)	N(5)−C(5)	1.38(2)
N(5)−C(51)	1.41(2)	C(1)−C(2)	1.49(3)
C(2)−C(3)	1.34(3)	C(3)−C(4)	1.45(2)
C(4)−C(5)	1.35(3)	C(5)−C(6)	1.53(3)
Angles			
C(1)−N(1)−C(11)	129(2)	C(2)−N(2)−C(21)	121(2)
C(3)−N(3)−C(6)	109(2)	C(3)−N(3)−C(31)	129(2)
C(6)−N(3)−C(31)	122(2)	C(1)−N(4)−C(4)	107(2)
C(1)−N(4)−C(41)	117(2)	C(4)−N(4)−C(41)	117(2)
C(5)−N(5)−C(51)	121(2)	N(1)−C(1)−N(4)	130(2)
N(1)−C(1)−C(2)	120(2)	N(4)−C(1)−C(2)	109(2)
N(2)−C(2)−C(1)	113(2)	N(2)−C(2)−C(3)	143(3)
C(1)−C(2)−C(3)	104(2)	N(3)−C(3)−C(2)	141(3)
N(3)−C(3)−C(4)	105(2)	C(2)−C(3)−C(4)	113(2)
N(4)−C(4)−C(3)	106(2)	N(4)−C(4)−C(5)	140(2)
C(3)−C(4)−C(5)	114(2)	N(5)−C(5)−C(4)	136(3)
N(5)−C(5)−C(6)	120(3)	C(4)−C(5)−C(6)	104(2)
O(1)−C(6)−N(3)	128(3)	O(1)−C(6)−C(5)	123(3)
N(3)−C(6)−C(5)	108(3)		

[a] Estimated standard deviations are given in parentheses. See Figure 3 for atom labels.

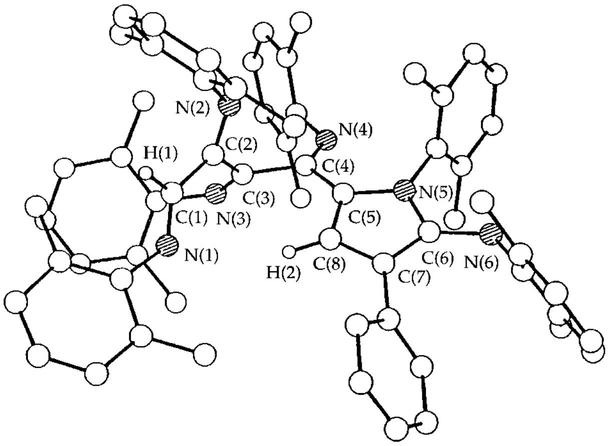
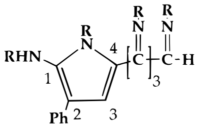


Figure 4. PLUTO view of 1-(2′,6′-xylylamino)-2-phenyl-4-R′-pyrole (R′ = C(=NR){C(=NR)}$_2$CH(=NR), R = Xyl)) (**7**). Aromatic hydrogen atoms are omitted for clarity.



(7) R = Xyl

Reaction of Complex 3 with Phenyl Acetylene. When complex **3** was treated with an excess amount of phenylacetylene in refluxing toluene, a red organic compound, formulated as $\{(XylNC)_6(PhC_2H)H_2\}$ (**7**) from the elemental analysis and the mass spectrum, was obtained in 22% yield. The UV−vis spectral pattern of **7** is quite different (λ_{max} 360, 320 nm) from those of the heterobicyclic compounds **4**−**6** (λ_{max} 420−440 nm). The IR spectrum indicated the presence of NH group at 3348 cm^{-1} and C=N and C=C groups at 1609, 1591, and 1505 cm^{-1}. In the ^{1}H NMR spectrum, six singlets assignable to the *o*-methyl groups of xylyl units were observed at δ 1.42, 1.64, 1.89, 1.99, 2.05, and 2.30 with the same intensity and one singlet assignable to an amino proton was observed at δ 4.91; however, resonances for olefinic and formimidoyl protons were not assigned owing to overlap with aromatic signals. Compound **7**·C_6H_6 was revealed by X-ray crystallography to be a pyrrole derivative, 1-(2′,6′-xylylamino)-2-phenyl-4-R′-*N*′-xylyl-pyrole (R′ = −C(=NXyl){C(=NXyl)}$_2$CH(=NXyl), as shown in Figure 4. Some selected bond distances and angles are summarized in Table 6. The pyrrole ring has xylyl, xylylamino, phenyl, and polyimino substituents. The polyimino side chain contained three internal imino and a terminal formimidoyl moieties connected by C−C single bonds; the average distances of C−N double and C−C single bonds are 1.26 and 1.49 Å, respectively. The C=NR groups in the side chain alternatively twisted around the C−C single bonds; the torsion angles are N(1)−C(1)−C(2)−N(2) = −161°, N(2)−C(2)−C(3)−N(3) = −133°, and N(3)−C(3)−C(4)−N(4) = 51°.

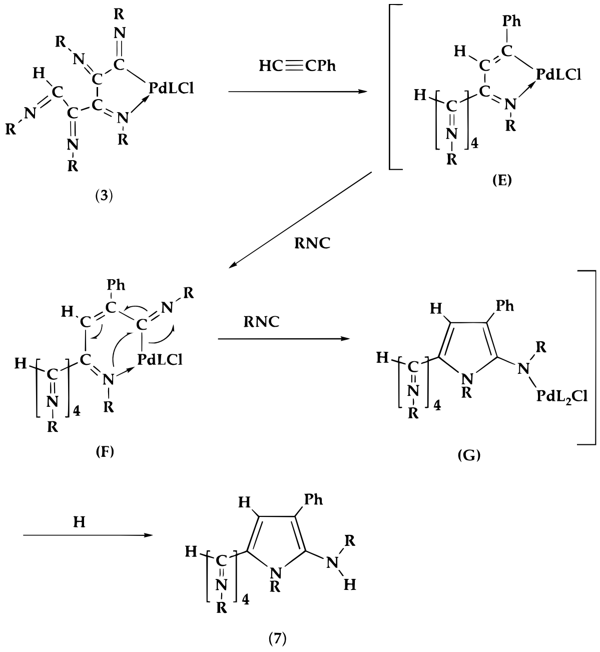
Table 6. Selected Interatomic Distances (Å) and Angles (deg) for 7[a]

Distances			
N(1)−C(1)	1.23(2)	N(1)−C(11)	1.43(2)
N(2)−C(2)	1.28(2)	N(2)−C(21)	1.45(2)
N(3)−C(3)	1.27(1)	N(3)−C(31)	1.44(2)
N(4)−C(4)	1.26(1)	N(4)−C(41)	1.42(2)
N(5)−C(5)	1.41(1)	N(5)−C(6)	1.37(1)
N(5)−C(51)	1.44(2)	N(6)−C(6)	1.39(2)
N(6)−C(61)	1.45(2)	C(1)−C(2)	1.49(2)
C(2)−C(3)	1.54(2)	C(3)−C(4)	1.50(2)
C(4)−C(5)	1.44(2)	C(5)−C(8)	1.39(2)
C(6)−C(7)	1.39(2)	C(7)−C(8)	1.41(2)
Angles			
C(1)−N(1)−C(11)	119(1)	C(2)−N(2)−C(21)	121(1)
C(3)−N(3)−C(31)	127(1)	C(4)−N(4)−C(41)	127(1)
C(5)−N(5)−C(51)	125(1)	C(5)−N(5)−C(6)	110(1)
C(6)−N(5)−C(51)	124(1)	C(6)−N(6)−C(61)	121(1)
N(1)−C(1)−C(2)	124(1)	N(2)−C(2)−C(1)	122(1)
N(2)−C(2)−C(3)	115(1)	C(1)−C(2)−C(3)	123(1)
N(3)−C(3)−C(2)	124(1)	N(3)−C(3)−C(4)	118(1)
C(2)−C(3)−C(4)	118(1)	N(4)−C(4)−C(3)	124(1)
N(4)−C(4)−C(5)	120(1)	C(3)−C(4)−C(5)	116(1)
N(5)−C(5)−C(4)	125(1)	N(5)−C(5)−C(8)	105(1)
C(4)−C(5)−C(8)	128(1)	N(5)−C(6)−N(6)	118(1)
N(5)−C(6)−C(7)	108(1)	N(6)−C(6)−C(7)	134(1)
C(6)−C(7)−C(8)	107(1)	C(6)−C(7)−C(71)	129(1)
C(8)−C(7)−C(71)	126(1)	C(5)−C(8)−C(7)	110(1)

[a] Estimated standard deviations are given in parentheses. See Figure 4 for atom labels.

Mechanism. One of the possible mechanisms for formation of the heterobicyclic compound **4a** is depicted in Schemes 1 and 2. The hydride complex, *trans*-[Pd(H)Cl(PPh$_3$)$_2$] (**2**), was assumed to be an incipient species in the reaction of **1** with XylNC and H$_2$SiMePh, on the basis of the fact that [PdCl$_2$(PPh$_3$)$_2$] (**1**) was readily transformed to **2** by treatment with H$_2$SiMePh. Complex **2** underwent multiple insertion of five isocyanide molecules into the Pd−H bond to afford the stable complex **3**. While no intervening species between **2** and **3** was isolated in the present system, the reaction may proceed through a successive fashion; a single insertion of isocyanide generates the η^1-formimidoyl compound, which is further converted to double- and triple-inserted compounds. The linear triimino species is stabilized by forming a five-membered chelation of the triimino part to afford complex A. A complex with a similar structure has been obtained from the reaction of PdI(CH$_3$)(PPh$_3$)$_2$ with XylNC.[18e] Complex A undergoes further insertion of two XylNC molecules into the Pd−C bond under vigorous conditions (reflux in toluene), leading to the formation of complex **3**. The successive insertion of bulky XylNC was remarkably fast; reaction of **2** with 4 equiv of XylNC gave only complex **3** without isolation of (A). Further, the reaction of **3** with XylNC in the presence of H$_2$SiMePh afforded the heterobicyclic compound **4a** (21% yield), suggesting that complex **3** is one of the precursors of **4a**. As to the steps between **3** and **4a**, we speculated a plausible mechanism as shown in Scheme 2. A nucleophilic attack of β-imino nitrogen atom on the formimidoyl carbon in **3** leads to the first cyclization, giving a Pd-containing [5.5]-membered bicyclic compound B. The strained metalla-bicyclic structure might destabilize the [PdCCCN] five-membered chelation and enhance the reactivity of the Pd−C σ-bond. One more isocyanide is, then, inserted into the Pd−C bond, resulting in a formation of [5.6]-membered metalla-bicyclic complex C. The second cyclization takes place by a nucleophilic attack of the δ imino nitrogen atom on the α imino carbon atom, followed by an abstraction of hydrogten atom, to give the bicyclic compound **4a**. The positions of the carbonyl and the mesityl groups in **5** and **6** are consistent with this mechanism.

Scheme 3[a]



[a] L = RNC, R = Xyl.

A plausible mechanism for **7** is depicted in Scheme 3. One phenylacetylene molecule is inserted into the Pd−C σ-bond of **3** to give (E), which is followed by insertion of an isocyanide molecule F. A nucleophilic attack of the coordinated imino nitrogen atom onto the α-imino carbon atom leads to a cyclization to form the pyrrole ring G, and an abstraction of hydrogen atom gives the pyrrole derivative **7**. The differential reactivity of phenylacetylene toward **3**, compared with RNC and CO, resulted in the formation of different types of heterocyclic compounds.

Conclusion

In the present study, we have successfully isolated and characterized the palladium polyimino complex [Pd{C(=NR)C(=NR)C(=NR)C(=NR)CH(=NR)}(CNR)Cl] (**3**) derived from multiple insertion of bulky XylNC into the Pd−H bond of *trans*-[Pd(H)Cl(PPh$_3$)$_2$] (**2**). This is the first structurally characterized example of multiple isocyanide insertion products into Pd−H bonds. We also demonstrated a self-cyclization of the polymino moiety on the metal center leading to the formation of novel heterobicyclic compounds (**4**). One of the imino groups in the heterobicyclic ring can be modified by the reaction of precursor **3** with MesNC and CO, providing asymmetric compounds **5** and **6**, respectively. The reaction of **3** with phenylacetylene afforded the pyrrole derivative **7** instead of heterobicycles, suggesting that the products of spontaneous oligomerization of isocyanides can be controlled by utilizing stable intermediate complexes.

Acknowledgment. We thank Dr. Matsuzaka for carrying out high-resolution mass spectroscopy.

Supporting Information Available: Tables of complete atomic positional parameters, anisotropic temperature factors, and bond distances and angles for $3\cdot{}^{1}/_{2}C_6H_6$, **4a**, **6**, and $7\cdot C_6H_6$ (31 pages). Ordering information is given on any current masthead page.

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