Cross-Coupling Reactions

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Rational Design of a Palladium-Catalyzed C_{sp}–C_{sp} Cross-Coupling Reaction Inspired by Kinetic Studies**

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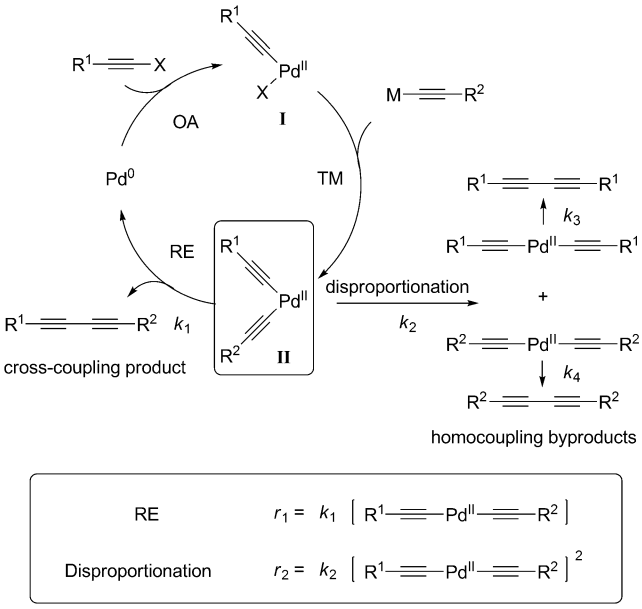
Owing to the unique chemical and physical properties of diynes, along with their wide applications in pharmaceuticals and materials chemistry, these compounds have attracted the attention of scientists for decades.[1] However, the synthesis of diynes still remains a great challenge. Compared with the intensively developed synthetic methods for biaryl and arylalkynes (C_{sp^2}–C_{sp^2} and C_{sp^2}–C_{sp} couplings), the methods for C_{sp}–C_{sp} coupling reactions are rare, and lack high efficiency in most cases.[2] To date, the Glaser–Hay coupling reaction, which was developed more than 100 years ago, still remains the most commonly used method to prepare conjugated diynes, mainly through the homo-coupling of terminal alkynes.[1a,3] Cadiot-Chodkiewicz cross-coupling, which involves alkynyl halides as electrophiles and terminal alkynes as nucleophiles, provides a solution to access some unsymmetrical 1,3-diynes in the presence of copper salts.[1a,4] Although powerful for some syntheses, this protocol suffers from poor selectivity, low efficiency, often complicated reaction conditions, and always produces homocoupled by-products.[1a,2j,k,5] Recently, some modified Cu-catalyzed C_{sp}–C_{sp} cross-couplings have also been reported for the construction of unsymmetrical diynes.[6]

Pd-catalysis has been extremely successful in various types of bond formation reactions,[2a–d,i,j] which also exhibit great potential for the synthesis of diynes. Recently, several Pd-catalyzed C_{sp}–C_{sp} cross-coupling reactions have been developed.[5,7] Improvements have been reported, although increasing the selectivity and turnover number (TON) still remains a challenge. A general catalytic cycle for Pd-catalyzed C_{sp}–C_{sp} cross-coupling is outlined in Scheme 1.[2j] We speculated that there is competition between reductive elimination of and disproportionation of intermediate **II**. The former leads to the cross-coupling product, whereas the latter results in homocoupled by-products. This inherent problem limits the general application of this synthetic method and makes favoring the reductive elimination process critical.



Scheme 1. Putative pathways for Pd-catalyzed C_{sp}–C_{sp} cross-coupling. OA = oxidative addition, TM = transmetalation, RE = reductive elimination.

Some efforts employing steric or π-acid ligands have been developed to promote the reductive elimination.[8] On the other hand, based on the kinetics rate law for the reductive elimination and disproportionation (Scheme 1), simply decreasing the loading of the Pd catalyst might be a solution to address the challenge. As indicated in Scheme 1, the reductive elimination rate (r_1) is first order in [**II**], and the rate of the disproportionation process (r_2) is second order in [**II**]. Thus, reducing the loading of Pd-catalyst would theoretically favor reductive elimination over disproportionation. Simply speaking, by reducing the Pd catalyst loading to 1/100, r_1 will be decreased to 1/100, but r_2 will be decreased to 1/10000. It seems clear that the reductive elimination pathway can be enhanced in this way.

Recently, a ligand-free $Pd(OAc)_2$ (OAc = acetate) catalytic system was extensively studied in which palladium nanoparticles (NPs) were proposed to be the active catalytic species.[7b,9] Many of these Pd-catalyzed reactions were reported with the use of very low catalyst loadings. This

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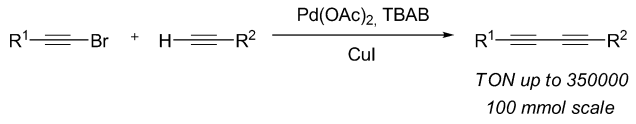
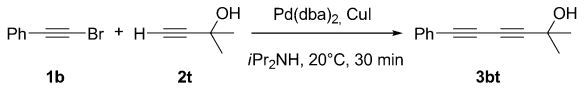
encouraged us to speculate that Pd(NPs) might also be a suitable catalyst for diynes synthesis. In fact, if Pd at the ppm level could effectively catalyze the reaction, not only there is economic value of the process (high TON), but it is also beneficial for addressing Pd-contamination problems in the work-up process. Even without a special protocol to remove the Pd species, the Pd contamination in the products would likely be within the limit of regulation because of the original lower loading of the Pd precursor. Herein, we describe a highly efficient and selective Pd-catalyzed C_{sp}–C_{sp} cross-coupling reaction with low catalyst loadings (Scheme 2).



Scheme 2. Pd-catalyzed C_{sp}–C_{sp} cross-coupling reaction. OAc = acetate, TBAB = tetrabutylammonium bromide.

Our initial efforts focused on the reaction of (bromoethynyl)benzene (**1b**) and 2-methylbut-3-yn-2-ol (**2t**). In the presence of 2 mol% $Pd(dba)_2$ (dba = dibenzylideneacetone), **3bt** was obtained in 78% yield and with 92:8 selectivity (Table 1, entry 1). Interestingly, increasing the Pd catalyst loading resulted in lower selectivity (Table 1, entries 2–4).

Table 1: The impact of $Pd(dba)_2$ loading on selectivity.[a]



Entry	$Pd(dba)_2$ [mol%]	Yield of **3bt** [%][b]	Selectivity[c]
1	2	78	92:8
2	4	75	91:9
3	6	80	91:9
4	8	75	89:11

[a] Reaction conditions: **1b** (1.0 mmol), **2t** (1.0 mmol), CuI (2 mol%) in iPr_2NH (3 mL) as solvent at 20°C; the amounts of $Pd(dba)_2$ are given in the table. [b] Determined by GC with biphenyl as an internal standard. [c] Molar ratio of **3bt**/1,4-diphenylbutadiyne. dba = dibenzylideneacetone.

Further kinetic investigation of this reaction was conducted (Figure 1). The kinetic profiles of [**3bt**] vs. time (Figure 1a) almost overlapped, regardless of the initial concentration of $Pd(dba)_2$. As shown in Figure 1b, plotting the reaction initial rate vs. Pd loading showed a zero-order kinetic dependence on the mol% of Pd used. This observation is abnormal, and clearly indicated that the roles of Pd catalysts in this reaction are complicated.

The selectivity of the Pd catalyzed C_{sp}–C_{sp} cross-coupling shown in Table 1 encouraged us to further examine the effectiveness of unsymmetrical 1,3-diynes synthesis. After some attempts, 4-bromo-2-methylbut-3-yn-2-ol (**1a**) and phenylacetylene (**2a**) were found to be better model substrates for further method development. Gratifyingly, upon reducing the Pd catalyst loading to 0.1 mol%, **1a** and **2a** gave improved results, producing the desired product in 96% yield in the presence of additive TBAB (tetrabutylammonium bromide) at 70°C (Table 2, entry 1). Usually, tetraalkylamonium halides are used as stabilizers for NPs, which would prevent them from further aggregation and precipitation from the reaction, as well as making the catalyst active.[10] The effects of different Pd and TBAB loadings in this C_{sp}–C_{sp} cross-coupling were also investigated (Table 2). In the absence of Pd or Cu salts, almost no reaction occurred (Table 2, entries 2 and 3). Without TBAB, the reaction yield decreased dramatically (Table 2, entry 4). Moreover, the combination of $Pd(OAc)_2$ and TBAB afforded a better result (Pd/TBAB = 1:30; Table 2, entry 5). However, other ratios of Pd/TBAB led to reduced yields (Table 2, entries 6–9).

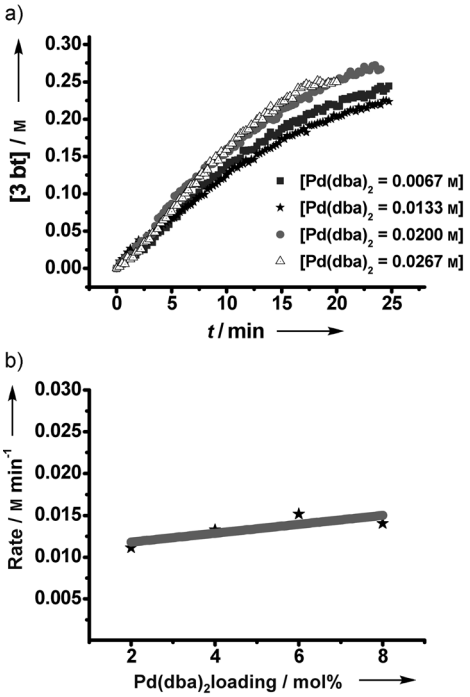
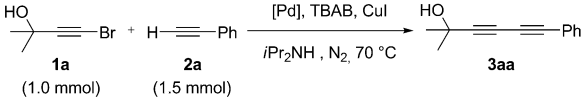


Figure 1. Kinetic profiles with different $Pd(dba)_2$ loadings. a) Concentration of **3bt** vs. time curve for the reactions of $Pd(dba)_2$ at 0.0067–0.0267 M monitored by in situ IR spectroscopy. Reaction conditions: **1b** (1.0 mmol), **2t** (1.0 mmol), CuI (2 mol%) in iPr_2NH (3 mL) as solvent at 20°C; the loading of $Pd(dba)_2$ is 2–8 mol%. b) Initial rate vs. Pd loading curve for the reactions.

To our delight, when 0.01 mol% $Pd(OAc)_2$ was employed, more than 99% of the cross-coupling product was obtained without any 1-haloalkyne homocoupled by-product (Table 2, entry 11). Varying the amount of CuI and iPr_2NH solvent also slightly affected the chemical yield (Table 2, entries 10–13).

The substrate scope of this transformation is shown in Scheme 3. With 4-bromo-2-methylbut-3-yn-2-ol (**1a**) as a substrate, the reaction was readily extended to a variety of aryl terminal alkynes in high yields. Both electron-donating and -withdrawing functional groups, such as Me, Ph, OMe, NMe_2, CN, acetyl (Ac), and CO_2Et, were well tolerated (Scheme 3,

Table 2: Conditions optimization for the C_{sp}–C_{sp} cross-coupling of 4-bromo-2-methylbut-3-yn-2-ol **1a** and phenylacetylene **2a**.[a]



1a (1.0 mmol) **2a** (1.5 mmol) **3aa**

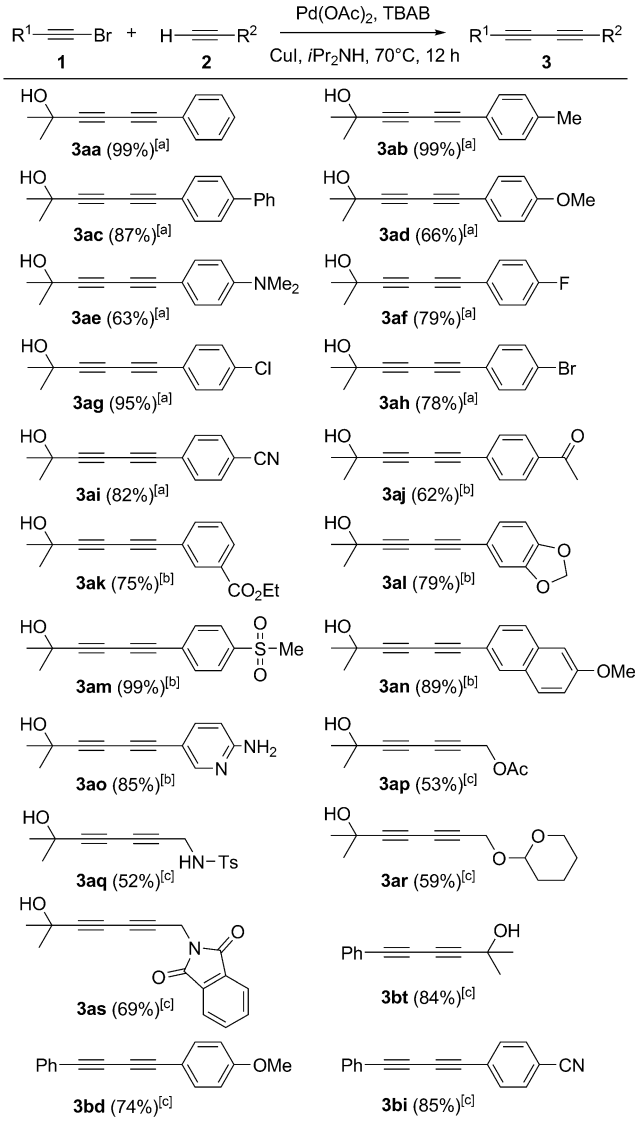
Entry	[Pd] (mol%)	TBAB [mol%]	CuI [mol%]	iPr_2NH [mL]	Yield [%][b]
1	$Pd(dba)_2$ (0.1)	3.0	2	5	96
2	none	none	2	5	trace
3	$Pd(dba)_2$ (0.1)	3.0	none	5	trace
4	$Pd(dba)_2$ (0.1)	none	2	5	58
5	$Pd(OAc)_2$ (0.1)	3.0	2	5	97
6	$Pd(OAc)_2$ (0.1)	1.0	2	5	77
7	$Pd(OAc)_2$ (0.1)	0.5	2	5	87
8	$Pd(OAc)_2$ (0.1)	0.1	2	5	73
9	$Pd(OAc)_2$ (0.1)	10.0	2	5	80
10	$Pd(OAc)_2$ (0.01)	0.3	2	5	94
11	**$Pd(OAc)_2$ (0.01)**	**0.3**	**0.2**	**5**	**>99**
12	$Pd(OAc)_2$ (0.01)	0.3	0.2	3	97
13	$Pd(OAc)_2$ (0.01)	0.3	0.2	10	97

[a] Reactions were carried out on **1a** (1.0 mmol) in the presence of [Pd]/TBAB and CuI in iPr_2NH solvent at 70°C. [b] Yield determined by GC analysis with biphenyl as an internal standard. dba = dibenzylideneacetone, TBAB = tetrabutylammonium bromide.

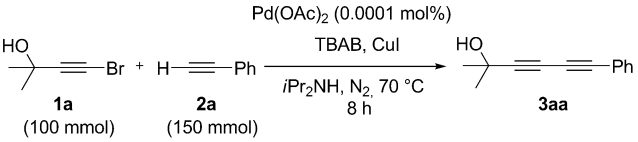
3ab–**3ae** and **3ai**–**3ak**). Aryl alkynes bearing fluoro, chloro, or bromo groups could also be introduced to give the desired cross-coupling products, demonstrating the exceptional chemoselectivity of this method (Scheme 3, **3af**–**3ah**). Furthermore, terminal alkynes containing benzodioxole, methylsulfonylbenzene, methoxynaphthalene, or aminopyridine moieties could be converted into the corresponding unsymmetrical 1,3-diyne scaffold in good to excellent yields (Scheme 3, **3al**–**3ao**). Alkyl terminal alkynes such as prop-2-ynyl acetate (**2p**), 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (**2q**), 2-(prop-2-ynyloxy)tetrahydro-2*H*-pyran (**2r**), and 2-(prop-2-ynyl)isoindoline-1,3-dione (**2s**) also reacted well under the standard conditions (Scheme 3, **3ap**–**3as**). Moreover, (bromoethynyl)benzene (**1b**) reacted smoothly with both aryl and alkyl terminal alkynes to afford the corresponding diyne products in good yields (Scheme 3, **3bt, 3bd,** and **3bi**).

This transformation could be readily scaled up. In fact, when 100 mmol (16.3 g) of **1a** was employed with $Pd(OAc)_2$ (0.0001 mol%) as the catalyst precursor, a TON of up to 350000 was achieved, along with a turnover frequency (TOF) of up to 43750 h^{-1} (Scheme 4). No homocoupled by-product was observed in this reaction, indicating that the selectivity was still high. To the best of our knowledge, this is the highest TON for the Pd-catalyzed C_{sp}–C_{sp} cross-coupling reaction reported to date.

To verify whether Pd(NPs) were involved in this cross-coupling reaction, a ligand poisoning experiment was carried out with in situ IR spectroscopy.[11] As shown in Figure 2, under the standard conditions this transformation proceeded smoothly, providing 96% yield of product (TON = 9600, TOF = 9600 h^{-1}) and the kinetic profile of [**3aa**] vs. time fit a nearly straight line. As a comparison, when the ligand PPh_3 was added into the reaction at 30 min, an obvious inflection point was observed and the reaction was suppressed.



Scheme 3. Substrate scope for the reactions of bromoalkynes **1** and terminal alkynes **2**. Isolated yields. [a] Reaction conditions: **1** (1.0 mmol) and **2** (1.5 mmol) in the presence of $Pd(OAc)_2$ (0.01 mol%), TBAB (0.3 mol%) and CuI (0.2 mol%) in iPr_2NH (5 mL) at 70°C. [b] Reaction conditions: **1** (0.5 mmol) and **2** (0.75 mmol) in the presence of $Pd(OAc)_2$ (0.01 mol%), TBAB (0.3 mol%) and CuI (2 mol%) in iPr_2NH (3 mL) at 70°C. [c] Reaction conditions: **1** (1.0 mmol) and **2** (1.5 mmol) in the presence of $Pd(OAc)_2$ (0.01 mol%), TBAB (0.3 mol%) and CuI (2 mol%) in iPr_2NH (5 mL) at 70°C.



Yield: 35% TON: 350000 TOF: 43750 h^{-1}

Scheme 4. Gram scale experiment. Reaction conditions: **1a** (100 mmol) and **2a** (150 mmol) in the presence of $Pd(OAc)_2$ (0.0001 mol%), TBAB (0.3 mol%) and CuI (2 mol%) in iPr_2NH (150 mL) at 70°C. Yield of isolated product shown.

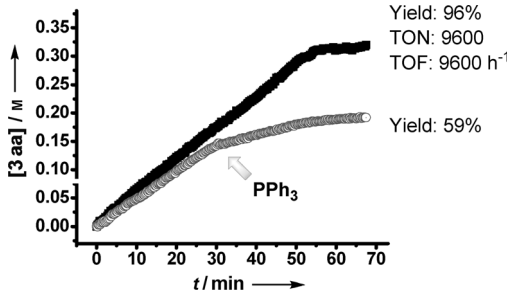


Figure 2. Concentration of **3 aa** vs. time curve for the reaction of **1 a** (0.33 M) with **2 a** (0.5 M) and $Pd(OAc)_2$ (0.01 mol%) as the catalyst precursor in the presence of TBAB (0.3 mol%) monitored by in situ IR spectroscopy at 70°C (■); ○: the same conditions, but with PPh_3 (0.05 mol%) added at 30 min.

Kinetic studies on the effect of the Pd catalyst loading were also performed by in situ IR spectroscopy (Pd loading of 0.008–0.5 mol%). As shown in Figure 3, the reaction rate was

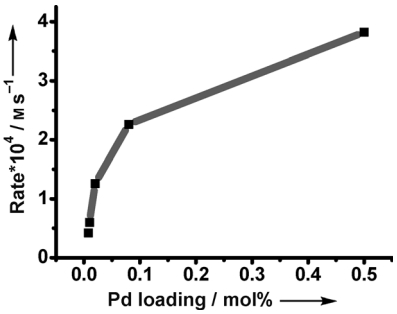


Figure 3. Rate vs. Pd loading curve for the reactions of **1 a** (0.33 M) and **2 a** (0.5 M), with different concentrations of $Pd(OAc)_2$ monitored by in situ IR spectroscopy at 70°C.

clearly not first order in Pd. The kinetic behavior of the catalyst indicated that the real catalytic species have multiple roles in the reaction vessel, and only part of the Pd species employed actually catalyzed the C_{sp}–C_{sp} cross-coupling. One rationalization for this observation is the existence of Pd(NPs).

In summary, guided by kinetics investigations, we have developed an efficient highly selective Pd-catalyzed C_{sp}–C_{sp} cross-coupling reaction between terminal alkynes and 1-bromoacetylenes. High selectivity and good to excellent yields could be attained with low catalyst loadings (only 0.0001–0.01 mol% of Pd is required). Preliminary kinetic studies indicated that this transformation might involve Pd(NPs). The TON of this highly active Pd-catalyst was up to 350000. From a synthetic point of view, this protocol is an extremely simple and efficient way to construct unsymmetrical 1,3-diynes under mild conditions.

Experimental Section

General procedure for the synthesis of unsymmetrical 1,3-diynes (**3 aa**): A mixture of 4-bromo-2-methylbut-3-yn-2-ol **1 a** (1.0 mmol), phenylacetylene **2 a** (1.5 mmol), TBAB (0.3 mol%), and CuI (0.2 mol%) in iPr_2NH (5 mL) was stirred under N_2 at 70°C for 5 min. Then $Pd(OAc)_2$ (0.01 mol%) was added in one portion. After reaction completion, as indicated by TLC and GC, the mixture was quenched with dilute hydrochloric acid (4 mL, 2 M), and the solution was extracted with ethyl acetate (3 × 15 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 20:1) to afford **3 aa** in 99% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$–7.40 (m, 2H), 7.26–7.24 (m, 3H), 2.34 (br, 1H), 1.52 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 132.7$, 129.4, 128.6, 121.7, 86.9, 79.0, 73.4, 67.3, 65.9, 31.3 ppm.

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[1] a) P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740–2767; *Angew. Chem. Int. Ed.* **2000**, *39*, 2632–2657; b) F. Diederich, *Chem. Commun.* **2001**, 219–227; c) S. Eisler, A. D. Slepkov, E. Elliott, T. Luu, R. McDonald, F. A. Hegmann, R. R. Tykwinski, *J. Am. Chem. Soc.* **2005**, *127*, 2666–2676; d) J. A. Marsden, M. M. Haley, *J. Org. Chem.* **2005**, *70*, 10213–10226; e) M. L. Lerch, M. K. Harper, D. J. Faulkner, *J. Nat. Prod.* **2003**, *66*, 667–670; f) Y. S. Kim, S. H. Jin, S. I. Kim, D. R. Hahn, *Arch. Pharmacal Res.* **1989**, *12*, 207–213; g) H. Matsunaga, M. Katano, H. Yamamoto, H. Fujito, M. Mori, K. Takata, *Chem. Pharm. Bull.* **1990**, *38*, 3480–3482; h) M. Ladika, T. E. Fisk, W. W. Wu, S. D. Jons, *J. Am. Chem. Soc.* **1994**, *116*, 12093–12094; i) Y. Nakai, I. Sakakibara, K. Hirakura, S. Terabayashi, S. Takeda, *Chem. Pharm. Bull.* **2005**, *53*, 1580–1581; j) D. A. M. Egbe, E. Birckner, E. Klemm, *J. Polym. Sci. Part A* **2002**, *40*, 2670–2679.

[2] a) F. Diederich, P. J. Stang, *Metal-catalyzed cross-coupling reactions*, Wiley-VCH, New York, **1998**; b) E.-i. Negishi, A. d. Meijere, *Handbook of organopalladium chemistry for organic synthesis*, Wiley-Interscience, New York, **2002**; c) A. d. Meijere, F. Diederich, *Metal-catalyzed cross-coupling reactions*, 2nd, completely rev. and enl. ed., Wiley-VCH, Weinheim, **2004**; d) L. Anastasia, E.-i. Negishi, *Handb. Organopalladium Chem. Org. Synth.* **2002**, *1*, 311–334; e) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1469; f) A. Suzuki, *Chem. Commun.* **2005**, 4759–4763; g) L.-C. Campeau, K. Fagnou, *Chem. Commun.* **2006**, 1253–1264; h) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447–2464; i) K. Sonogashira, *Handb. Organopalladium Chem. Org. Synth.* **2002**, *1*, 493–529; j) E.-I. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017; k) A. L. K. Shi Shun, R. R. Tykwinski, *Angew. Chem.* **2006**, *118*, 1050–1073; *Angew. Chem. Int. Ed.* **2006**, *45*, 1034–1057; l) R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874–922; m) H. Doucet, J.-C. Hierso, *Angew. Chem.* **2007**, *119*, 850–888; *Angew. Chem. Int. Ed.* **2007**, *46*, 834–871; n) R. Chinchilla, C. Najera, *Chem. Soc. Rev.* **2011**, *40*, 5084–5121.

[3] a) C. Glaser, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422–424; b) C. Glaser, *Ann. Chem. Pharm.* **1870**, *154*, 137–171; c) A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320–3321.

[4] a) W. Chodkiewicz, P. Cadiot, *C. R. Hebd. Seances Acad. Sci.* **1955**, *241*, 1055–1057; b) W. Chodkiewicz, *Ann. Chim. (Paris)* **1957**, *2*, 819–869.

[5] M. Alami, F. Ferri, *Tetrahedron Lett.* **1996**, *37*, 2763–2766.

[6] a) H.-F. Jiang, A. Z. Wang, *Synthesis* **2007**, 1649–1654; b) F. Bellina, A. Carpita, L. Mannocci, R. Rossi, *Eur. J. Org. Chem.* **2004**, 2610–2619; c) B. W. Gung, H. Dickson, *Org. Lett.* **2002**, *4*,

2517 – 2519; d) S. López, F. Fernandez-Trillo, P. Midon, L. Castedo, C. Saa, *J. Org. Chem.* **2006**, *71*, 2802 – 2810; e) J. M. Montierth, D. R. DeMario, M. J. Kurth, N. E. Schore, *Tetrahedron* **1998**, *54*, 11741 – 11748; f) S. Wang, L. Yu, P. Li, L. Meng, L. Wang, *Synthesis* **2011**, 1541 – 1546; g) M. Yu, D. Pan, W. Jia, W. Chen, N. Jiao, *Tetrahedron Lett.* **2010**, *51*, 1287 – 1290.

[7] a) W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang, A. Lei, *J. Am. Chem. Soc.* **2008**, *130*, 14713 – 14720; b) H. Li, L. Wang, M. Yang, Y. Qi, *Catal. Commun.* **2012**, *17*, 179 – 183; c) S. Kim, S. Kim, T. Lee, H. Ko, D. Kim, *Org. Lett.* **2004**, *6*, 3601 – 3604; d) S. A. Nye, K. T. Potts, *Synthesis* **1988**, 375 – 377; e) J. Wityak, J. B. Chan, *Synth. Commun.* **1991**, *21*, 977 – 979; f) C. Amatore, E. Blart, J. P. Genet, A. Jutand, S. Lemaire-Audoire, M. Savignac, *J. Org. Chem.* **1995**, *60*, 6829 – 6839.

[8] a) E. A. Bercot, T. Rovis, *J. Am. Chem. Soc.* **2002**, *124*, 174 – 175; b) I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, *Org. Lett.* **2004**, *6*, 4435 – 4438; c) R. Shintani, W.-L. Duan, T. Nagano, A. Okada, T. Hayashi, *Angew. Chem.* **2005**, *117*, 4687 – 4690; *Angew. Chem. Int. Ed.* **2005**, *44*, 4611 – 4614; d) Z.-Q. Wang, C.-G. Feng, M.-H. Xu, G.-Q. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 5336 – 5337; e) D. B. G. Williams, M. L. Shaw, *Tetrahedron* **2007**, *63*, 1624 – 1629; f) X. Luo, H. Zhang, H. Duan, Q. Liu, L. Zhu, T. Zhang, A. Lei, *Org. Lett.* **2007**, *9*, 4571 – 4574.

[9] a) J. D. Aiken III, R. G. Finke, *J. Mol. Catal. A* **1999**, *145*, 1 – 44; b) D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884 – 1894; c) D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem.* **2005**, *117*, 8062 – 8083; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852 – 7872; d) A. Balanta, C. Godard, C. Claver, *Chem. Soc. Rev.* **2011**, *40*, 4973 – 4985; e) H. Bönnemann, R. M. Richards, *Eur. J. Inorg. Chem.* **2001**, 2455 – 2480; f) J. Durand, E. Teuma, M. Gomez, *Eur. J. Inorg. Chem.* **2008**, 3577 – 3586; g) A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181 – 5203; h) B. F. G. Johnson, *Top. Catal.* **2003**, *24*, 147 – 159; i) J. Liu, Y. Deng, H. Wang, H. Zhang, G. Yu, B. Wu, H. Zhang, Q. Li, T. B. Marder, Z. Yang, A. Lei, *Org. Lett.* **2008**, *10*, 2661 – 2664; j) M. Moreno-Mañas, R. Pleixats, *Acc. Chem. Res.* **2003**, *36*, 638 – 643; k) M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559 – 1563; l) M. B. Thathagar, P. J. Kooyman, R. Boerleider, E. Jansen, C. J. Elsevier, G. Rothenberg, *Adv. Synth. Catal.* **2005**, *347*, 1965 – 1968; m) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317 – 341; n) A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285 – 3288.

[10] a) M. T. Reetz, E. Westermann, *Angew. Chem.* **2000**, *112*, 170 – 173; *Angew. Chem. Int. Ed.* **2000**, *39*, 165 – 168; b) M. T. Reetz, E. Westermann, R. Lohmer, G. Lohmer, *Tetrahedron Lett.* **1998**, *39*, 8449 – 8452; c) Q. Yao, E. P. Kinney, Z. Yang, *J. Org. Chem.* **2003**, *68*, 7528 – 7531; d) K. Yu, W. Sommer, M. Weck, C. W. Jones, *J. Catal.* **2004**, *226*, 101 – 110.

[11] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317 – 341.

