# Reactions of Heterodinuclear $\mu$-Ethynediyl Palladium–Platinum Complexes with Isocyanides: Living Polymerization of Aryl Isocyanides

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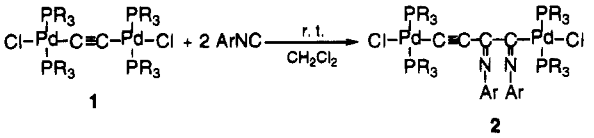
The heterodinuclear $\mu$-ethynediyl complex $Cl(R_3P)_2PtC{\equiv}CPd(PR_3)_2Cl$ (**3**) reacts with aryl isocyanides in the molar ratio 1:2 to give the double-insertion product $Cl(R_3P)_2PtC{\equiv}CC({=}NAr)C({=}NAr)Pd(PR_3)_2Cl$ (**5**). Treatment of **3** with aryl isocyanides in the molar ratio 1:100 causes a multiple and successive insertion of isocyanides into the Pd–C bond of **3**, leading to isocyanide polymers **7** which have a narrow distribution of molecular weight, suggesting that the reaction is a living polymerization. The living behaviors are confirmed by trace experiments using gel permeation chromatography and the syntheses of isocyanide block copolymers (**9**). The ($\mu$-ethynediyl)dipalladium complex $Cl(R_3P)_2PdC{\equiv}CPd(PR_3)_2Cl$ (**1**) similarly produces isocyanide polymers (**10**), while the ($\mu$-butadiynediyl)dipalladium complex **11** and mononuclear palladium acetylide **13** give only single-insertion products **12** and **14**, respectively.

## Introduction

Polyisocyanides, some of which have unique properties due to their rigid helical structure, have been dealt with as an object of study over the last few decades.[1] The first report on the synthesis of polyisocyanides using transition-metal catalysts was made by Yamamoto and Hagihara.[2] They found that an isocyanide was polymerized by transition-metal carbonyl complexes such as $Ni(CO)_4$ and $Co_2(CO)_8$. Drenth and Nolte investigated the polymerization of isocyanides with Ni(II) salts.[1c]

On the other hand, it is well-known that isocyanides insert into M–C bonds of various transition-metal complexes to give imino–metal complexes. Although multiple insertion sometimes occurs,[3] few examples of multiple and successive insertion giving isocyanide polymers have appeared in the literature.[4] However, polymerization by multiple and successive insertion of isocyanide monomers into an M–C bond is of special interest because the reaction would be expected to be essentially a living process and may be understood on the basis of organometallic chemistry.

Previously we reported the first synthesis of $\mu$-ethynediyl dinuclear complexes, in which two metal atoms are linked together by one acetylene unit.[5] The complexes may be expected to have unique properties due to the mutual interaction between the two metals through a C≡C triple bond. Indeed, ($\mu$-ethynediyl)dipalladium complexes **1** reacted with aryl isocyanides to afford a selective double-insertion product (**2**).[6] This reactivity is peculiar to the $\mu$-ethynediyl complexes, since other dipalladium complexes such as ($\mu$-butadiynediyl)- and ($\mu$-phenylenebis(ethynediyl))dipalladium complexes and mononuclear palladium acetylides gave normal single-insertion products. Recently we have also reported the synthesis of heterodinuclear $\mu$-ethynediyl complexes (**3**) containing palladium and platinum.[7] We have also examined the reactivity of heterodinuclear complexes **3** toward isocyanides and found multiple and successive insertion of isocyanide into the Pd–C bond of the complexes which leads to a novel living polymerization of isocyanides. Herein we wish to describe full details of our study on the living polymerization of aryl isocyanides catalyzed by heterodinuclear $\mu$-ethynediyl complexes **3** containing palladium and platinum. A portion of this work has previously been communicated.[8]



$$Cl{-}\underset{PR_3}{\overset{PR_3}{Pd}}{-}C{\equiv}C{-}\underset{PR_3}{\overset{PR_3}{Pd}}{-}Cl \underset{\mathbf{1}}{} + 2\,ArNC \xrightarrow[CH_2Cl_2]{r.t.} Cl{-}\underset{PR_3}{\overset{PR_3}{Pd}}{-}C{\equiv}C{-}\underset{\underset{Ar}{N}}{C}{-}\underset{\underset{Ar}{N}}{C}{-}\underset{PR_3}{\overset{PR_3}{Pd}}{-}Cl \quad \mathbf{2} \qquad (1)$$

## Results and Discussion

Although ($\mu$-ethynediyl)dipalladium complexes **1** smoothly react with 2 equiv of phenyl isocyanide at room

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[1] (a) Millich, F. *Chem. Rev.* **1972**, *72*, 101. (b) Millich, F. *Adv. Polym. Sci.* **1975**, *19*, 117. (c) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30.

[2] Yamamoto, Y.; Takizawa, T.; Hagihara, N. *Nippon Kagaku Zasshi* **1966**, *87*, 1355.

[3] (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.

[4] (a) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7198. (b) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1977**, *16*, 3182.

[5] (a) Ogawa, H.; Joh, T.; Takahashi, S.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1220. (b) Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 22.

[6] (a) Ogawa, H.; Joh, T.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1988**, 561. (b) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531.

[7] Onitsuka, K.; Joh, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1992**, *32*, 851.

[8] Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 851.

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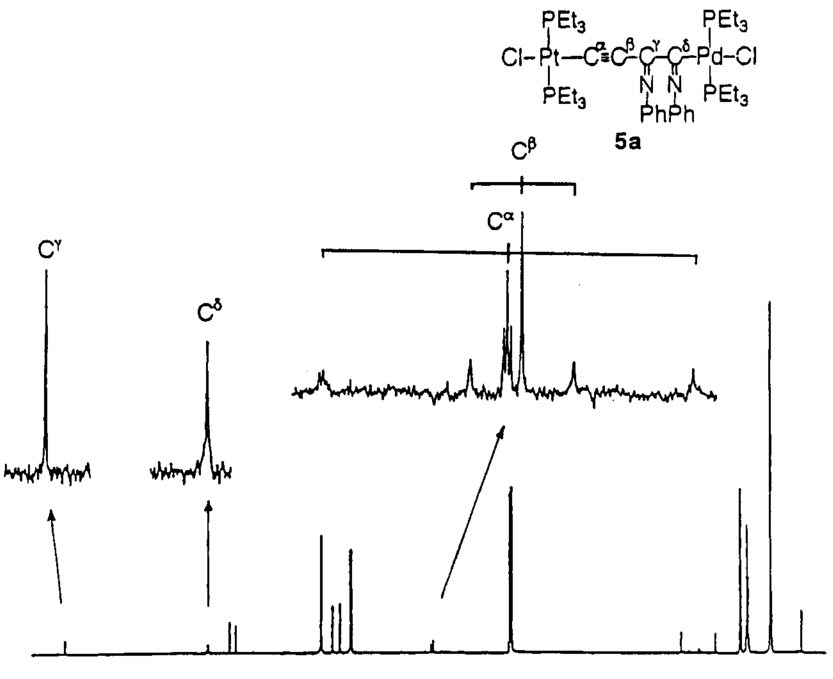
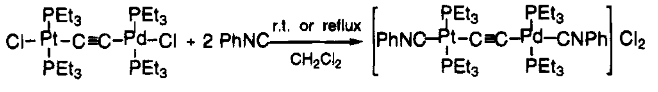


**Figure 1.** $^{13}C$ NMR spectrum of complex **5a**.

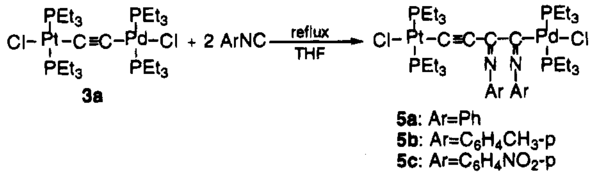
temperature to afford double-insertion products **2** in good yield, under the same reaction conditions heterodinuclear μ-ethynediyl complex **3a** did not give any insertion products. The similar reaction under reflux in dichloromethane also gave no insertion products, but the IR spectrum of the reaction mixture exhibited an absorption at 2180 cm$^{-1}$ due to ν(C≡N), indicating the formation of a cationic complex (**4a**) which corresponds to an initial product[6] of the insertion reaction.



$$\mathrm{Cl{-}Pt(PEt_3)_2{-}C{\equiv}C{-}Pd(PEt_3)_2{-}Cl} + 2\,\mathrm{PhNC} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{r.t. or reflux}} \left[\mathrm{PhNC{-}Pt(PEt_3)_2{-}C{\equiv}C{-}Pd(PEt_3)_2{-}CNPh}\right]\mathrm{Cl_2} \quad (2)$$

**3a** **4a**

When complex **3a** was treated with 2 equiv of phenyl isocyanide in THF under reflux for 13 h, an orange oily product (**5a**) was obtained in good yield. Spectroscopic measurements and elemental analysis have indicated that complex **5a** is a double-insertion product in which two molecules of phenyl isocyanide insert exclusively into the Pd—C bond of **3a**. It was specifically suggested by the $^{13}C$ NMR spectrum that the insertion of isocyanide did not occur at the Pt—C bond but at the Pd—C bond (Figure 1). The resonances of acetylene carbons appeared at δ 99.09 as a triplet and 98.06 as a singlet with attendant satellites due to the coupling of a $^{195}Pt$ nucleus, while the signals of imino carbons were observed at δ 195.02 and 158.28 without satellite signals, showing that the Pt atom is bonded to an acetylenic carbon. In the $^{31}P$ NMR spectrum of **5a** two singlets at



$$\mathrm{Cl{-}Pt(PEt_3)_2{-}C{\equiv}C{-}Pd(PEt_3)_2{-}Cl} + 2\,\mathrm{ArNC} \xrightarrow[\mathrm{THF}]{\text{reflux}} \mathrm{Cl{-}Pt(PEt_3)_2{-}C{\equiv}C{-}C({=}NAr){-}C({=}NAr){-}Pd(PEt_3)_2{-}Cl} \quad (3)$$

**3a**

**5a**: Ar=Ph
**5b**: Ar=$C_6H_4CH_3$-p
**5c**: Ar=$C_6H_4NO_2$-p

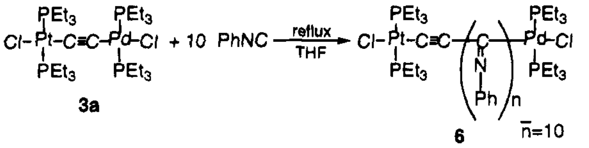
**Table 1. Selected Spectral Data for Complexes 5, 6, and 8**

| | IR (cm$^{-1}$) | | $^{31}P$ NMR (δ) | |
|---|---|---|---|---|
| complex | $\nu_{C\equiv C}$ | $\nu_{C=N}$ | P on Pd | P on Pt ($^1J_{Pt-P}$) |
| **5a** | 2090 | 1575 | 18.8 | 21.8 (2350) |
| **5b** | 2090 | 1565 | 17.8 | 21.1 (2356) |
| **5c** | 2075 | 1565 | 20.2 | 21.9 (2332) |
| **6** | 2085 | 1640 | 18.7 | 21.6 (2331) |
| **8** | 2090 | 1640 | 17.6 | 21.0[a] |

[a] The coupling constant could not be determined exactly due to broadening of the signal.

δ 18.8 and 21.8 were observed, the latter of which was accompanied by satellite signals due to the coupling ($J$ = 2350 Hz) with a $^{195}Pt$ nucleus. The spectrum of **3a** exhibits two singlets at δ 19.6 with satellites ($J$ = 2518 Hz) and δ 21.8. After the isocyanide insertion into the Pd—C bond of **3a** the signal for the $PEt_3$ ligand coordinating to palladium is shifted to higher magnetic field and the signal for $PEt_3$ on platinum moves to lower field. An analogous phenomenon was observed in the reaction of dipalladium complexes with isocyanides, and the resonance of phosphorus on palladium linked to the imino group in **2** was observed at lower magnetic field, whereas that on palladium bonded to the ethynyl group was observed at higher magnetic field, than the phosphorus atoms of **1**. Thus, $^{31}P$ NMR is useful in finding the reaction point where isocyanides insert in the dinuclear μ-ethynediyl complexes. Similarly, **3a** reacted with *p*-tolyl and *p*-nitrophenyl isocyanides to afford the double-insertion products **5b** and **5c**, respectively. However, alkyl isocyanides such as cyclohexyl and *tert*-butyl isocyanides did not give insertion products at all.

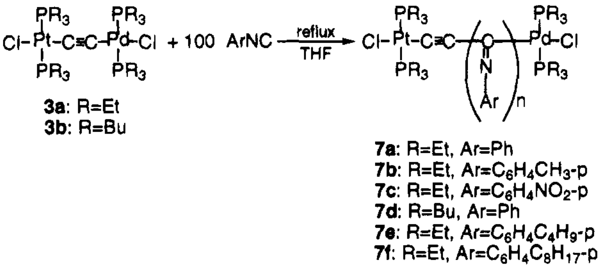
On treatment of **3a** with phenyl isocyanide in the molecular ratio 1:10 under reflux in THF, an oligomeric complex (**6**) was obtained and no isocyanide was recovered. The IR spectrum of **6** showed absorptions at 2085 cm$^{-1}$ due to ν(C≡C) and at 1640 cm$^{-1}$ due to ν(C=N), the latter being characteristic of isocyanide polymers.[9]



(4)

The average molecular weight of **6** was determined to be 1850 by vapor pressure osmometry (in benzene), which is consistent with the calculated molecular weight of a product derived from one molecular of **3a** and ten molecules of phenyl isocyanide. The composition of **6** was also suggested by the ratio of aromatic protons of the PhN=C group to aliphatic protons of triethylphosphine on metals in the $^1$H NMR. The $^{13}$P NMR spectrum of complex **6** is very similar to that of **5a**, indicating that **6** contains organometallic end groups and has a structure similar to that of **5a**. As oligomeric complex **6** is available from a successive insertion of isocyanides into the Pd—C bond of **3a**, it is likely that complex **3** acts as a good catalyst for polymerization of isocyanides.

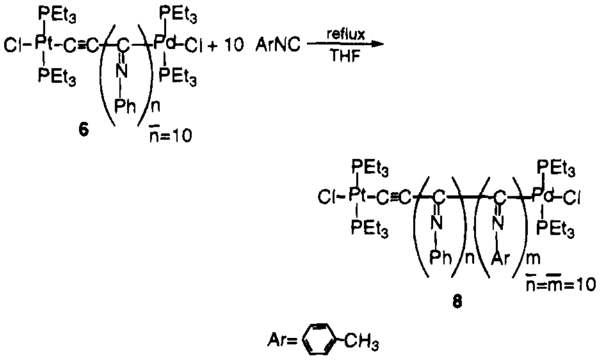
Indeed, the reaction of **3a** with phenyl isocyanide in the molar ratio of 1:100 quantitatively gave yellow solids (**7a**) which precipitated from the reaction solution.



(5)

Observation of the C=N stretching at 1660 cm$^{-1}$ suggested **7a** to be an isocyanide polymer. Similar treatment of **3a** with *p*-tolyl isocyanide also gave a polymer (**7b**) in a quantitative yield. However, the reaction of **3a** with *p*-nitrophenyl isocyanide under the same conditions afforded a polymer (**7c**) in 55% yield and about 40% of the isocyanide was recovered. The low yield of the polymer and the recovery of the monomer may be due to very low solubility of the polymeric product which was separated from the solution as a precipitate during the reaction. 2,6-Xylyl isocyanide, which reacted with **3a** to yield a double-insertion product (**5d**), did not give any polymeric products due to the steric hindrance of the xylyl group. Complex **3b**, bearing a tributylphosphine ligand, also reacted with phenyl isocyanide to produce a polymer (**7d**). Unfortunately, further characterization of the polymers obtained from phenyl, tolyl, and nitrophenyl isocyanides could not be done because of their low solubility in common organic solvents. Therefore, in order to improve the solubility of isocyanide polymers, we have prepared polymers from aryl isocyanides having a long alkyl chain. The reaction of **3a** with *p*-butyl- and *p*-octylphenyl isocyanides in molar ratios of 1:100 afforded polymers **7e** and **7f**, respectively, which are soluble in benzene and THF and insoluble in methanol. Polymers **7e** and **7f** were characterized by spectroscopic methods and gel permeation chromatography (GPC). The GPC analysis using polystyrene standards showed a very narrow distribution of molecular weight, $M_w/M_n = 1.02$ ($M_n = 13\ 000$) for **7e** and 1.01 ($M_n = 17\ 000$) for **7f**, suggesting that the reactions are living polymerizations, as expected.

The living nature of the polymerization of aryl isocyanides catalyzed with **3** has been demonstrated by several experiments. Not only **3** but also **5** and **6** initiate the polymerization of isocyanides, since the last two still possess an active end group, —C(=NR)-Pd(PEt$_3$)$_2$Cl. For example, the reactions of **5a** and **6** with 100 equiv of phenyl isocyanide produced polymer **7a** quantitatively. One of the characteristic features of living polymerization is to produce block copolymers. Thus, oligomer complex **6** was treated with 10 equiv of *p*-tolyl isocyanide to yield the soluble block cooligomer **8** (eq 6). Cooligomer complex **8** was characterized by the ratio of aromatic protons to aliphatic ones in $^1$H NMR and by the comparison of the signals attributed to the triethylphosphine with that of **5b**. Block copolymers **9** were prepared in high yields from the polymerization of ArNC with **3a** followed by addition of a different kind of monomer, Ar′NC, to the reaction solution (eq 7). The block copolymerization can also be performed by using isolated polymer complex **5** as an initiator, because **5** as well as **6** is not deactivated during the isolation procedure and reused for the second polymerization of isocyanides (Table 2).



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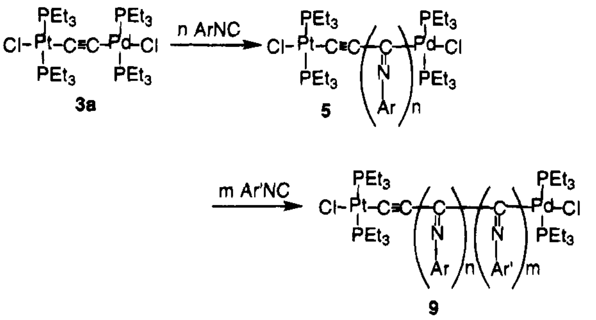

(7)

Furthermore, the average molecular weight of the isolated polymers has been confirmed to vary linearly with the initial ratio of isocyanide monomer to complex **3a**, which is also characteristic of a living system. Monitoring the polymerization by GPC revealed a linear increase in the average molecular weight of polymer as a function of monomer conversion (Figure 2).

Recently two examples of a living polymerization of isocyanides using a transition-metal complex as a catalyst have been reported. One is the polymerization of 1,2-diisocyanoarenes catalyzed by palladium or nickel complexes to give poly(2,3-quinoxaline).[10] The other is the polymerization of alkyl isocyanides by [($\eta^3$-C$_3$H$_5$)-

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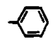
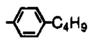
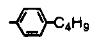
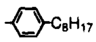
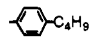
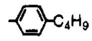
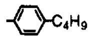
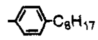
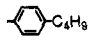
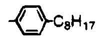
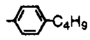
(9) Millich, F.; Sinclain, R. G. *J. Polym. Sci., Part C* **1968**, *22*, 23.

**Table 2. Averaged Molecular Weight of Block Copolymer Complexes (9)**

| run no. | Ar | $n$ | $\bar{M}_n^1$ | Ar′ | $m$ | $\bar{M}_n^2$ |
|---|---|---|---|---|---|---|
| 1 |  | 10 | 1 900$^a$ |  | 100 | 14 000 |
| 2 |  | 30 | 3 900$^b$ |  | 50 | 12 000 |
| 3 |  | 100 | 13 000$^b$ |  | 30 | 16 000 |
| 4 |  | 100 | 13 000$^a$ |  | 30 | 17 000 |
| 5 |  | 30 | 5 900$^b$ |  | 30 | 10 000 |
| 6 |  | 80 | 12 000$^b$ |  | 30 | 15 000 |

$^a$ Isolated. $^b$ Not isolated.

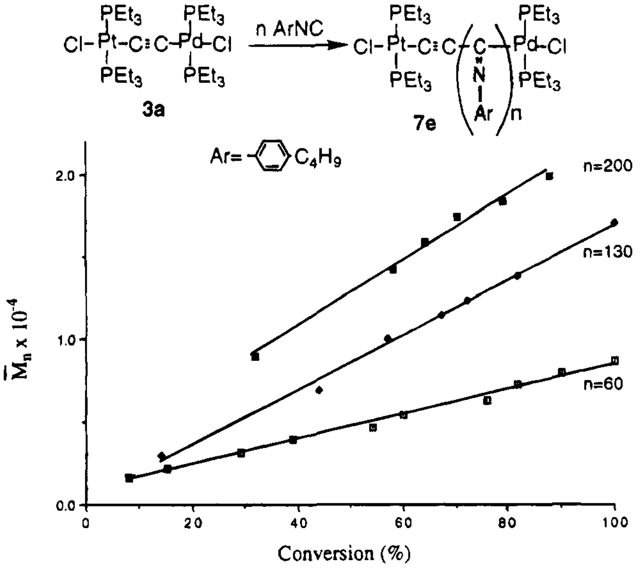


**Figure 2.** Molecular weight vs percent conversion of isocyanide.

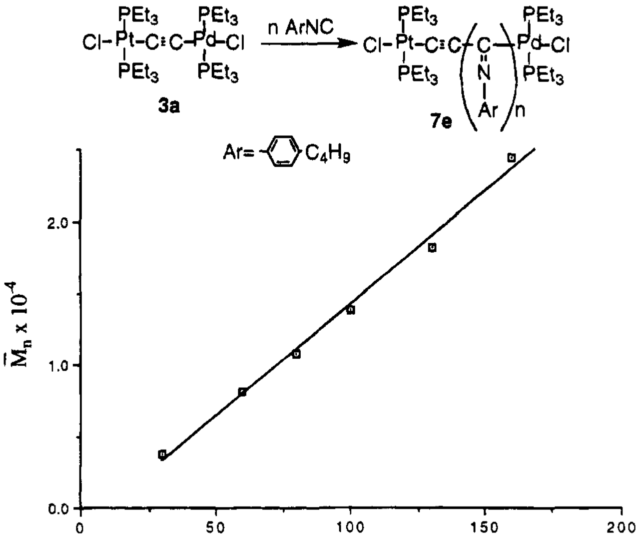
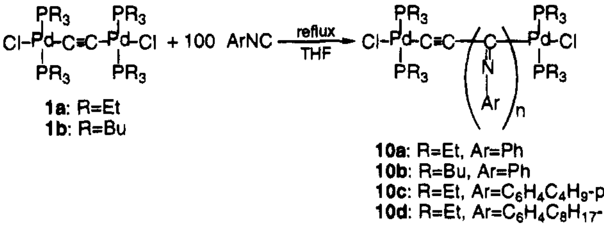


**Figure 3.** Variation of molecular weight with isocyanide/**3a** ratio.

$Ni(OC(O)CF_3)]_2$; the polymers produced in this case, however, have a rather broad distribution of molecular weight, $M_w/M_n$ = 1.1–1.6.[11] Our catalysts are active for aryl isocyanides and yield polymers of a sharp molecular weight distribution. It should be noted that all the complexes **5** and oligo- and polyisocyanide complexes prepared and isolated here have the active end group "$-Pd(PR_3)_2Cl$" so that they are still "living" and able to undergo further insertion of isocyanides. Hence, these complexes as well as complex **3** provide a novel system for living polymerization of isocyanides giving polymers structurally designed in terms of molecular weight, composition, sequence, *etc.*

The reaction of the (μ-ethynediyl)dipalladium complex **1** with 10 equiv of phenyl isocyanide at room temperature gave selectively the double-insertion product **2**, and further insertion was not observed. Similar treatment under THF reflux afforded **2** as the main product along with small amounts of an oligomer complex. However, it is worth noting that complex **1**, on treatment with phenyl isocyanide in the molar ratio 1:100, gave the isocyanide polymer **10**. The average molecular weights of soluble polymers **10c** and **10d** prepared from the respective reaction of **1a** with *p*-*n*-butylphenyl and *p*-*n*-octylphenyl isocyanides were determined by GPC to be $M_n$ = 12 000 for **10c** and $M_n$ = 17 000 for **10d**. On the other hand, the (μ-butadiynediyl)dipalladium complex **11** did not initiate the polymerization of isocyanides but yielded only a single-insertion complex (**12**), even when treated with 100 equiv of phenyl isocyanide. Similar treatment of palladium acetylide **13** with 100 equiv of phenyl isocyanide gave a single-insertion complex (**14**), and most of the isocyanide was recovered. These results indicate the catalytic feature in the present living polymerization of isocyanides; that is, the multiple and successive insertion of isocyanides into a Pd–C bond is specific to (μ-ethynediyl)dimetal complexes and the platinum or palladium moiety in complex **3** or **1** plays a very important role as an end group in the reaction with isocyanides.



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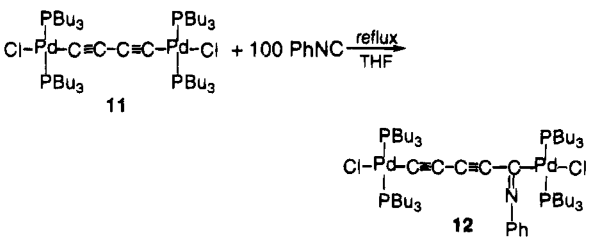
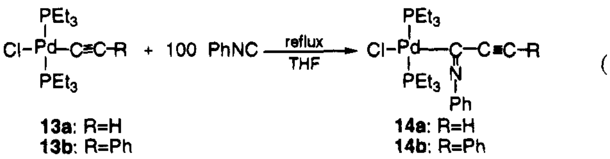


(9)



(10)

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(10) (a) Ito, Y.; Ihara, E.; Murakami, M.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 6446. (b) Ito, Y.; Ihara, E.; Murakami, M. *Polym. J.* **1992**, *24*, 297.

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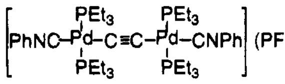
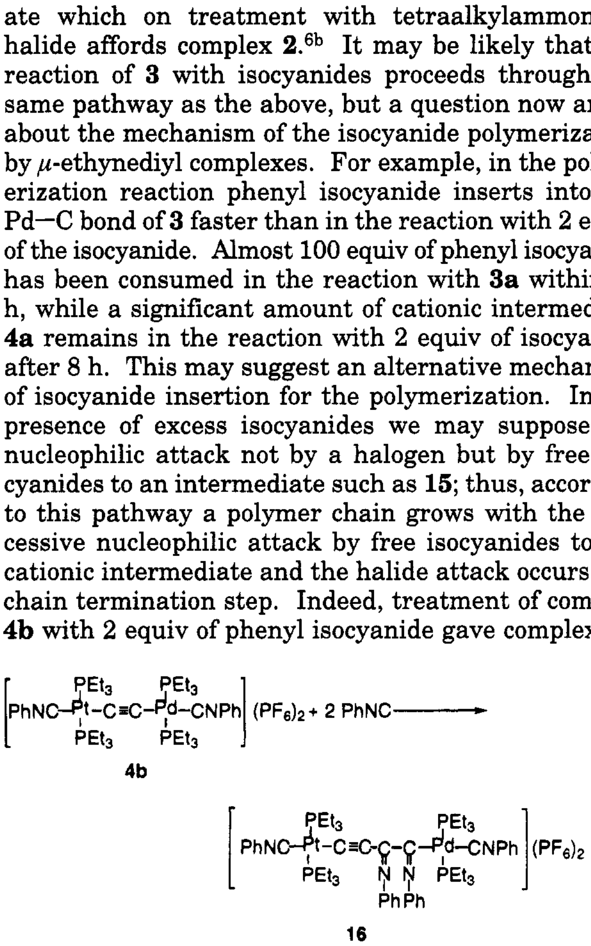
Insertion of isocyanides into an M—C bond in the complex $L_nM(R)X$ is believed to proceed by nucleophilic attack of a halide to a cationic intermediate, in which both isocyanide and alkyl groups are bonded to the metal, and simultaneous alkyl migration.[12] In the reaction of complex **1** with isocyanides, a cationic complex (**15**) has already been isolated as an intermediate which on treatment with tetraalkylammonium halide affords complex **2**.[6b] It may be likely that the reaction of **3** with isocyanides proceeds through the same pathway as the above, but a question now arises about the mechanism of the isocyanide polymerization by μ-ethynediyl complexes. For example, in the polymerization reaction phenyl isocyanide inserts into the Pd—C bond of **3** faster than in the reaction with 2 equiv of the isocyanide. Almost 100 equiv of phenyl isocyanide has been consumed in the reaction with **3a** within 20 h, while a significant amount of cationic intermediate **4a** remains in the reaction with 2 equiv of isocyanide after 8 h. This may suggest an alternative mechanism of isocyanide insertion for the polymerization. In the presence of excess isocyanides we may suppose the nucleophilic attack not by a halogen but by free isocyanides to an intermediate such as **15**; thus, according to this pathway a polymer chain grows with the successive nucleophilic attack by free isocyanides to the cationic intermediate and the halide attack occurs at a chain termination step. Indeed, treatment of complex **4b** with 2 equiv of phenyl isocyanide gave complex **16**, and complexes **4b** and **15**, having no halogen, are also active for the polymerization to produce isocyanide polymers. It has already been shown by Novak et al.[11c] that the nucleophilic attack of isocyanide monomers is commonly involved in the mechanism of isocyanide polymerization by nickel catalysts.



$$\left[\mathrm{PhNC{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}CNPh}\right](\mathrm{PF_6})_2$$

**15**



$$\left[\mathrm{PhNC{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}CNPh}\right](\mathrm{PF_6})_2 + 2\,\mathrm{PhNC} \longrightarrow \left[\mathrm{PhNC{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}\underset{\underset{Ph}{N}}{\overset{\|}{C}}{-}\underset{\underset{Ph}{N}}{\overset{\|}{C}}{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}CNPh}\right](\mathrm{PF_6})_2 \quad (11)$$

**4b**

**16**

## Experimental Section

All the reactions were carried out under an atmosphere of nitrogen, but workup was performed in air. THF was dried over sodium/benzophenone and freshly distilled prior to use. $^1H$ and $^{13}C$ NMR (in $CDCl_3$) were measured on a Bruker AM-360 spectrometer using $SiMe_4$ as an internal standard and $^{31}P$ NMR (in 1/1 $CD_2Cl_2/CH_2Cl_2$) spectra on a JEOL FX-100 spectrometer against an external $PPh_3$ (in $C_6D_6$) reference. FAB mass spectra were obtained on a JMX-DX300 spectrometer and IR spectra on a Hitachi 295 spectrophotometer. Elemental analyses and the measurement of average molecular weight by VPO were performed by The Material Analysis Center, ISIR, Osaka University. Gel permeation chromatography was run on a Shimadzu HSG-20 column using a Shimadzu LC-3A and Shimadzu 840 liquid chromatograph.

Heterodinuclear μ-ethynediyl complexes **3** containing palladium and platinum,[7] (μ-ethynediyl)dipalladium complexes **1**,[5] (μ-butadiynediyl)dipalladium complexes, and mononuclear palladium acetylide complexes[13] were prepared by the method described previously. Aryl isocyanides were prepared by a carbylamine reaction in the presence of a phase transfer catalyst.[14] Alkyl isocyanides were purchased from Aldrich and used without further purification.

**Reaction of Complex 3a with 2 Equiv of Phenyl Isocyanide.** Complex **3a** (261 mg, 0.3 mmol) was dissolved in 20 mL of THF and treated with phenyl isocyanide (62 mg, 0.6 mmol) under reflux for 13 h. The solvent was evaporated under reduced pressure, and the product was isolated by alumina column chromatography. Elution with benzene/dichloromethane (1/1 v/v) gave the yellow-orange oil **5a** (304 mg, 94%).

IR: $\nu(C{\equiv}C)$ 2090, $\nu(C{=}N)$ 1575 $cm^{-1}$. $^{13}C$ NMR: $\delta$ 195.02 (s, $C{\equiv}C\mathit{C}({=}NPh)$), 158.28 (s, $Pd\mathit{C}({=}NPh)$), 152.58 (s, Ph), 150.94 (s, Ph), 128.51 (s, Ph), 128.41 (s, Ph), 125.45 (s, (Ph), 123.46 (s, Ph), 120.74 (s, Ph), 120.39 (s, Ph), 99.09 (t, $^1J_{Pt-C}$ = 1439, $^2J_{P-C}$ = 14 Hz, $Pt\mathit{C}{\equiv}C$), 98.46 (s, $^2J_{Pt-C}$ = 408 Hz, $PtC{\equiv}\mathit{C}$), 16.07 (vt, $J$ = 12 Hz, $PCH_2$), 14.21 (vt, $J$ = 16 Hz, $PCH_2$), 8.22 (s, $PCH_2\mathit{C}H_3$), 8.01 (s, $PCH_2\mathit{C}H_3$). $^{31}P$ NMR: $\delta$ 21.8 (s, $^1J_{Pt-P}$ = 2350 Hz, PtP), 18.8 (s, PdP). Mass: *m/z* 1076 ($M^+$). Anal. Calcd for $C_{40}H_{70}N_2Cl_2P_4PdPt$: C, 44.68; H, 6.56; N, 2.61; Cl, 6.59; P, 11.52. Found: C, 44.71; H, 6.36; N, 2.68; Cl, 6.81; P, 11.54.

**Reactions of Complex 3a with 2 Equiv of *p*-Tolyl and *p*-Nitrophenyl Isocyanides.** These reactions were carried out by a procedure similar to that with phenyl isocyanide.

**5b**: orange oil; yield 69%. IR: $\nu(C{\equiv}C)$ 2090, $\nu(C{=}N)$ 1565 $cm^{-1}$. $^{31}P$ NMR: $\delta$ 21.1 (s, $^1J_{Pt-P}$ = 2356 Hz, PtP), 17.8 (s, PdP). Mass: *m/z* 1105 ($M^+$). Anal. Calcd for $C_{42}H_{74}N_2Cl_2P_4PdPt$: C, 45.72; H, 6.76; N, 2.54; Cl, 6.43; P, 11.23. Found: C, 45.71; H, 6.48; N, 2.39; Cl, 6.64; P, 11.42.

**5c**: red oil; yield 88%. IR: $\nu(C{\equiv}C)$ 2075, $\nu(C{=}N)$ 1565 $cm^{-1}$. $^{13}C$ NMR: $\delta$ 202.45 (s, $C{\equiv}C\mathit{C}({=}NAr)$), 159.47 (s, $Pd\mathit{C}({=}NAr)$), 158.50 (s, Ar), 156.50 (s, Ar), 145.07 (s, Ar), 143.95 (s, Ar), 124.81 (s, Ar), 124.54 (s, Ar), 120.53 (s, Ar), 120.43 (s, Ar), 106.90 (t, $^2J_{P-C}$ = 14 Hz, $Pt(\mathit{C}{\equiv}C)$, 98.32 (s, $PtC{\equiv}\mathit{C}$), 16.12 (vt, $J$ = 13 Hz, $PCH_2$), 14.22 (vt, $J$ = 16 Hz, $PCH_2$), 8.28 (s, $PCH_2\mathit{C}H_3$), 7.93 (s, $PCH_2\mathit{C}H_3$). $^{3P}$ NMR: $\delta$ 21.9 (s, $^1J_{Pt-P}$ = 2332 Hz, PtP), 20.2 (s, PdP). Mass: *m/z* 1166 ($M^+$). Anal. Calcd for $C_{40}H_{60}N_4O_4Cl_2P_4PdPt$: C, 41.23; H, 5.88; N, 4.81; Cl, 6.08; P, 10.63. Found: C, 41.28; H, 5.59; N, 4.70; Cl, 6.36; P, 10.69.

**Reaction of Complex 3a with 10 Equiv of Phenyl Isocyanide.** To a solution of complex **3a** (435 mg, 0.5 mmol) in 20 mL of THF was added phenyl isocyanide (516 mg, 5 mmol). After being stirred for 20 h under reflux, the solvent was removed in vacuo. The residue was purified by chromatography on alumina with benzene/dichloromethane (2/1 v/v) as eluent to give the brown-yellow solid **6** (444 mg, 47%).

IR: $\nu(C{\equiv}C)$ 2085, $\nu(C{=}N)$ 1640 $cm^{-1}$. $^{31}P$ NMR: $\delta$ 21.6 (s, $^1J_{Pt-P}$ = 2331 Hz, PtP), 18.7 (s, PdP). Anal. Calcd for $C_{96}H_{110}N_{10}Cl_2P_4PdPt$ ($n$ = 10): C, 60.68; H, 5.83; N, 7.37. Found: C, 60.39; H, 5.79; N, 7.19.

**Reaction of Complex 3a with 100 Equiv of Phenyl Isocyanide.** Complex **3a** (113 mg, 0.13 mmol) was added to a solution of phenyl isocyanide (1.321 g, 12.8 mmol) in 20 mL

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of THF. The reaction mixture was stirred for 20 h under reflux, and a yellow precipitate was produced. After the mixture was poured into 100 mL of methanol, the precipitate was filtered off and washed with methanol to give the yellow polymer **7a** (1.326 g, 92%).

IR: $\nu$(C=N) 1640 cm$^{-1}$. Anal. Calcd for $C_{726}H_{560}N_{100}Cl_2P_4PdPt$ ($n$ = 100): C, 77.99; H, 5.05; N, 12.53. Found: C, 78.10; H, 4.97; N, 12.44.

**Reactions of Complex 3a with 100 Equiv of *p*-Tolyl and *p*-Nitrophenyl Isocyanides.** Treatment of complex **3a** with these isocyanides by a method similar to that with phenyl isocyanide gave the yellow polymers **7b** in 88% yield and **7c** in 55% yield. In the case of the reaction with *p*-nitrophenyl isocyanide, approximately 40% of the isocyanide was recovered.

**7b**: yellow solid. IR: $\nu$(C=N) 1645 cm$^{-1}$. Anal. Calcd for $C_{826}H_{760}N_{100}Cl_2P_4PdPt$ ($n$ = 100): C, 78.84; H, 6.08; N, 11.13. Found: C, 77.23; H, 5.80; N, 10.44.

**7c**: brown-yellow solid. IR: $\nu$(C=N) 1650 cm$^{-1}$. Anal. Calcd for $C_{446}H_{300}N_{120}O_{120}Cl_2P_4PdPt$ ($n$ = 60): C, 54.91; H, 3.10; N, 17.23. Found: C, 55.59; H, 3.40; N, 16.86.

**Reaction of Complex 3b with 100 Equiv of Phenyl Isocyanide.** This reaction, carried out by a method similar to that for **3b**, gave the yellow polymer **7d** in 89% yield.

IR: $\nu$(C=N) 1640 cm$^{-1}$. Anal. Calcd for $C_{750}H_{608}N_{100}Cl_2P_4PdPt$ ($n$ = 100): C, 78.21; H, 5.32; N, 12.16. Found: C, 76.39; H, 5.40; N, 11.77.

**Reaction of Complex 3a with 100 Equiv of *p-n*-Butylphenyl Isocyanide.** To a solution of *p-n*-butylphenyl isocyanide (478 mg, 3 mmol) in 10 mL of THF was added complex **3a** (26 mg, 0.03 mmol). After being stirred for 20 h under reflux, the solution was concentrated to about 1 mL. Addition of methanol (100 mL) gave a precipitate, which was dried in vacuo to afford the yellow polymer **7e** (440 mg, 87%).

IR: $\nu$(C=N) 1650 cm$^{-1}$. Anal. Calcd for $C_{1126}H_{1360}N_{100}Cl_2P_4PdPt$ ($n$ = 100): C, 80.54; H, 8.16; N, 8.34. Found: C, 79.64; H, 8.21; N, 8.34.

**Reaction of Complex 3a with 100 Equiv of *p-n*-Octylphenyl Isocyanide.** A treatment similar to that with *p-n*-butylphenyl isocyanide gave the brown-yellow polymer **7f** (88%).

IR: $\nu$(C=N) 1650 cm$^{-1}$. Anal. Calcd for $C_{1526}H_{2160}N_{100}Cl_2P_4PdPt$ ($n$ = 100): C, 81.81; H, 9.72; N, 6.25. Found: C, 81.39; H, 9.79; N, 6.25.

**Reaction of Oligomer Complex 6 with 10 Equiv of *p*-Tolyl Isocyanide.** Complex **6** (190 mg, 0.1 mmol) was treated with *p*-tolyl isocyanide (117 mg, 1.0 mmol) in THF under reflux for 24 h. After the solvent was evaporated, the residue was purified by alumina column chromatography to give the brown solid **8** (249 mg, 81%).

IR: $\nu$(C≡C) 2090, $\nu$(C=N) 1640 cm$^{-1}$. $^{31}$P NMR: $\delta$ 21.0 (br, PtP), 17.6 (br, PdP). Anal. Calcd for $C_{176}H_{180}N_{20}Cl_2P_4PdPt$ ($n = m$ = 10): C, 68.82; H, 5.91; N, 9.08. Found: C, 67.93; H, 5.91; N, 9.12.

**Reactions of Complexes 5a and 6 with 100 Equiv of Phenyl Isocyanide.** A THF solution of complex **5a** (32 mg, 0.03 mmol) was added to a solution of phenyl isocyanide (309 mg, 3.0 mmol) in 10 mL of THF. The reaction mixture was stirred under reflux for 20 h and poured into 100 mL of methanol. The precipitate was filtered off, washed with methanol, and dried under reduced pressure to give the yellow polymer **7a** (316 mg, 93%).

The reaction of complex **6** with 100 equiv of phenyl isocyanide was performed by a method similar to that for **5a** to produce the yellow polymer **7a** in 93% yield.

**Reactions of Complexes 1a and 1b with 100 Equiv of Phenyl Isocyanide.** These reactions were carried out by a procedure similar to that for **3a**; yellow polymers were produced in 92% yield for **10a** and 90% yield for **10b**, respectively.

**10a**: yellow solid. IR: $\nu$(C=N) 1650 cm$^{-1}$. Anal. Calcd for $C_{726}H_{560}N_{100}Cl_2P_4Pd_2$ ($n$ = 100): C, 78.61; H, 5.09; N, 12.63. Found: C, 78.04; H, 4.79; N, 12.45.

**10b**: yellow solid. IR: $\nu$(C=N) 1660 cm$^{-1}$. Anal. Calcd for $C_{750}H_{608}N_{100}Cl_2P_4Pd_2$ ($n$ = 100): C, 78.82; H, 5.36; N, 12.26. Found: C, 78.15; H, 5.26; N, 12.21.

**Reactions of Complexes 1a and 1b with 100 Equiv of *p-n*-Butylphenyl and *p-n*-Octylphenyl Isocyanides.** Treatment of complex **1a** with these isocyanides by a procedure similar to that for **3a** gave brown-yellow polymers **10c** in 71% yield and **10d** in 94% yield, respectively.

**10c**: IR: $\nu$(C=N) 1645 cm$^{-1}$. Anal. Calcd for $C_{1126}H_{1360}N_{100}Cl_2P_4Pd_2$ ($n$ = 100): C, 80.97; H, 8.21; N, 8.39. Found: C, 80.95; H, 8.20; N, 8.32.

**10d**: IR: $\nu$(C=N) 1645 cm$^{-1}$. Anal. Calcd for $C_{1526}H_{2160}N_{100}Cl_2P_4Pd_2$ ($n$ = 100): C, 82.14; H, 9.76; N, 6.28. Found: C, 80.79; H, 9.75; N, 6.06.

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