CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200900022

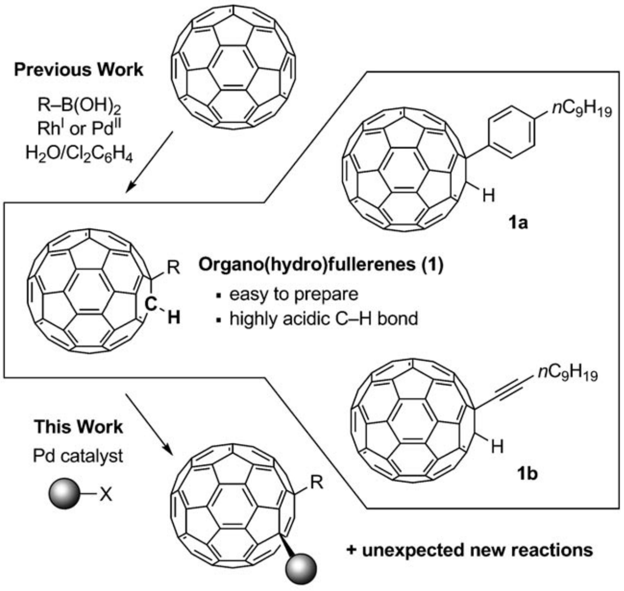
Palladium-Catalyzed Carbon–Carbon Bond Formation and Cleavage of Organo(hydro)fullerenes

Masakazu Nambo and Kenichiro Itami*[a]

Nanocarbons such as fullerenes and carbon nanotubes have attracted the interest of scientists from many disciplines due to their unique structures and properties.[1] The chemical modification of fullerenes has proven to be a promising approach for the preparation of new nanocarbon-based materials, providing the opportunity to tune the properties of these interesting materials. A number of privileged reactions for the functionalization of fullerenes have emerged.[1] Cyclopropanation with α-halomalonates,[2] Diels–Alder-type [4+2] cycloadditions with 1,3-dienes,[3] [3+2] cycloaddition with azomethine ylides,[4] nucleophilic addition with organolithium and organomagnesium reagents,[5] multifold addition with organocopper reagents,[6] radical additions,[7] and electrophilic additions[8] are the representative synthetic methods that have contributed significantly to the development of this field. The chemical modification of carbon nanotubes[9] or graphene sheets[10] is another emerging area of extensive research. However, despite these significant advances, the synthetic toolbox for fullerene functionalization remains comparatively limited. Thus a novel synthetic methodology is required for the development of new nanocarbon-based materials.

Transition-metal catalysis has been a fundamental tool in organic synthesis, enabling a variety of chemical transformations that are otherwise difficult or impossible to achieve with traditional methods.[11] In many instances, remarkable levels of reactivity/selectivity control in chemical transformations can be accomplished. To explore new directions in metal catalysis and nanocarbon chemistry,[12] we recently initiated a program aimed at developing new functionalization chemistry of nanocarbons using transition-metal catalysts.[13] Herein we report several Pd-catalyzed reactions of organo(hydro)fullerenes. In addition to anticipated coupling reactions, unexpected new C–C bond forming and cleaving processes were also uncovered during this study.

As our initial foray into the area of nanocarbon chemistry, we developed a new organoboron-based functionalization of C_{60} catalyzed by Rh^{I} or Pd^{II} complexes (Scheme 1).[13] These reactions enable the introduction of various organic fragments and a hydrogen atom to the fullerene surface in a highly regioselective and mono-addition selective manner.[13] A notable feature of the resultant hydrofullerenes **1** is that they possess an acidic C–H bond reflecting the highly conjugated fullerene backbone.[14] For example, Fagan and Evans have experimentally determined the pK_a of $t\mathrm{BuC_{60}H}$ to be 5.7 (in DMSO at 25 °C) by voltammetric techniques.[14a] Geerlings has also identified several highly acidic organo-



Scheme 1. Organo(hydro)fullerenes **1** as key molecules in fullerene functionalization.

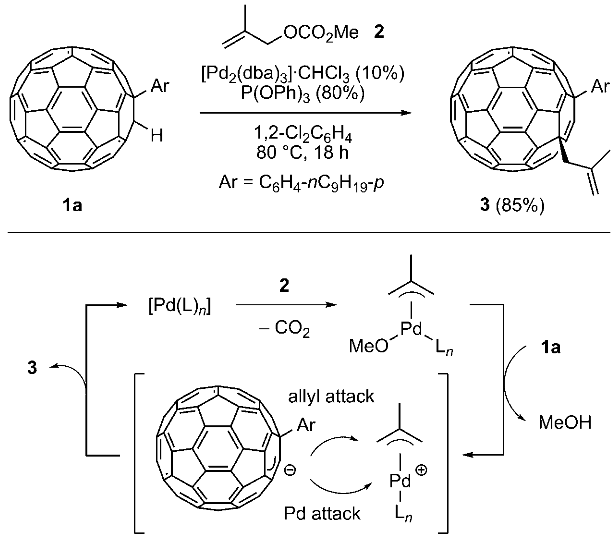
---

[a] M. Nambo, Prof. Dr. K. Itami
Department of Chemistry
Graduate School of Science
Nagoya University, and
PRESTO, Japan Science and Technology Agency
Chikusa, Nagoya 464-8602 (Japan)
Fax: (+81) 52-788-6098
E-mail: itami@chem.nagoya-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200900022.

(hydro)fullerenes by theoretical calculations.[14c] Considering the ample precedents demonstrating that Pd catalysts can functionalize a range of acidic C–H bonds of organic molecules,[15] we surmised that such catalytic transformations should also be possible at the C–H bonds of organo(hydro)fullerenes **1** (Scheme 1).

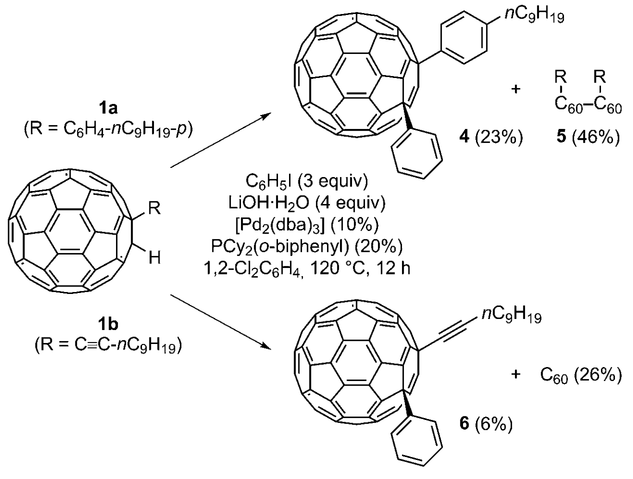
As a first model reaction of C–H bond functionalization of **1**, we examined the Pd-catalyzed allylation reaction.[15] In early experiments, the use of methallyl methyl carbonate (**2**) was found to be optimal as a source of allylic electrophile.[15–17] As for the Pd catalyst, the Pd/P(OPh)$_3$ complex turned out to be the best choice. For example, the treatment of aryl(hydro)fullerene **1a** (1 equiv) with **2** (2 equiv) in 1,2-$Cl_2C_6H_4$ at 80 °C under the influence of [$Pd_2(dba)_3$]·$CHCl_3$ (10 mol %; dba = *trans,trans*-dibenzylideneacetone) and P(OPh)$_3$ (80 mol %) furnished the C–H bond allylation product **3** in 85 % isolated yield (Scheme 2).[18] The ^{13}C NMR spectrum of **3** showed 55 signals for sp^2-hybridized carbon atoms (though there exist some overlapped peaks), indicating the C_1-symmetric structure (1,4-isomer) of the product. The magnetic non-equivalence of two hydrogen atoms between C_{60} core and the vinyl group (δ = 3.64 and 3.73 ppm) in the ^{1}H NMR spectrum also indicates the 1,4-isomeric structure.[19] However, without an X-ray crystal structure analysis, the proposed structure is tentative and we cannot completely rule out other isomers at this stage.



Scheme 2. Pd-catalyzed C–H bond allylation of organo(hydro)fullerene **1a**.

A possible mechanism for this catalytic allylation reaction is also depicted in Scheme 2. We believe that the catalytic cycle is initiated by the reaction of [Pd^0(L)$_n$] (L = ligand) with **2** generating (π-allyl)Pd^{II}–OMe species,[16] which then deprotonates the acidic hydrogen atom of **1a**. The reaction of the thus-generated delocalized fullerenyl anion and cationic (π-allyl)Pd^{II} species would lead to the coupling products **3** with the regeneration of [Pd^0(L)$_n$]. The preferential attack of fullerenyl anion at 4-position might be due to steric reasons. The mechanism of the key C_{60}–allyl bond formation may be either 1) nucleophilic attack of fullerenyl anion on the allyl ligand on Pd, or 2) its attack on the Pd center followed by subsequent C_{60}–allyl bond-forming reductive elimination from diorganopalladium(II) species.

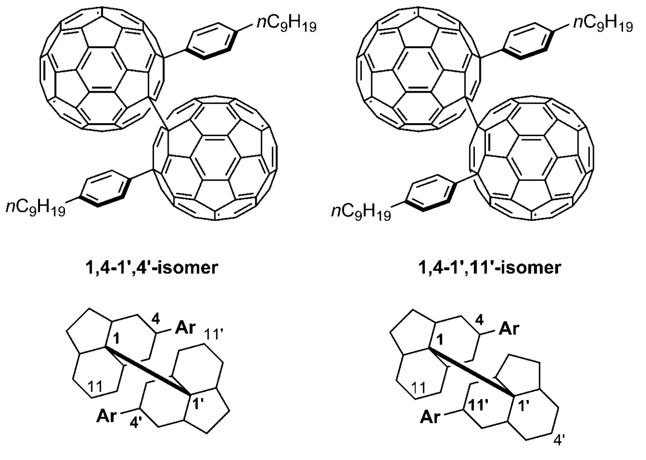
Having developed an efficient protocol for the allylation reaction, we next investigated the C–H bond arylation reaction of **1** using aryl halides as electrophilic partners.[15,20] After extensive screening, a catalytic system producing the desired arylation product was identified. The treatment of **1a**, C_6H_5I, LiOH, and Pd/PCy$_2$(*o*-biphenyl) catalyst in 1,2-$Cl_2C_6H_4$ at 120 °C afforded the arylation product **4** in 23 % isolated yield (Scheme 3). Similar to the previous allylation reaction, arylation occured exclusively at the 4-position resulting in the 1,4-isomer. The arylation also took place with **1b**, albeit less efficiently (**6**: 6 % yield).



Scheme 3. Pd-catalyzed C–H bond arylation of **1** and discovery of two unexpected reactions.

Although C–H bond arylation products can be obtained from **1** under Pd catalysis, the reaction efficiency is low in comparison to that of allylation. During our investigation to identify the mass balance in these arylation reactions, we discovered two unexpected reactions that take place in parallel and are also catalyzed by Pd.

In the case of the reaction with **1a**, the interesting fullerene dimer **5** ($ArC_{60}C_{60}Ar$) was produced in 46 % yield (Scheme 3).[21] Dimer **5** was not obtained in the absence of Pd, providing evidence that the observed C–H bond dimerization is catalyzed by the Pd complex. The ^{1}H NMR spectrum and LC-MS analyses indicate that **5** consists of two isomers. Because of the bulkiness of the aryl group, it is likely that **5** results from dimerization at positions remote from the aryl groups. Thus, the 1,4-1′,4′-isomer and the 1,4-1′,11′-isomer are the possible two isomers obtained in the reaction (Scheme 4). As highly indicated by theoretical calculations,[22] the corresponding isomers containing a 1,2-linkage of a pivot carbon and an aryl-attached carbon should be



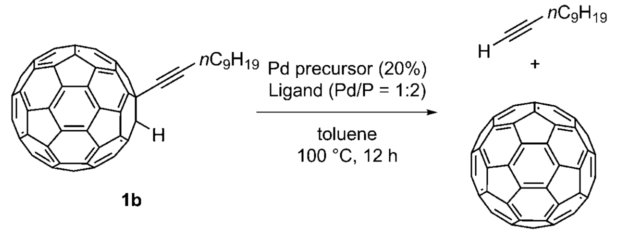
Scheme 4. Possible isomers of fullerene dimer **5**.

very unstable. However, we cannot completely rule out such isomers at this stage.

In the case of the reaction using **1b**, the corresponding dimer was not formed along with the arylation product **6**. Rather, pristine C_{60} was produced in 26 % yield (Scheme 3). Although some retro-reactions of functionalized fullerene derivatives have been reported,[23] the present reaction represents the first example using organo(hydro)fullerenes with the aid of transition-metal catalyst.

This C–C bond-cleaving process is intriguing also from the point of view of transition-metal catalysis.[24] Therefore, to gain a better grasp of reaction, the conditions were further optimized (Table 1). In early experiments, it was identified that iodobenzene and base (LiOH) are spectators in the production of C_{60}. The treatment of **1b** with a catalytic amount of $Pd(OAc)_2$ in toluene at 100 °C for 12 h gave C_{60} in 2 % yield (entry 1). While the addition of PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe), PCy_3 (Cy = cyclohexyl), and $P(p\text{-tol})_3$ (*p*-tol = *para*-tolyl) as supporting ligands on Pd resulted in somewhat higher yield of C_{60} (entries 2–5), $P(o\text{-tol})_3$ (*o*-tol = *ortho*-tolyl) was found to be a far superior ligand, yielding C_{60} in 79 % yield (entry 6). Concomitant with production of C_{60}, the alkynyl group and hydrogen atom were released from the fullerene core as the terminal alkyne (54 % yield). Other potential alkyne-derived products, such as enyne or diyne, were not obtained, as judged by the GC analysis of reaction mixture. Considering the fact that the related $Pd(OCOCF_3)_2/P(o\text{-Tol})_3$ and $PdCl_2/P(o\text{-Tol})_3$ systems possess virtually no activity (entries 7 and 8), the exceptionally high catalytic activity of $Pd(OAc)_2/P(o\text{-Tol})_3$ is interesting.

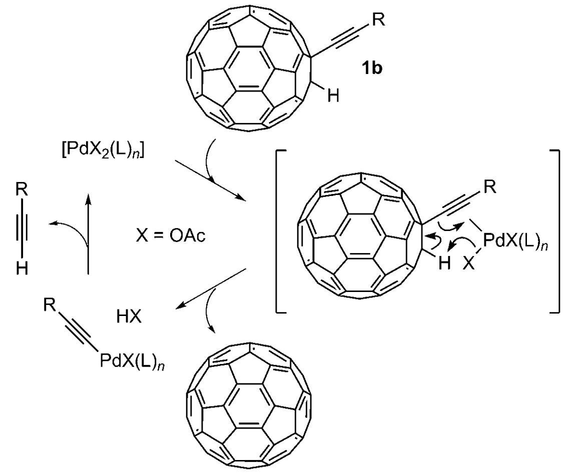
Table 1. Pd-catalyzed C–C bond cleavage of **1b**.[a]



Entry	Pd precursor	Ligand	Yield (C_{60}) [%][b]
1	$Pd(OAc)_2$	–	2
2	$Pd(OAc)_2$	PPh_3	7
3	$Pd(OAc)_2$	$Ph_2PCH_2CH_2PPh_2$	5
4	$Pd(OAc)_2$	PCy_3	4
5	$Pd(OAc)_2$	$P(p\text{-tol})_3$	18
6[c]	$Pd(OAc)_2$	$P(o\text{-tol})_3$	79
7	$Pd(OCOCF_3)_2$	$P(o\text{-tol})_3$	<1
8	$[PdCl_2(P(o\text{-tol})_3)_2]$	–	<1
9	–	$P(o\text{-tol})_3$	<1

[a] Conditions: **1b**, (1 equiv), Pd (20 mol %), ligand (Pd/P = 1:2), toluene, 100 °C, 12 h. [b] Determined by HPLC using C_{70} as an internal standard. [c] The yield of 1-undecyne was determined to be 54 % yield.

The driving force of this reaction is evidently the formation of stable, pristine C_{60}. Shown in Scheme 5 is our current working model for a possible Pd-catalyzed pathway. Molecular modeling (DFT) of the alkynyl(hydro)fullerene suggests that the alkynyl group and the hydrogen atom at the surface of C_{60} are perfectly synperiplanar (0.1°). Thus, the coordination of alkynyl group to Pd would bring the basic acetate moiety and acidic hydrogen atom in close proximity, thereby promoting the concerted bond formation (H–OAc, $C_{fullerene}$–$C_{fullerene}$, $C_{alkynyl}$–Pd) and cleavage ($C_{fullerene}$–H, $C_{fullerene}$–$C_{alkynyl}$, Pd–OAc) to release pristine C_{60}. Subsequent protodepalladation of thus-obtained alkynyl–PdOAc with HOAc would produce the terminal alkyne and regenerate the $Pd(OAc)_2/P(o\text{-Tol})_3$ catalyst. However, pathways initiated by Pd^0 cannot be ruled out at this moment.



Scheme 5. A possible mechanism for the Pd-catalyzed C–C bond cleavage of alkynyl(hydro)fullerene **1b**.

In summary, we have established that Pd catalysts enable several C–H bond transformations of organo(hydro)fullerenes. The allylation reaction can be a versatile and general method to functionalize fullerenes. Subsequent transformations of thus-formed allylated fullerenes might be achieved by various methods including the well-established olefin metathesis reaction. Although the arylation reaction is still in its infancy, the two new reactions found while investigating the arylation reaction are intriguing. The C–H bond dimerization reaction might contribute in the generation of new fullerene-assembled materials that are otherwise difficult to make. The C–C bond-cleaving reaction may find use in the "deprotection" of fullerenes, assuming an alkynyl(hydro)fullerene as a "masked" soluble fullerene. The present finding of multidexterous Pd catalysis in transforming organo(hydro)fullerenes not only highlights the potential of transition-metal catalysis for fullerene functionalization, but also unlocks opportunities for markedly different strategies in nanocarbon synthesis.

Experimental Section

Procedure for Pd-catalyzed C–H bond allylation of 1a (Scheme 2): A 20 mL glass Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. $[Pd_2(dba)_3]\cdot CHCl_3$ (1.7 mg, 1.6 μmol), $P(OPh)_3$ (3.1 μL, 12 μmol), and dry *o*-dichlorobenzene (2.0 mL) were added at room temperature to this flask under a stream of argon. After stirring the mixture at this temperature for 30 min, **1a** (13.8 mg, 15 μmol) and methallyl methyl carbonate (**2**: 3.8 mg, 29 μmol) were added to the flask under a stream of argon. After stirring at 80 °C for 18 h, the mixture was cooled to room temperature. The mixture was passed through a pad of silica gel with copious washings with toluene (~30 mL). The filtrate was concentrated (~5 mL) and subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford the coupling product (**3**: 12.4 mg, 85 %) as dark brown solid. ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 7.0$ Hz, 3H), 1.20–1.50 (m, 12H), 1.65–1.80 (m, 2H), 2.11 (s, 3H), 2.77 (t, $J = 7.8$ Hz, 2H), 3.64 (d, $J = 13.0$ Hz, 1H), 3.73 (d, $J = 13.0$ Hz, 1H), 5.12 (s, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 8.21 ppm (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 14.13$, 22.70, 24.97, 29.36, 29.40, 29.57, 29.61, 31.55, 31.92, 35.77, 50.20, 59.31, 61.50, 117.56, 127.06, 129.54, 137.11, 138.42, 138.60, 138.80, 139.26, 140.53, 140.90, 142.08, 142.23, 142.59, 142.65, 142.74, 143.09, 143.14, 143.22, 143.26, 143.28, 143.85, 143.88, 143.94, 143.96, 144.07, 144.18, 144.25, 144.32, 144.40, 144.44, 144.48, 144.55, 144.67, 144.90, 144.95, 144.96, 145.07, 145.13, 145.53, 145.60, 146.61, 146.91, 146.94, 146.96, 147.03, 147.10, 147.24, 147.62, 148.65, 148.70, 148.82, 150.96, 151.98, 157.16, 157.69 ppm; HRMS (ESI-TOF, negative): *m/z* calcd for $C_{79}H_{30}$: 978.2348, found 978.2354.

Procedure for Pd-catalyzed C–C bond cleavage of 1b (Table 1, Entry 6): A 50 mL glass Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. $Pd(OAc)_2$ (1.3 mg, 6 μmol), $P(o\text{-}Tol)_3$ (3.7 mg, 12 μmol), and dry toluene (20 mL) were added at room temperature to this flask under a stream of argon. After stirring the mixture for 30 min, **1b** (26.2 mg, 30 μmol) was added under a stream of argon. After stirring at 100 °C for 12 h, the reaction mixture was cooled to room temperature. The yield of C_{60} was determined to be 79 % by HPLC analysis (Buckyprep column; toluene as eluent; flow rate 0.5 mL min^{-1}; UV detection at 326 nm) of this crude mixture using C_{70} as an internal standard. Thereafter, the mixture was passed through a pad of silica gel with copious washings with toluene (~30 mL) and the solvent was evaporated. The yield of 1-undecyne was determined to be 54 % by GC analysis using *n*-nonane as an internal standard.

Acknowledgements

This work was supported in part by the PRESTO program of Japan Science and Technology Agency, and a grant-in-aid for scientific research from MEXT and JSPS. M.N. is a recipient of the JSPS Predoctoral Fellowships for Young Scientists. We thank Dr. Olivier Coutelier and Dr. Jean Bouffard (Nagoya University) for critical comments and discussion.

Keywords: C–C cleavage · C–C coupling · fullerenes · homogeneous catalysis · palladium

---

[1] a) A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**; b) *Fullerenes: Chemistry, Physics, and Technology* (Eds.: K. M. Kadish, R. S. Ruoff), Wiley, New York, **2000**; c) *Fullerenes: Principles and Applications* (Eds.: F. Langa, J.-F. Nierengarten), RSC, Cambridge, **2007**; d) N. Martín, *Chem. Commun.* **2006**, 2093; e) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, *Synlett* **2007**, 3077.

[2] a) C. Bingel, *Chem. Ber.* **1993**, *126*, 1957; b) J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem.* **1996**, *108*, 2242; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2101; c) X. Camps, A. Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595.

[3] a) V. M. Rotello, J. B. Howard, T. Yadav, M. M. Conn, E. Viani, L. M. Giovane, A. L. Lafleur, *Tetrahedron Lett.* **1993**, *34*, 1561; b) M. Tsuda, T. Ishida, T. Nogami, S. Kurono, M. Ohashi, *J. Chem. Soc. Chem. Commun.* **1993**, 1296; c) K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, T. S. M. Wan, *Tetrahedron Lett.* **1993**, *34*, 8473; d) I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem.* **1995**, *107*, 1755; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1607; e) Y. Murata, N. Kato, K. Fujiwara, K. Komatsu, *J. Org. Chem.* **1999**, *64*, 3483; f) K. Mikami, S. Matsumoto, T. Tonoi, Y. Okubo, T. Suenobu, S. Fukuzumi, *Tetrahedron Lett.* **1998**, *39*, 3733; g) J. L. Segura, N. Martín, *Chem. Rev.* **1999**, *99*, 3199; h) Y. Takaguchi, T. Tajima, K. Ohta, J. Motoyoshiya, H. Aoyama, T. Wakahara, T. Akasaka, M. Fujitsuka, O. Ito, *Angew. Chem.* **2002**, *114*, 845; *Angew. Chem. Int. Ed.* **2002**, *41*, 817.

[4] a) M. Maggini, G. Scorrano, *J. Am. Chem. Soc.* **1993**, *115*, 9798; b) M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519; c) H. Imahori, H. Norteda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 100; d) G.-W. Wang, T.-H. Zhang, E.-H. Hao, L.-J. Jiao, Y. Murata, K. Komatsu, *Tetrahedron* **2002**, *58*, 55.

[5] a) F. Wudl, A. Hirsch, K. C. Khemani, T. Suzuki, P. M. Allemand, A. Kosch, H. Eckert, G. Srdanov, H. M. Webb, *ACS Symp. Ser.* **1992**, *481*, 161; b) A. Hirsch, A. Soi, H. R. Karfunkel, *Angew. Chem.* **1992**, *104*, 808; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 766; c) P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke, E. Johnston, *J. Am. Chem. Soc.* **1992**, *114*, 9697; d) A. Hirsch, T. Grösser, A. Skiebe, A. Soi, *Chem. Ber.* **1993**, *126*, 1061; e) H. Nagashima, H. Terasaki, E. Kimura, K. Nakajima, K. Itoh, *J. Org. Chem.* **1994**, *59*, 1246; f) K. Komatsu, Y. Murata, N. Takimoto, S. Mori, N. Sugita, T. S. M. Wan, *J. Org. Chem.* **1994**, *59*, 6101.

[6] a) M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 12850; b) S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe, E. Nakamura, *Science* **2001**, *291*, 1944; c) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato, E. Nakamura, *Nature* **2002**, *419*, 702; d) Y. Matsuo, K. Tahara, M. Sawamura, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 8725; e) Y.-W. Zhong, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 3052; f) Y. Matsuo, K. Tahara, K. Morita, K. Matsuo, E. Nakamura, *Angew. Chem.* **2007**, *119*, 2902; *Angew. Chem. Int. Ed.* **2007**, *46*, 2844; g) T. Nakae, Y. Matsuo, E. Nakamura, *Org. Lett.* **2008**, *10*, 621.

[7] a) P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton, K. F. Preston, *Science* **1991**, *254*, 1183; b) M. D. Tzirakis, M. Orfanopoulos, *Org. Lett.* **2008**, *10*, 873; c) Y. Matsuo, Y. Zhang, E. Nakamura, *Org. Lett.* **2008**, *10*, 1251.

[8] a) G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma, G. K. Prakash, *J. Am. Chem. Soc.* **1991**, *113*, 9387; b) L. Y. Chiang, R. B. Upasani, J. W. Swirczewski, *J. Am. Chem. Soc.* **1992**, *114*, 10154; c) T. Kitagawa, H. Sakamoto, K. Takeuchi, *J. Am. Chem. Soc.* **1999**, *121*, 4298; d) A. Iwashita, Y. Matsuo, E. Nakamura, *Angew. Chem.* **2007**, *119*, 3583; *Angew. Chem. Int. Ed.* **2007**, *46*, 3513; e) K. Kokubo, S. Tochika, M. Kato, Y. Sol, T. Oshima, *Org. Lett.* **2008**, *10*, 3335.

[9] For selected examples and reviews on functionalization of carbon nanotubes, see: a) J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, J. M. Tour, *J. Am. Chem. Soc.* **2001**, *123*, 6536; b) V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002**, *124*, 760; c) A. Hirsch, *Angew. Chem.* **2002**, *114*, 1933; *Angew. Chem. Int. Ed.* **2002**, *41*, 1853; d) G. Viswanathan, N. Chakrapani, H. Yang, B. Wei, H. Chung, K. Cho, C. Y. Ryu, P. M. Ajayan, *J. Am. Chem. Soc.* **2003**, *125*, 9258; e) D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **2006**, *106*, 1105; f) R. Graupner, J. Abraham, D. Wunderlich, A. Vencelová, P. Lauffer, J. Röhrl, M. Hundhausen, L. Ley, A. Hirsch, *J. Am. Chem. Soc.* **2006**, *128*, 6683; g) W. Zhang, T. M. Swager, *J. Am. Chem. Soc.* **2007**, *129*, 7714; h) Z. Syrgiannis, F. Hauke, J. Röhrl, M. Hundhausen, R. Graupner, Y. Elemes, A. Hirsch, *Eur. J. Org. Chem.* **2008**, 2544.

[10] D. Li, R. B. Kaner, *Science* **2008**, *320*, 1170.

[11] a) *Transition Metals for Organic Synthesis* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**; b) J. Tsuji, *Transition Metal Reagents and Catalysts*, Wiley, New York, **2000**; c) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.

[12] Chemical transformations of fullerenes by means of metal catalysis: a) L. Becker, T. P. Evans, J. L. Bada, *J. Org. Chem.* **1993**, *58*, 7630; b) L.-L. Shiu, T.-I. Lin, S.-M. Peng, G.-R. Her, D. D. Ju, S.-K. Lin, J.-H. Hwang, C. Y. Mou, T.-Y. Luh, *J. Chem. Soc. Chem. Commun.* **1994**, 647; c) C. K. F. Shen, K.-M. Chien, T.-Y. Liu, T.-I. Lin, G.-R. Her, T.-Y. Luh, *Tetrahedron Lett.* **1995**, *36*, 5383; d) L. Gan, S. Huang, X. Zhang, A. Zhang, B. Cheng, H. Cheng, X. Li, G. Shang, *J. Am. Chem. Soc.* **2002**, *124*, 13384; e) N. Martín, M. Altable, S. Filippone, Á. Martín-Domenech, *Chem. Commun.* **2004**, 1338; f) N. Martín, M. Altable, S. Filippone, Á. Martín-Domenech, A. Poater, M. Solà, *Chem. Eur. J.* **2005**, *11*, 2716; g) Y. Matsuo, A. Iwashita, E. Nakamura, *Chem. Lett.* **2006**, *35*, 858.

[13] a) M. Nambo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2007**, *129*, 8080; b) S. Mori, M. Nambo, L.-C. Chi, J. Bouffard, K. Itami, *Org. Lett.* **2008**, *10*, 4609.

[14] a) See reference [5c]; b) M. E. Niyazymbetov, D. H. Evans, S. A. Lerke, P. A. Cahill, C. C. Henderson, *J. Phys. Chem.* **1994**, *98*, 13093; c) G. V. Lier, B. Safi, P. Geerlings, *J. Phys. Chem. Solids* **1997**, *58*, 1719.

[15] J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, New York, **2004**.

[16] The use of allylic carbonates in Pd-catalyzed allylation reactions: J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura, K. Takahashi, *J. Org. Chem.* **1985**, *50*, 1523.

[17] The use of allyl acetate resulted in much lower conversion.

[18] The use of allyl methyl carbonate resulted in the formation of two inseparable regioisomers. The allylation of alkynyl(hydro)fullerene **1b** also resulted in the formation of two inseparable regioisomers.

[19] K. M. Kadish, X. Gao, E. Van Caemelbecke, T. Suenobu, S. Fukuzumi, *J. Phys. Chem. A* **2000**, *104*, 3878.

[20] Selected examples on Pd-catalyzed arylation of relatively acidic C–H bonds: a) M. Uno, K. Seto, W. Ueda, M. Masuda, S. Takahashi, *Synthesis* **1985**, 506; b) M. Miura, S. Pivsa-Art, G. Dyker, J. Heiermann, T. Satoh, M. Nomura, *Chem. Commun.* **1998**, 1889; c) G. Dyker, J. Heiermann, M. Miura, J. Inoh, S. Pivsa-Art, T. Satoh, M. Nomura, *Chem. Eur. J.* **2000**, *6*, 3426; d) M. Lafrance, C. N. Rowley, T. K. Woo, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 8754.

[21] The chemistry of fullerene dimers: a) Y. Murata, K. Motoyama, K. Komatsu, *Tetrahedron* **1996**, *52*, 5077; b) J. R. Morton, K. F. Preston, P. J. Krusic, S. A. Hill, E. Wasserman, *J. Am. Chem. Soc.* **1992**, *114*, 5454; c) G. Schick, K.-D. Kampe, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1995**, 2023; d) G.-W. Wang, K. Komatsu, Y. Murata, M. Shiro, *Nature* **1997**, *387*, 583; e) T. Tanaka, K. Komatsu, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1671; f) J. Segura, N. Martín, *Chem. Soc. Rev.* **2000**, *29*, 13; g) F. Cheng, Y. Murata, K. Komatsu, *Org. Lett.* **2002**, *4*, 2541.

[22] S. Osawa, E. Osawa, M. Harada, *J. Org. Chem.* **1996**, *61*, 257.

[23] a) M. A. Herranz, F. Diederich, L. Echegoyen, *Eur. J. Org. Chem.* **2004**, 2299; b) M. A. Herranz, N. Martín, J. Ramey, D. M. Guldi, *Chem. Commun.* **2002**, 2968; c) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, L. Echegoyen, C. M. Cardona, *Angew. Chem.* **2006**, *118*, 116; *Angew. Chem. Int. Ed.* **2006**, *45*, 110; d) J. L. Delgado, F. Oswald, F. Cardinali, F. Langa, N. Martín, *J. Org. Chem.* **2008**, *73*, 3184; e) S. Filippone, M. I. Barroso, Á. Martín-Domenech, S. Osuna, M. Solà, N. Martín, *Chem. Eur. J.* **2008**, *14*, 5198.

[24] Reviews on catalytic C–C bond cleavage reactions: a) M. Murakami, M. Makino, S. Ashida, T. Matsuda, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1315; b) T. Mitsudo, T. Kondo, *Synlett* **2001**, 309; c) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610.

Received: January 5, 2009