Intramolecular Insertion of Acetylene into a Palladium−Carbon Bond in (Iminoacyl)palladium Complexes

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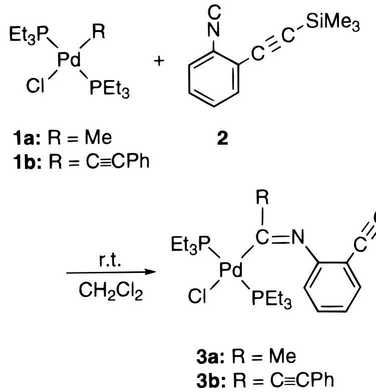
*Summary: An (iminoacyl)palladium complex (**3a**) prepared from the reaction of methylpalladium complex **1a** with o-((trimethylsilyl)ethynyl)phenyl isocyanide (**2**) undergoes an intramolecular insertion of acetylene at 45 °C in chloroform to give the ((E)-indolidenemethyl)-palladium complex **4a** quantitatively. The treatment of **3** with $AgPF_6$ followed by Et_4NCl at room temperature causes smooth insertion of acetylene, giving the ((Z)-indolidenemethyl)palladium complex **5** as a main product.*

The alternative copolymerization of olefins and carbon monoxide, which proceeds through alternating insertion of olefins and carbon monoxide into metal−carbon bonds, is a promising new type of polymerization catalyzed by transition-metal complexes.[1] Since isocyanide is isoelectronic with carbon monoxide and has a similar reactivity toward organometallic complexes, i.e., facile insertion into metal−carbon bonds,[2] copolymerization of isocyanide with unsaturated hydrocarbons giving polyimines may be possible via transition-metal catalysts. One of the most remarkable reactivity differences of isocyanide compared to carbon monoxide is the ability of the former to undergo multiple and successive insertions, leading to the formation of isocyanide homopolymers.[3] Therefore, a key step in the copolymerization of isocyanide with unsaturated hydrocarbons is insertion into metal−carbon bonds of iminoacyl complexes, which are produced by the initial insertion of isocyanides. However, there are few reports on the reactions of iminoacylmetal complexes with unsaturated hydrocarbons.[4] We present herein a novel intramolecular insertion of acetylene into a palladium−carbon bond of iminoacyl complexes which are produced by the reaction of organopalladium complexes with *o*-ethynylphenyl isocyanide.

The addition of *o*-((trimethylsilyl)ethynyl)phenyl isocyanide (**2**) to a dichloromethane solution of **1a** at room-temperature results in the quantitative formation of an iminoacyl complex (**3a**), which was isolated in 83% yield.[5] The IR spectrum of **3a** showed absorptions at 2153 cm^{-1} due to ν(C≡C) and 1557 cm^{-1} due to ν(C=N). In the ^{13}C NMR of **3a** a signal assignable to an imino carbon was observed at δ 194.1 and acetylene resonances appeared at δ 98.6 and 103.4. These data strongly suggest that **3a** was produced by the insertion of the isocyano group of **2** into the Pd−C bond of **1a**. The structure of **3a** was unequivocally identified by an X-ray diffraction study, as shown in Figure 1.[6] Treatment of the (phenylethynyl)palladium complex **1b** with **2** also produced an insertion product (**3b**), which was isolated in 80% yield.



(1)

Heating a chloroform solution of **3a** at 45 °C for 19 h caused the high-yield intramolecular insertion of acety-

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[2] For reviews, see: (a) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225. (b) Treichel. P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21. (c) Shingleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

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[5] The preparation of **3a** is as follows. Complex **1a** (590 mg, 1.5 mmol) was treated with **2** (299 mg, 1.5 mmol) in 30 mL of dichloromethane for 2 h at room temperature. After it was concentrated under reduced pressure, the residue was dissolved in about 20 mL of hexane and cooled to −30 °C to give pale yellow crystals of **3a** (742 mg, 83%). **3a**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9H), 1.06 (dt, $J = 17.1$, 7.7 Hz, 18H), 1.75−1.81 (m, 12H), 2.52 (t, $J = 1.1$ Hz, 3H), 7.04 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.23 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.42 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.97 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.1, 8.3, 15.4 (vt, $N = 13$ Hz), 35.8 (t, $J = 8$ Hz), 98.6, 103.4, 116.7, 117.7, 124.0, 128.5, 132.8, 152.5 (t, $J = 2$ Hz), 194.1 (t, $J = 5$ Hz); ^{31}P NMR ($CDCl_3$) δ 13.9; IR (KBr) 2153 ($\nu_{C\equiv C}$), 1557 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{25}H_{46}ClNP_2PdSi$: C, 50.68; H, 7.82; N, 2.36. Found: C, 50.74; H, 8.02; N, 2.27.

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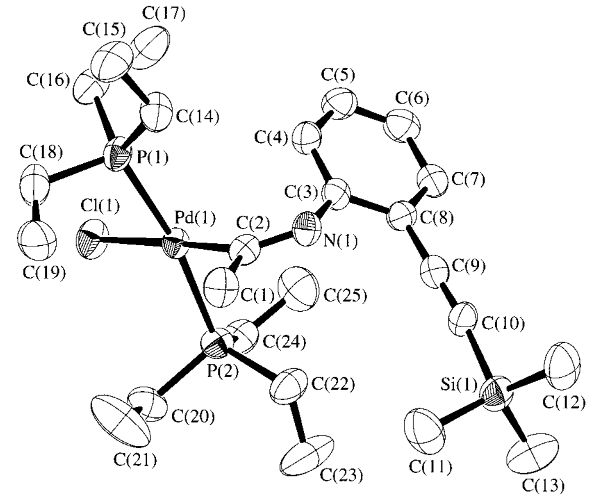
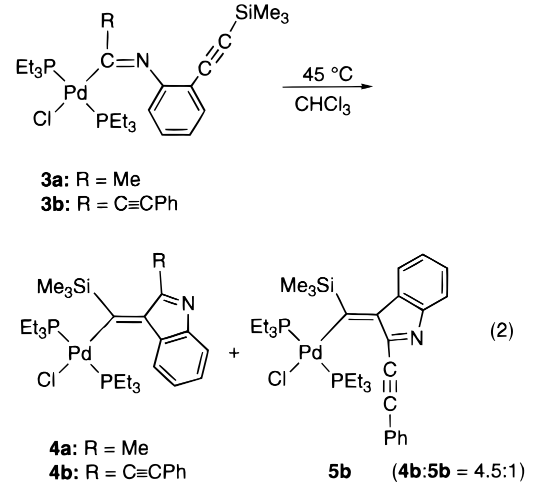


Figure 1. ORTEP drawing of **3a**. Hydrogen atoms and the solvent molecule are omitted for clarity. Bond distances and angles are included in the Supporting Information.

lene to give a new complex (**4a**) possessing an indole skeleton. Complex **4a** was isolated by alumina column chromatography followed by recrystallization from dichloromethane–hexane in 61% yield.[7] Acetylene insertion was confirmed by the disappearance of characteristic acetylene peaks in the IR and ^{13}C NMR spectra of **4a**, as well as by an X-ray analysis.[8] The ORTEP diagram of **4a** is shown in Figure 2. The molecule of **4a** sits on a crystallographic mirror plane defined by Pd(1), Cl(1), Si(1), and an indolidenemethyl group. The most striking structural feature of **4a** is that the Pd moiety and the imino group are linked to the olefin, which is generated by the trans insertion of acetylene.[9]



When complex **3b** was treated under similar conditions, the insertion of acetylene occurred with 12% conversion to give **4b** along with another complex (**5b**) in a molar ratio of 4.5:1. Longer reaction time and higher temperature caused decomposition of **3b** to Pd$(PEt_3)_2Cl_2$ and unidentified organic compounds. It should be noted that the addition of 0.3 equiv of PEt_3 inhibited the reaction from **3a** to **4a**, suggesting that the insertion of acetylene in **3** proceeds via initial dissociation of PEt_3 to give a vacant site for coordination of the acetylene.[10b,11] (Iminoacyl)palladium complexes prepared from the reaction of methylpalladium complex **1a** with *p*-tolyl or *p*-nitrophenyl isocyanide were treated with unsaturated hydrocarbons such as phenylacetylene and norbornene under various conditions, but no intermolecular insertion products were obtained. This result suggests that the insertion of acetylene into a Pd–C bond in (iminoacyl)palladium complexes is only effective when occurring intramolecularly.[10]

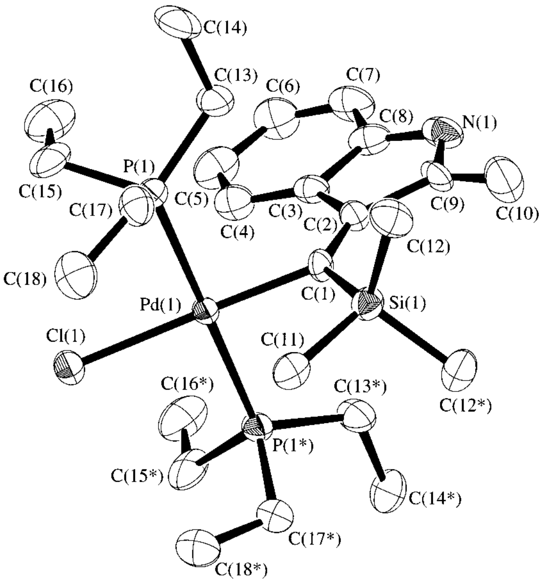


Figure 2. ORTEP drawing of **4a**. Hydrogen atoms are omitted for clarity. Bond distances and angles are included in the Supporting Information.

It has already been reported that cationic palladium complexes having a weakly coordinated ligand show a higher reactivity toward insertion of olefins and acety-

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(6) Crystallographic data for **3a**·CH_2Cl_2: fw = 677.47, monoclinic, space group $P2_1/n$ (No. 14), a = 15.705(3) Å, b = 11.122(3) Å, c = 20.765(3) Å, β = 108.67(1)°, V = 3436(1) Å^3, Z = 4, d_{calcd} = 1.309 g cm^{-3}, −75 °C, ω−2θ scan, 6° < 2θ < 55°, μ(Mo Kα) = 9.16 cm^{-1}, R (R_w) = 0.045 (0.062) for 307 parameters against 5519 reflections with $I > 3.0\,\sigma(I)$ out of 8297 unique reflections by full-matrix least-squares method, GOF = 1.17.

(7) The preparation of **4a** is as follows. Complex **3a** (300 mg, 0.506 mmol) was dissolved in 10 mL of chloroform and warmed to 45 °C for 19 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina using ethyl acetate as an eluent. A fraction containing the yellow band was collected and concentrated under reduced pressure. Recrystallization from dichloromethane–hexane gave a yellow powder of **4a** (183 mg, 61%). **4a**: ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 9H), 1.07 (dt, J = 17.1, 7.6 Hz, 18H), 1.48–1.56 (m, 6H), 1.67–1.75 (m, 6H), 2.56 (s, 3H), 7.16 (dt, J = 7.4, 1.1 Hz, 1H), 7.32 (dt, J = 7.4, 1.1 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 9.39 (d, J = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 5.1, 8.1, 15.5 (vt, N = 13 Hz), 20.8, 118.3, 121.9 (t, J = 2 Hz), 123.4, 127.6, 134.3, 150.3 (t, J = 3 Hz), 155.3, 161.6, 208.5; ^{31}P NMR ($CDCl_3$) δ 5.5; IR (KBr) 1514 ($\nu_{C=N}$) cm^{-1}. Anal. Calcd for $C_{25}H_{46}ClNP_2PdSi$: C, 50.68; H, 7.82; N, 2.36. Found: C, 51.05; H, 7.50; N, 2.39.

(8) Crystallographic data for **4a**: fw = 592.54, orthorhombic, space group $Pnma$ (No. 62), a = 15.838(4) Å, b = 12.923(3) Å, c = 14.358(3) Å, V = 2938.8(10) Å^3, Z = 4, d_{calcd} = 1.339 g cm^{-3}, −75 °C, ω−2θ scan, 6° < 2θ < 55°, μ(Mo Kα) = 8.85 cm^{-1}, R (R_w) = 0.059 (0.093) for 163 parameters against 2152 reflections with $I > 3.0\sigma(I)$ out of 3790 unique reflections by full-matrix least-squares method, GOF = 1.25.

(9) The stereochemistry is cis in the usual acetylene insertion: (a) Appleton, T. G.; Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1972**, *11*, 2074. (b) Tohda, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1975**, 54. (c) Tohda, Y.; Sonogashira, K.; Hagihara, N. *J. Organomet. Chem.* **1976**, *110*, C53.

(10) (a) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107. (b) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

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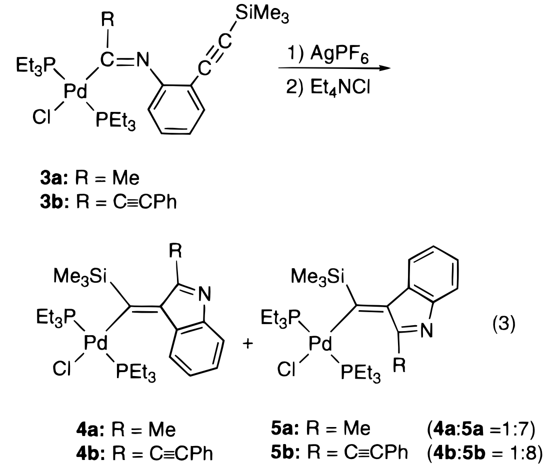

3a: R = Me
3b: R = C≡CPh

4a: R = Me
4b: R = C≡CPh

5a: R = Me (**4a**:**5a** =1:7)
5b: R = C≡CPh (**4b**:**5b** = 1:8)

(3)

lenes into their Pd−C bonds than neutral analogues.[1,11,12] We converted **3a** into a cationic complex by treatment with AgPF$_6$ in the expectation that acetylene insertion would be facilitated. The resulting cationic complex, however, proved too unstable for characterization. The addition of Et$_4$NCl to the reaction mixture after 30 min gave neutral products that could be characterized. The ^{31}P NMR spectrum of the reaction mixture indicated the formation of **4a** and a new complex (**5a**) in a 1:7 molar ratio. Isolation by column chromatography on alumina followed by recrystallization from dichloromethane−hexane afforded a pure sample of **5a** in 66% yield.[13] The molecular structure of **5a** is shown in Figure 3.[14] The molecule of **5a** sits on a crystallographic mirror plane defined by Pd(1), Cl(1), Si(1), and an indolidenemethyl group. Although complex **5a** is also derived from the intramolecular acetylene insertion of **3a**, it can be that, in contrast to **4a**, the stereochemistry in the acetylene insertion is cis.[9] Similar treatment of **3b** with AgPF$_6$, followed by Et$_4$NCl, also gave **4b** and **5b** in a 1:8 molar ratio. No isomerization of **5a** into **4a** was observed after heating a chloroform solution of **5a** at 45 °C overnight, suggesting that **5a** is not an intermediate in the formation of **4a** from **3a**.

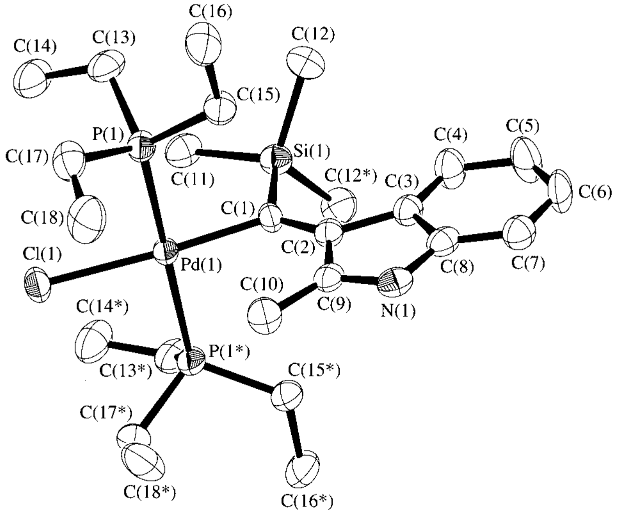

Figure 3. ORTEP drawing of **5a**. Hydrogen atoms are omitted for clarity. Bond distances and angles are included in the Supporting Information.

The reaction presented herein may be regarded as an elementary process in the alternative copolymerization of isocyanide with acetylene. We are trying to extend the present finding into a cyclopolymerization system to give poly(indolidenemethyl)s.

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Supporting Information Available: Text giving experimental details and full characterization data for all new complexes and tables of X-ray crystallographic data for complexes **3a**, **4a**, and **5a** (20 pages). Ordering information is given on any current masthead page.

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(13) The preparation of **5a** is as follows. To a solution of complex **3a** (660 mg, 1.11 mmol) in 30 mL of acetone was added silver hexafluorophosphate (338 mg, 1.34 mmol). After the mixture was stirred for 30 min at room temperature, the precipitates were filtered off. The filtrate was treated with tetraethylammonium chloride (740 mg, 4.47 mmol) for 30 min at room temperature. About 10 mL of water was added to the reaction mixture, followed by extraction with dichloromethane. After the extract was dried over sodium sulfate, the solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with dichloromethane. Concentration of the yellow fraction followed by recrystallization from dichloromethane−hexane gave a yellow powder of **5a** (613 mg, 66%). **5a**: ^{1}H NMR (CDCl$_3$) δ 0.63 (br, 9H), 1.07 (dt, $J = 17.1$, 7.6 Hz, 18H), 1.48−1.56 (m, 6H), 1.67−1.75 (m, 6H), 2.56 (s, 3H), 7.16 (dt, $J = 7.4$, 1.1 Hz, 1H), 7.32 (dt, $J = 7.4$, 1.1 Hz, 1H), 7.39 (d, $J = 7.4$ Hz, 1H), 9.39 (d, $J = 7.4$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ −0.1, 8.1, 15.8 (vt, $N =$ 13 Hz), 19.6, 118.8, 123.3, 123.4, 126.0, 127.4, 150.1, 155.1, 168.2, 208.7; ^{31}P NMR (CDCl$_3$) δ 4.0. Anal. Calcd for $C_{25}H_{46}ClNP_2PdSi$: C, 50.68; H, 7.82; N, 2.36. Found: C, 50.92; H, 7.53; N, 2.15.

(14) Crystallographic data for **5a**: fw = 592.54, hexagonal, space group $P6_3/m$ (No. 176), $a = 20.811(4)$ Å, $c = 12.970(3)$ Å, $V = 4864(2)$ Å^3, $Z = 6$, $d_{calcd} = 1.213$ g cm^{-3}, −75 °C, $\omega-2\theta$ scan, $6° < 2\theta < 55°$, μ(Mo Kα) = 8.02 cm^{-1}, R (R_w) = 0.040 (0.060) for 163 parameters against 2252 reflections with $I > 3.0\sigma(I)$ out of 3890 unique reflections by full-matrix least-squares method, GOF = 1.13.