ELSEVIER

A study on ligand-coupling reactions of imidoyl palladium complexes

Masashi Morishita, Hideki Amii *

Department of Chemistry, Faculty of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

Abstract

A new ligand-coupling reaction of imidoylpalladium(II) complexes is described. Heating a toluene solution of imidoylpalladium complexes gave rise to the α-diimines (1,4-diazabutadienes).
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

In various catalytic transformations, α-diimines **1** are useful catalyst ligands for transition-metal catalyzed reactions, because they are characteristic of good σ-donor and π-acceptor properties which stabilize organometallic complexes [1,2]. The diimine complexes have been utilized as catalysts for a wide repertoire of reactions, such as alkene polymerization [3a,3b], alkene–CO copolymerization [3c], aziridination [3d], allylic amination [3e], C–H bond activation [3f], Si–H bond activation [3g], Suzuki–Miyaura cross-coupling [3h], alkyne hydrogenation [3i], alkyne coupling reactions [3j,3k] and many others.

The preparative methods for α-diimines **1** have involved (a) condensation of α-diketones with primary amines [4,5], (b) homologation of bis(imidoyl chlorides) [6], and (c) dimerization of iminoacyl compounds such as aldimines [7], iminoethers [8], imidoyl iodides [9], nitriles [10] (Scheme 1). One of the effective methodologies for the preparation of α-diimines is (d) multi-component coupling of organic halides (or alkynes) and isonitriles [11,12]. In 1991, Murakami and Ito reported SmI$_2$-mediated double insertion reactions of aryl isocyanides into organic halides to afford vicinal di- and tricarbonyl compounds [11]. They proposed

stepwise insertion mechanism involving (i) initial insertion of an isocyanide into an alkylsamarium species to generate an imidoylsamarium(III) intermediate and (ii) the subsequent insertion of the second equivalent of isocyanide into a C–Sm bond in the imidoylsamarium species.

Herein, we report a new example of Pd-mediated 2:2 coupling reactions of aryl iodides and isocyanides to provide α-diimines **1** via ligand-coupling reactions of the imidoylpalladium(II) species **2** (Eq. (1)).

$$(Xy = 2,6\text{-Me}_2C_6H_3)$$

(1)
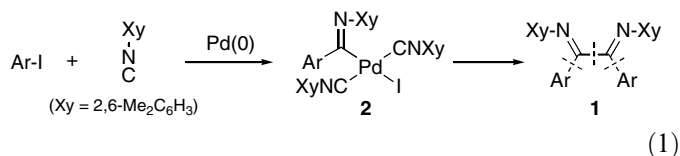
2. Results and discussion

Heating a mixture of tris(dibenzylideneacetone)dipalladium (Pd$_2$(dba)$_3$CHCl$_3$), iodobenzene (1.5 equiv to Pd) and 2,6-dimethylphenylisocyanide (XyNC, 3.0 equiv to Pd) in toluene at 100 °C led to complete consumption of the starting materials. A 2:2 coupling reaction of iodobenzene and isonitrile occurred to afford α-diimine **1a** in 34% yield (Scheme 2).

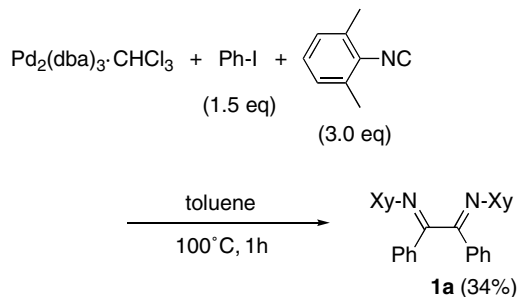The reaction to provide α-diimine **1a** would proceed via the following pathway; (i) oxidative addition of Ph–I into

---

* Corresponding author. Tel./fax: +81 78 803 5799.
E-mail address: amii@kobe-u.ac.jp (H. Amii).
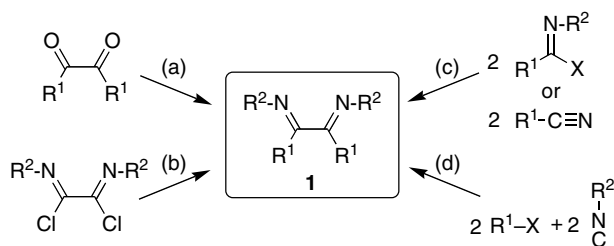
Scheme 1.

Scheme 2.

Pd(0), (ii) insertion of the isocyanide into the carbon–metal σ-bond in the phenylpalladium complex to give the imidoylpalladium(II) intermediate [13], and (iii) ligand-coupling of the imidoylpalladium complex to yield α-diimine **1a**. In order to elucidate the reaction mechanism, isolation of imidoylpalladium complexes and investigation of their reactivities are considered to be significant.

As shown in Table 1, Pd$_2$(dba)$_3$ · CHCl$_3$ was treated with iodobenzene (1.5 equiv to Pd) and XyNC (3.0 equiv to Pd) in toluene at 26 °C for 24 h, oxidative addition and isocyanide-insertion took place to give imidoylpalladium(II) complex **2a** in 48% isolated yield (entry 1). Conducting the reaction at 26 °C led to selective formation of imidoylpalladium complex **2a**, whereas heating the reaction mixture of Pd$_2$(dba)$_3$CHCl$_3$, Ph–I and XyNC at 100 °C gave α-diimine **1a** (Scheme 2). Other examples of the formation of **2** are given in Table 1. Under the same experimental conditions, the reactions of aryl iodides endowed

with either electron-donating or -withdrawing substituents on the aryl rings provided the corresponding palladium(II) isocynaide complexes **2** (entries 2, 4–6). Obviously, aryl iodides possessing electron-withdrawing substituents (Cl, CO$_2$Et and Ac) on the aryl ring provided **2d**–**f** in high yields (entries 4–6) due to their great ability of oxidative addition to Pd(0).

Next, the reactions of isolated palladium complexes **2** leading to α-diimines **1** have been investigated. Heating a toluene solution of bis(xylylisocyanide)imidoylpalladium(II) complex **2a** at 100 °C for 1 h afforded **1a**, a bis-imine of benzil in 43% yield (Table 2, entry 1).

Under the similar conditions, the ligand homocoupling reactions of imidoylpalladium complexes **2b** and **2d** which possess *p*-tolyl and *p*-chlorophenyl groups in the iminoacyl groups, provided α-diimines **1b** and **1d**, respectively (entries 2 and 3) [14]. However, the imidoylpalladium complexes having electron-withdrawing substituents, such as ethoxy-carbonyl and acetyl groups on the aryl rings of **2** did not undergo the desired ligand homocoupling reactions (entries 4 and 5).

The formation of α-diimines **1** from imidoylpalladium complexes **2** can be explained by assuming a disproportionation mechanism pictured in Scheme 3. The ligand-exchange reactions of imidoylpalladium complexes **2** provide diiodobis(isocyanide)palladium **3** and bis(imidoyl)palladium(II) intermediates **4**, which yield α-diimines **1** via reductive elimination.
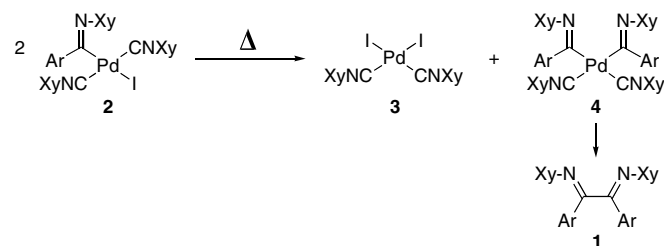
When a toluene solution of a 1:1 mixture of imidoylpalladium complexes **2b** and **2d** was heated to 100 °C, the

Table 1

Entry	R	**2** (Yield (%))
1	H	**2a** (48)
2	Me	**2b** (65)
3	OMe	**2c** (0)
4	Cl	**2d** (83)
5	CO$_2$Et	**2e** (79)
6	Ac	**2f** (84)

Table 2

Entry	R	**1**	Yield[a] (%)
1	H	**1a**	43
2	Me	**1b**	32
3	Cl	**1d**	32
4	CO$_2$Et	**1e**	[b]
5	Ac	**1f**	[b]

[a] Isolated yield.
[b] Not detected.

Scheme 3.
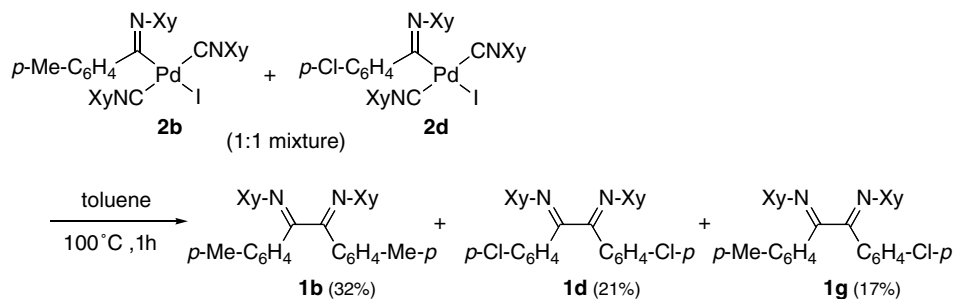
Scheme 4.

homocoupling products **1b** and **1d** were obtained in 32% and 21% yields, respectively (Scheme 4). Beside symmetrical bis-imines **1b** and **1d**, cross-coupling product **1g**, an unsymmetrical α-diimine containing both iminoacyl groups of **2b** and **2d** was formed in 17% yield. The present crossover experiment suggests that the ligand-exchange reactions of imidoylpalladium complexes **2** proceed in an intermolecular fashion [15].

In conclusion, we have demonstrated the 2:2 coupling reactions of aryl halides and isocyanides. The key intermediates are imidoylpalladium complexes **2**, which undergo intermolecular ligand-exchange reactions to provide α-diimines **1**. At present, the use of a stoichiometric amount of a Pd(0) complex is required for the present transformation. Fine-tuning of the catalyst system to make a stoichiometric transformation catalytic is one of the practical subjects worthy of further investigation.

3. Experimental

3.1. General remarks

IR spectra were measured on Perkin–Elmer FT-IR Spectrometer SPECTRUM 1000 apparatus. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded by JEOL JNM-LA apparatus and the chemical shift are reported in δ (ppm) values relative to TMS (δ 0 ppm). Coupling constants (J) are reported in hertz. Mass spectra were measured on Shimadzu GCMS-QP 2000 A instrument. Elemental analysis was performed on Yanaco CHN CORDER MT-5. All reactions were carried out under an argon atmosphere. Toluene was dried over CaH$_2$ and then distilled. All other reagents and solvents were employed without further purification. Fuji-Silysia BW-820MH silica gel was employed for column chromatography and Merck silica gel 60 PF$_{254}$ was used for preparative thin layer chromatography (PTLC).

3.2. [Pd{C(=NXy)Ph}I(XyNC)$_2$] (2a)

To a solution of Pd$_2$(dba)$_3$ · CHCl$_3$ (20 mg, 19 μmol) and XyNC (15 mg, 0.19 mmol) in 1 mL of toluene was added iodobenzene (12 mg, 57 μmol). After stirring for

24 h at 26 °C, the solvent was evaporated. Then, the residue was purified by silica gel column chromatography (hexane:AcOEt = 5:1) to afford imidoylpalladium complex **2a** (24 mg, 48%) as a yellow solid. Mp 118.0–120.0 °C (dec.). IR (KBr): 2178, 1617, 1581 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.20 (dd, J = 9.2, 1.6, 2H), 7.47–7.43 (m, 3H), 7.22 (t, J = 7.6, 2H), 7.05 (d, J = 7.6, 4H), 6.94–6.91 (m, 3H), 2.20 (s, 12H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 176.9, 145.0, 135.9, 130.0 128.1, 128.0, 126.6, 123.4, 18.8, 18.7. Anal. Calc. for C$_{33}$H$_{32}$NPdI: C, 56.30; H, 4.58; N, 5.97. Found: C, 56.15; H, 4.59; N, 5.97%.

3.3. [Pd{C(=NXy)C$_6$H$_4$Me-p}I(XyNC)$_2$] (2b)

By a procedure similar to that for **2a**, the title compound was obtained (18 mg, 65%) from Pd$_2$(dba)$_3$ · CHCl$_3$ (20 mg, 19 μmol), XyNC (15 mg, 0.19 mmol), and p-iodotoluene (13 mg, 57 μmol) as a yellow solid. Mp 118.0–119.0 °C (dec.). IR (KBr): 2171, 1621, 1588 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.20 (d, J = 8.4, 2H), 7.26–7.24 (m, 2H), 7.22 (t, J = 7.6, 2H), 7.04 (d, J = 7.6, 4H), 6.96–6.90 (m, 3H), 2.41 (s, 3H), 2.20 (s, 12H), 2.12 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 176.4, 149.6, 140.1, 136.7, 135.9, 129.9, 129.8, 128.7, 128.0, 126.6, 123.2, 110.9, 110.8, 21.3, 18.8, 18.6. Anal. Calc. for C$_{34}$H$_{34}$N$_3$PdI: C, 56.88; H, 4.77; N, 5.85. Found: C, 56.62; H, 6.62; N, 5.78%.

3.4. [Pd{C(=NXy)C$_6$H$_4$Cl-p}I(XyNC)$_2$] (2d)

By a procedure similar to that for **2a**, the title compound was obtained (23 mg, 83%) from Pd$_2$(dba)$_3$ · CHCl$_3$ (20 mg, 19 μmol), XyNC (15 mg, 0.19 mmol), and p-chloroiodobenzene (14 mg, 57 μmol) as a yellow solid. Mp 128.0–129.0 °C (dec.). IR (KBr): 2181, 1619, 1585 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.27 (d, J = 8.8, 2H), 7.43 (d, J = 8.8, 2H), 7.22 (t, J = 7.6, 2H), 7.06 (d, J = 7.6, 4H), 6.95–6.89 (m, 3H), 2.21 (s, 12H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 175.8, 143.4, 136.7, 135.9, 135.8, 130.9, 130.1, 128.8, 128.3, 128.0, 126.5, 123.4, 18.7, 18.6. Anal. Calc. for C$_{33}$H$_{31}$N$_3$ClPdI: C, 53.68; H, 4.23; N, 5.69. Found: C, 54.03; H, 4.53; N, 6.06%.

3.5. [Pd{C(=NXy)C₆H₄(CO₂Et)-p}I(XyNC)₂] (2e)

3.5. [Pd{C(=NXy)C_6H_4(CO_2Et)-p}I(XyNC)_2] (2e)

By a procedure similar to that for **2a**, the title compound was obtained (23 mg, 79%) from Pd$_2$(dba)$_3$·CHCl$_3$ (20 mg, 19 μmol), XyNC (15 mg, 0.19 mmol), and ethyl *p*-iodobenzoate (16 mg, 57 μmol) as a yellow solid. Mp 129.0–130.0 °C (dec.). IR (KBr): 2177, 1706, 1612, 1584 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.34 (d, *J* = 8.8, 2H), 8.13 (d, *J* = 8.8, 2H), 7.21 (t, *J* = 7.6, 2H), 7.05 (d, *J* = 7.6, 4H), 6.96–6.90 (m, 3H), 4.42 (q, *J* = 7.2, 2H), 2.20 (s, 12H), 2.12 (s, 6H), 1.43 (t, *J* = 7.2, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 177.0, 166.3, 149.6, 148.6, 148.5, 143.0, 135.8, 131.3, 130.1, 129.3, 128.0, 126.3 126.3, 123.5, 61.1 18.7, 18.6, 14.3. Anal. Calc. for C$_{36}$H$_{36}$N$_3$O$_2$PdI: C, 55.72; H, 4.68; N, 5.41. Found: C, 55.81; H, 4.69; N, 5.54%.

3.6. [Pd{C(=NXy)C₆H₄(COCH₃)-p}I(XyNC)₂] (2f)

3.6. [Pd{C(=NXy)C_6H_4(COCH_3)-p}I(XyNC)_2] (2f)

By a procedure similar to that for **2a**, the title compound was obtained (24 mg, 84%) from Pd$_2$(dba)$_3$·CHCl$_3$ (20 mg, 19 μmol), XyNC (15 mg, 0.19 mmol), and *p*-iodo-acetophenone (14 mg, 57 μmol) as a yellow solid. Mp 139.0–140.0 °C (dec.). IR (KBr): 2186, 1689, 1617, 1604, 1583 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37 (d, *J* = 8.4, 2H), 8.05 (d, *J* = 8.4, 2H), 7.21 (t, *J* = 7.6, 2H), 7.05 (d, *J* = 7.6, 4H), 6.96–6.90 (m, 3H), 2.67 (s, 3H), 2.20 (s, 12H), 2.12 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.8, 177.1, 149.7, 148.6, 137.6, 135.8, 130.1, 129.6, 128.2, 128.0, 126.4, 123.6, 26.8, 18.8, 18.7, 18.6. Anal. Calc. for C$_{35}$H$_{34}$N$_3$OPdI: C, 56.35; H, 4.59; N, 5.63. Found: C, 56.57; H, 4.74; N, 5.40%.

3.7. 1,2-Bis[N-(2,6-dimethylphenyl)imino]-1,2-diphenylethane (1a)

Under an argon atmosphere, a toluene solution (5.0 mL) of imidoylpalladium complex **2a** (7.9 mg, 1.1 μmol) was heated at 100 °C for 1 h. Then, the reaction mixture was concentrated under reduce pressure, purified by PTLC (hexane:AcOEt = 4:1) to afford α-diimine **1a** (1.0 mg, 43%) as a viscous yellow oil. IR (neat): 1634, 1592 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [as a mixture of two geometrical isomers, an isomer ratio of 8:1]: δ 8.26 (d, *J* = 6.4, 4H), 7.54–6.64 (m, 12H), 2.23–1.82 (m, 12H). GC–MS: *m/z* (%) 416 (0.9) [M$^+$], 401 (7.0), 208 (100), 193 (17.1), 105 (22.2), 77 (39.2). Anal. Calc. for C$_{30}$H$_{28}$N$_2$: C, 86.50; H, 6.78; N, 6.73. Found: C, 86.44; H, 6.98; N, 6.57%.

3.8. 1,2-Bis[N-(2,6-dimethylphenyl)imino]-1,2-di(4-methylphenyl)ethane (1b)

A viscous yellow oil. IR (neat): 1628, 1605, 1591 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [as a mixture of two geometrical isomers, an isomer ratio of 9:1]: δ 8.12 (d, *J* = 7.2, 4H), 7.71–6.72 (m,10H), 2.45–1.77 (m, 18H). GC–MS: *m/z* (%) 444 (1.5) [M$^+$], 429 (6.3), 222 (100), 207 (27.9)

103 (20.7), 79 (34.4). Anal. Calc. for C$_{32}$H$_{32}$N$_2$: C, 86.44; H, 7.25; N, 6.30. Found: C, 85.88; H, 7.50; N, 5.98%.

3.9. 1,2-Bis[N-(2,6-dimethylphenyl)imino]-1,2-di(4-chlorophenyl)ethane (1d)

A viscous yellow oil. IR (neat): 1633, 1591 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [as a mixture of two geometrical isomers, an isomer ratio of 4:1]: δ 8.18–6.84 (m, 14H), 2.03–1.78 (m, 12H). GC–MS: *m/z* (%) 488 (0.4) 486 (0.8), 484 (1.2) [M$^+$], 244 (33.4), 242 (100), 105 (3.8), 77 (51.4). Anal. Calc. for C$_{30}$H$_{26}$N$_2$Cl$_2$: C, 74.22; H, 5.40; N, 5.77. Found: C, 72.43; H, 5.87; N, 5.39%.

Acknowledgement

References

[1] For a review of metal–diimine complexes, see: G. van Koten, K. Vrieze, Advances in Organometallic Chemistry, vol. 21, Academic Press, New York, 1982, pp. 151–239.

[2] M. Lersch, B. Dalhus, J.E. Bercaw, J. Labinger, M. Tilset, Organometallics 25 (2006) 1055–1058.

[3] (a) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169–1204;
(b) D.J. Tempel, L.K. Johnson, R.L. Huff, P.S. White, M. Brookhart, J. Am. Chem. Soc. 122 (2000) 6686–6700;
(c) J.H. Groen, J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, Organometallics 16 (1997) 68–77;
(d) D.B. Llewellyn, D. Adamson, B.A. Arndtsen, Org. Lett. 2 (2000) 4165–4168;
(e) S. Cenini, F. Ragaini, S. Tollari, D. Paone, J. Am. Chem. Soc. 118 (1996) 11964–11965;
(f) L. Johansson, O.B. Ryan, C. Rømming, M. Tilset, J. Am. Chem. Soc. 123 (2001) 6579–6590;
(g) X. Fang, B.L. Scott, J.G. Watkin, G.J. Kubas, Organometallics 19 (2000) 4193–4195;
(h) G.A. Grasa, A.C. Hillier, S.P. Nolan, Org. Lett. 3 (2001) 1077–1080;
(i) M.W. van Laren, C.J. Elsevier, Angew. Chem., Int. Ed. 38 (1999) 3715–3717;
(j) R. van Belzen, H. Hoffmannand, C.J. Elsevier, Angew. Chem., Int. Ed. 36 (1997) 1743–1745;
(k) E. Shirakawa, H. Yoshida, Y. Nakao, T. Hiyama, J. Am. Chem. Soc. 121 (1999) 4290–4291.

[4] (a) H. tom Dieck, M. Svoboda, T. Greieser, Z. Naturforsh. 36b (1981) 823–832;
(b) H. tom Dieck, J. Dietrich, Chem. Ber. 117 (1984) 694–701;
(c) R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, R. Benedix, Recl. Trav. Chim. Pays-Bas 113 (1994) 88–89.

[5] M. Gasperini, F. Ragaini, S. Cenini, Organometallics 21 (2002) 2950–2957.

[6] R. Faust, B. Göbelt, Tetrahedron Lett. 38 (1997) 8017–8020.

[7] (a) S.J. Walia, J. Singh, S.M. Chattha, M. Satyanarayana, Tetrahedron Lett. 3 (1969) 195–198;

(b) W. Jin, Y. Makioka, Y. Taniguchi, T. Kitamura, Y. Fujiwara, Chem. Commun. (1998) 1101–1102;
(c) W. Jin, Y. Makioka, Y. Taniguchi, T. Kitamura, Y. Fujiwara, J. Org. Chem. 66 (2001) 514–520.

[8] R. Jaunin, G. Sechaud, Helv. Chim. Acta 37 (1954) 2088–2093.

[9] (a) H. Amii, M. Kohda, M. Seo, K. Uneyama, Chem. Commun. (2003) 1752–1753;
(b) J.P. Sadighi, L.M. Henling, J.A. Labinger, J.E. Bercaw, Tetrahedron Lett. 44 (2003) 8073–8076.

[10] B.N. Diel, P.J. Deardorff, C.M. Zelenski, C. Incarvito, L. Liable-Sands, A.M. Rheingold, Inorg. Chim. Acta 357 (2004) 3902–3910.

[11] M. Murakami, H. Masuda, T. Kawano, H. Nakamura, Y. Ito, J. Org. Chem. 56 (1991) 1–2.

[12] N. Chatani, S. Murai, T. Hanafusa, Chem. Exp. 6 (1991) 339–342.

[13] (a) S. Otsuka, A. Nakamura, T. Yoshida, J. Am. Chem. Soc. 91 (1969) 7196–7198;
(b) Y. Yamamoto, H. Yamazaki, Bull. Chem. Soc. Jpn. 43 (1970) 2653;
(c) S. Otsuka, M. Naruto, T. Yoshida, A. Nakamura, J. Chem. Soc., Chem. Commun. (1972) 396–397;
(d) R. Usón, J. Forniés, P. Espinet, E. Lalinde, P.G. Jones, G.M. Sheldrich, J. Chem. Soc., Dalton Trans. (1982) 2389–2395;
(e) R. Usón, J. Forniés, P. Espinet, A. Garcia, C.F. Foces, F.H. Cano, J. Organomet. Chem. 282 (1985) C35–C38;
(f) K. Onitsuka, K. Yanai, F. Takei, T. Joh, S. Takahashi, Organometallics 13 (1994) 3862–3867;
(g) Y. Kayaki, I. Shimizu, A. Yamamoto, Bull. Chem. Soc. Jpn. 70 (1997) 917–927;
(h) J. Vicente, I. Saura-Llamas, C. Grunwald, C. Alcaraz, P.G. Jones, D. Bautista, Organometallics 21 (2002) 3587–3595;
(i) J. Vicente, J.A. Abad, E. Martinez-Viviente, P.G. Jones, Organometallics 21 (2002) 4454–4467.

[14] Although the yields of α-diimines **1** were low, other organic compounds endowed with imidoyl moieties were not detected. After heating of the imidoylpalladium complexes **2** at 100 °C, we observed the formation of $[PdI(CNXy)]_n$ oligomers [Ref. [13h]] besides α-diimines.

[15] There exists a possibility of other reaction pathway such as scrambling of the aryl groups in the Pd complexes **2**. When a mixture of the imidoylpalladium complex **2b** and p-Cl–C_6H_4–I (1 equiv) was heated at 100 °C for 1 h, homocoupling product **1b** was obtained selectively in 60% yield. And also heating a mixture of Pd complex **2d** and p-Me–C_6H_4–I (1 equiv) under the same conditions gave α-diimine **1d** in 38% yield. In each experiment, the formation of the cross-coupling product **1g** was not observed. These results suggest that the imidoyl–imidoyl coupling reactions would proceed via bimolecular ligand-exchange pathway.