Nucleophile-Selective Cross-Coupling

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Highly Tin-Selective Stille Coupling: Synthesis of a Polymer Containing a Stannole in the Main Chain**

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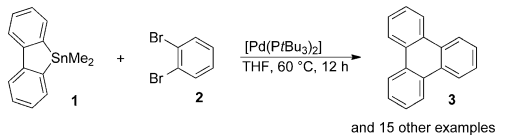
Abstract: *The incorporation of heavier Group 14 element heteroles into semiconducting polymers leads to unusual optoelectronic properties. However, polymers containing stannoles have not been accessible to date. We report a synthetic route to a well-defined, stannole-containing polymer, the first example of this class of π-conjugated polymers. This route was made possible by developing difunctionalized stannole monomers and highly tin-selective Stille coupling reactions that leave the tin in the stannole untouched. Compared to poly(3-n-hexylthiophene), the resulting polymer displays a remarkable bathochromic shift in its absorption.*

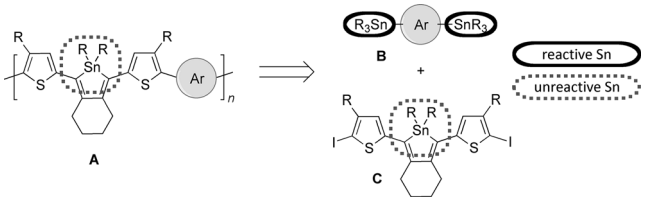
The formal replacement of the methylene group in cyclopentadienes by heavier Group 14 elements drastically changes their electronic properties:[1] With the incorporation of Si, Ge, or Sn the two σ*-orbitals of the exocylic E–R bonds (with E = Si, Ge, Sn) are much lower in energy than those of C–R bonds, allowing efficient mixing with the π*-orbital of the diene system. This mixing distinctly lowers their LUMO levels compared to carbon cyclopentadienes.[1b,d,e] Therefore, these higher Group 14 heteroles are interesting heterocycles for incorporation into semiconducting polymers: They are expected to have low band gaps and to display novel charge-transporting properties.[2] Sila- and germafluorenes have been incorporated in polymers[3] as have siloles and germoles,[4] which led to distinct improvements in device performances.[5] Furthermore, Group 14 heteroles were also incorporated as 1,1-bridged heteroles.[1b,6] As far as tin is concerned, there is some work on stannafluorenes,[7] but the chemistry of stannoles is much less studied.[1e,8]

To date, no stannole has been published that contains a reactive halogen functional group that could be used for cross-coupling reactions—on either the dienyl ring itself or on any further aromatic substituents on this ring. The problem is that stannacycles themselves are very versatile nucleophilic compounds in Stille cross-coupling reactions. Indeed, stannoles may be viewed as cyclic vinyl tin compounds that are regularly used in cross-coupling reactions[10] and which, depending on the reaction conditions, can be even more reactive than aryl tin compounds.[11] The recently reported reactivity of the related stannafluorenes illustrates the problem of being able to use reactive organo tin compounds in cross-coupling reactions, if reactions at the tin center are not wanted: it was shown that stannafluorenes **1** react cleanly with dibromobenzenes **2** to give triphenylenes **3** in high yields (Scheme 1).[9,12]

Herein, we demonstrate the first highly nucleophile selective Stille reaction, differentiating between an endo- and two exocyclic tin functional groups (Scheme 2). This



Scheme 1. The reaction of stannafluorenes **1** with di-electrophiles **2** can lead to cross-coupled products **3** (in this example, isolated in 87% yield).[9]



Scheme 2. Tin-selective cross-coupling reactions allow the synthesis of stannole containing polymers.

allowed the synthesis of the first well-defined non-annulated stannole-containing polymer of type **A** (Scheme 2), which shows a strong bathochromic shift compared to the related poly(3-*n*-hexylthiophene) (P3HT). To synthesize a monomer of type **C**, two major challenges had to be overcome: First, a synthetic route had to be developed to prepare a stannole monomer that contained electrophilic functional groups (bromides or iodides) on the carbon scaffold for the subsequent polymerization. The second issue was to protect the Sn center in the heterocycle so that it would be stable under polymerization conditions. We envisioned that this

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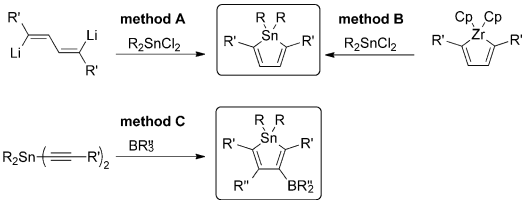
could be achieved based on a kinetically deactivated tin center in the stannole monomer.

The reactivity and functionalization possibilities of stannoles are almost entirely unexplored. Crucially, there is no report of stannoles that are substituted with bromides or iodides. This does not only concern bromide/iodide substituents on the ring, but also, no stannoles with brominated/iodinated aryl substituents have been synthesized.

There are three established methods for the preparation of stannoles: Generally, they can be prepared by synthesizing a dilithiated butadiene species in situ and then quenching it with R_2SnCl_2[8a,13] (method A, Scheme 3). The second route

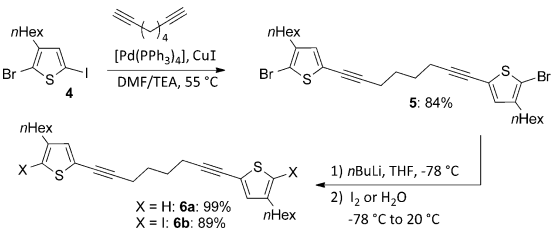


Scheme 3. Common preparation methods for stannoles.

involves a Zr–Sn exchange[1e,14] of zirconacyclopentadienes with R_2SnCl_2 (method B). Another possibility is the 1,1-carboboration of activated tin diacetylides, also known as Wrackmeyer reaction, which generally gives the desired stannoles in high yields (method C).[15]

Because the presence of halides (R′ =-Ar-X; Scheme 3) is essential for the intended monomer, a route via a dilithiated butadiene is problematic owing to potential unselective halogen–lithium exchange reactions. Although method C is an excellent and straightforward route for the synthesis of stannoles (and other heteroles),[16] it was not pursued at this stage because it would result in a boron atom in the 3 or 4 position. Such an asymmetric monomer would be expected in the subsequent polycondensation to lead to a regioirregular polymer.

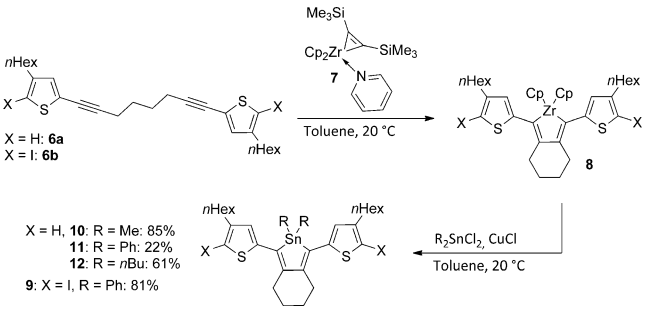
Therefore, a zirconacyclopentadiene was envisaged as a stannole precursor, flanked by two halide substituted 3-*n*-hexylthiophenes. For this route, the octadiyne linked bis(thiophene) **5** was prepared in an electrophile selective Sonogashira cross-coupling reaction, without observing any unselective coupling reaction with the bromide (Scheme 4). Bromine–lithium exchange and subsequent quenching with water or iodine at −78 °C led to the protonated and iodinated species **6a** and **6b**, respectively. The bromide–iodide



Scheme 4. Synthesis of thiophene-flanked octadiyne **6**.

exchange was carried out because of the higher reactivity of iodides in cross-coupling reactions,[17] thus facilitating a later polymerization process.

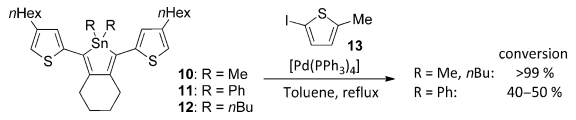
The commonly used reagent for the formation of zirconacyclopentadienes from diynes is the in situ prepared Negishi reagent.[18] However, this highly reactive reagent is problematic for halide-functionalized compounds, because it is capable of C–X insertion reactions.[19] A much milder reagent is Rosenthal's zirconocene,[20] which has been used for a bromide-functionalized zirconacyclopentadiene.[4a] Because of these advantageous properties, Rosenthal's zirconocene **7** was used in a reaction with **6** in toluene at 20 °C for 18 h, giving a dark red solution (Scheme 5). Copper chloride



Scheme 5. Synthesis of a variety of stannoles by a zirconacyclopentadiene one-pot procedure.

promotes the Zr–Sn exchange not only in THF,[14a–c] but also in toluene, making it possible to carry out the reaction as a simple one-pot procedure: The air- and moisture-sensitive zirconacyclopentadiene **8** was directly transformed into the corresponding stannoles within 3 h, using R_2SnCl_2 (with R = Me, *n*Bu, Ph) and catalytic amounts of copper chloride at 20 °C. The reaction was accompanied by a distinct color change from the dark **8** to the bright orange stannoles in all cases. For the isolation of **10** and **12**, carried out by column chromatography, it was necessary to condition the silica with triethylamine to prevent decomposition of the stannoles. The need for this procedure already gave some indication of their lower stability compared to the phenyl-substituted stannole **11**, which did not show any decomposition on silica. Initially, stannoles without halides and with substituents of different steric hindrance at the tin atom were prepared (R = Me, *n*Bu, Ph, **10**–**12**) to investigate the stability of the different stannoles under cross-coupling conditions, which would be later used for polymerization.

The stabilities of these stannoles (**10**–**12**) were examined by performing reactions with a 2-iodo thiophene **13**, applying standard cross-coupling conditions (Scheme 6).[21] In the case of R = Me and R = *n*Bu (**10** and **12**), a conversion of the starting material of over 99 % was found, but the reaction mixture was highly complex and the stannoles had completely decomposed.[22] The phenyl substituted stannole **11** however, showed a much higher stability under cross-coupling conditions, with a conversion of 40 to 50 %. These results indicated that the use of phenyl-substituted stannoles should offer a much higher stability.



Scheme 6. Examination of the stability of stannoles **10**, **11**, and **12** under cross-coupling (polymerization) conditions.

Based on these results, an iodinated stannole **9**, bearing phenyl groups at the tin, was prepared in a yield of 81% (Scheme 5) and fully characterized. The determined $^{n}J(^{119}Sn,^{13}C)$ values support the assignment of carbon signals, showing similar coupling constants to hexaphenylstannole (see the Supporting Information).[23] The molecular structure of **9** was determined by X-ray crystallography (Figure 1): the

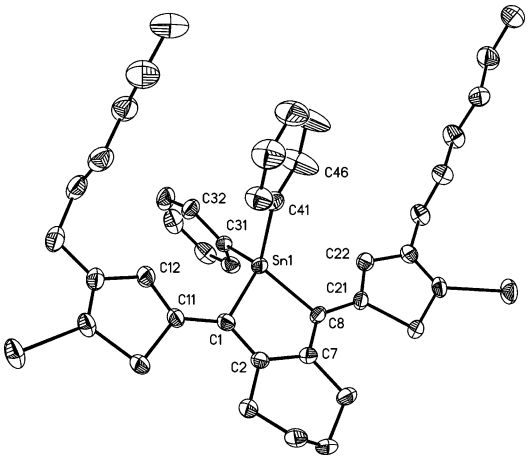
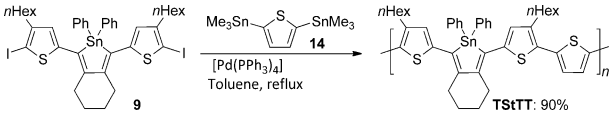


Figure 1. ORTEP drawing of **9**, thermal ellipsoids set at 50% probability. Hydrogen atoms and two disordered carbon atoms are omitted for clarity. Selected bond lengths [Å]: Sn1–C8 2.1328(3), Sn1–C1 2.1385(4), C1–C2 1.3724(5), C2–C7 1.4882(5), C7–C8 1.3675(5).

stannole ring is essentially planar, while the two phenyl rings are twisted from this plane, with torsion angles of 85.98° (C32-C31-Sn1-C1) and 83.11° (C46-C41-Sn1-C8). The smallest angle of the strongly distorted tetrahedral environment of the tin atom is 83.85° (C1-Sn1-C8), which is similar to other reported values.[1e,16c,23] Compared to other Group 14 metalloles, this endocyclic angle increases from stannoles to germoles to siloles, showing the influence of the large atomic radius of tin and the long carbon–tin bonds.[1e] The Sn1–C8 and Sn1–C1 bonds are, as expected, much longer than the C–C bonds of the stannole. The C–C bond alternation of the 1,3-dienyl moiety is comparable to the values of another thiophene-substituted stannole,[1e] but less pronounced than in other reported structures without thiophenes attached to the stannole, possibly because of extended conjugation.[16c,23,24] The two thiophene rings are arranged anti-coplanar to the central stannole ring, with dihedral angles of 178.04° (C7-C8-C21-C22) and 177.77° (C2-C1-C11-C12). This high planarity of the whole molecule should ensure an effective conjugation, an important factor for a semiconducting polymer. The bulky phenyl groups do not perturb this planarity, making them good candidates as stabilizing substituents for stannoles.

Having solved the problems of synthesizing a halide-containing stannole and of finding an appropriate, stable-enough substituent for the tin, the polymerization was carried out by a Stille cross-coupling reaction between **9** and the double-stannylated thiophene **14** (Scheme 7). The reaction



Scheme 7. Cross-coupling of **9** and **14**, yielding 90% of the polymer TStTT ($M_w = 17.0$ kDa, PDI = 2.5).

was heated to reflux in toluene, using 5 mol% $[Pd(PPh_3)_4]$ as a catalyst, to afford a purple-black polymer in 90% yield after purification by precipitation. ^{119}Sn NMR spectroscopy and MALDI mass spectrometry indicated that the reaction was completely tin selective, without any noticeable decomposition of the stannole: the ^{119}Sn NMR of the monomer **9** showed one signal at $\delta = -79.9$ ppm which was slightly shifted to $\delta = -81.1$ ppm in the polymer TStTT, and no additional signal was observed. The MALDI-MS analysis showed a mass difference of 792.2 Da between corresponding peaks, which corresponds to the mass of the expected repeat unit.[25]

The polymer showed good solubility in common solvents ($CHCl_3$, CH_2Cl_2, chlorobenzene, toluene, THF) at 20°C. Number-and weight-average molecular weights were determined by gel permeation chromatography (GPC) to be $M_n = 6.8$ kDa and $M_w = 17.0$ kDa (calibrated with polystyrene standards), giving a polydispersity index (PDI) of 2.5. As the chain length of polymers prepared by step-growth polymerizations is extremely sensitive to unwanted side reactions, this comparatively high molecular weight underlines the extremely high nucleophile-selectivity of the reaction. The polymer was thermally stable up to 300°C and, somewhat unusually for a phenyl-containing polymer, not completely X-ray amorphous.[25]

UV/Vis spectra (for luminescence spectra, see the Supporting Information) from polymer TStTT were obtained in chloroform and compared to those of monomer **9** (Figure 2). The polymer TStTT shows a broad absorption in solution with a $\lambda_{max} = 536$ nm. This value displays a significant bathochro-

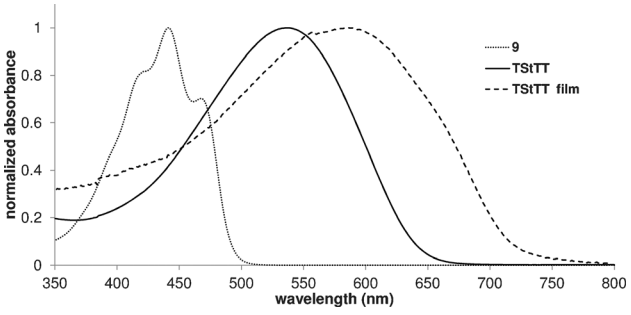


Figure 2. Absorption spectra of **9** and TStTT in chloroform and as a film.

mic shift compared to $\lambda_{max} = 441$ nm of the monomer **9** and $\lambda_{max} \approx 450$ nm of standard rrP3AT (regioregular poly(3-alkylthiophene)),[26] showing the increased conjugation length of TStTT compared to the monomer and the large influence of the tin atom on the absorption as predicted. A film of TStTT was obtained by spin-coating, leading to broader absorption and a distinct red-shift of 49 nm ($\lambda_{max} =$ 585 nm) compared to the spectrum in solution. This results in a band gap of E_g (film, TStTT) = 1.7 eV. This low band gap implies the excellent applicability of stannoles for semiconducting polymers.

In conclusion, we have developed a synthetic route to a stannole monomer with peripheral iodide (**9**) functionalities. This compound is the first stannole that allows nucleophile-selective cross-coupling reactions in the exocyclic position, leaving the stannole intact. With our method, it was possible to obtain a new class of well-defined low band gap polymers, which contain non-annulated stannoles. Future work will involve the exploration of the photophysical properties of stannole polymers in devices. Furthermore, further functionalization of stannole monomers and regioregular polymerization methods of asymmetric monomers are of high interest. In this context, method C will be explored which leads to a boryl group on the stannole that can be potentially cross-coupled.

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[1] a) E. Colomer, R. J. P. Corriu, M. Lheureux, *Chem. Rev.* **1990**, *90*, 265 – 282; b) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1 – 44; c) J. Dubac, A. Laporterie, G. Manuel, *Chem. Rev.* **1990**, *90*, 215 – 263; d) S. Yamaguchi, K. Tamao, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327 – 2334; e) S. Yamaguchi, Y. Itami, K. Tamao, *Organometallics* **1998**, *17*, 4910 – 4916.

[2] There has been one report of an oligomer containing stannoles, which was prepared by a polymeranalogous reaction. However, in this case the oligomer was short ($M_w < 3$ kDa), structurally ill-defined, and the extent of the stannole incorporation is unclear from the data presented: W.-M. Zhou, I. Tomita, *J. Inorg. Organomet. Polym. Mater.* **2009**, *19*, 113 – 117.

[3] For example: a) H. Usta, G. Lu, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2006**, *128*, 9034 – 9035; b) G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2008**, *130*, 7670 – 7685; c) K. L. Chan, M. J. McKiernan, C. R. Towns, A. B. Holmes, *J. Am. Chem. Soc.* **2005**, *127*, 7662 – 7663; d) Y. Zou, D. Gendron, R. Neagu-Plesu, M. Leclerc, *Macromolecules* **2009**, *42*, 6361 – 6365; e) N. Allard, R. d. B. Aïch, D. Gendron, P.-L. T. Boudreault, C. Tessier, S. Alem, S.-C. Tse, Y. Tao, M. Leclerc, *Macromolecules* **2010**, *43*, 2328 – 2333.

[4] a) B. L. Lucht, M. A. Buretea, T. D. Tilley, *Organometallics* **2000**, *19*, 3469 – 3475; b) S. Yamaguchi, R.-Z. Jin, Y. Itami, T. Goto, K. Tamao, *J. Am. Chem. Soc.* **1999**, *121*, 10420 – 10421; c) W.-M. Zhou, I. Tomita, *Polym. Bull.* **2008**, *61*, 603 – 609; d) J. Chen, Y. Cao, B. Z. Tang, in *Macromolecules Containing Metal and Metal-Like Elements*, Wiley, Hoboken, **2010**, p. 191 – 204; e) K. Tamao, S. Yamaguchi, M. Shiozaki, Y. Nakagawa, Y. Ito, *J. Am. Chem. Soc.* **1992**, *114*, 5867 – 5869; f) K. Tamao, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc.* **1994**, *116*, 11715 – 11722; g) K. Tamao, S. Yamaguchi, Y. Ito, Y. Matsuzaki, T. Yamabe, M. Fukushima, S. Mori, *Macromolecules* **1995**, *28*, 8668 – 8675.

[5] a) M. C. Scharber, M. Koppe, J. Gao, F. Cordella, M. A. Loi, P. Denk, M. Morana, H.-J. Egelhaaf, K. Forberich, G. Dennler, R. Gaudiana, D. Waller, Z. Zhu, X. Shi, C. J. Brabec, *Adv. Mater.* **2010**, *22*, 367 – 370; b) H.-Y. Chen, J. Hou, A. E. Hayden, H. Yang, K. N. Houk, Y. Yang, *Adv. Mater.* **2010**, *22*, 371 – 375; c) E. Wang, C. Li, Y. Mo, Y. Zhang, G. Ma, W. Shi, J. Peng, W. Yang, Y. Cao, *J. Mater. Chem.* **2006**, *16*, 4133 – 4140; d) H. Xiao, B. Leng, H. Tian, *Polymer* **2005**, *46*, 5707 – 5713; e) C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S.-W. Tsang, T.-H. Lai, J. R. Reynolds, F. So, *Nat. Photonics* **2012**, *6*, 115 – 120; f) C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So, J. R. Reynolds, *J. Am. Chem. Soc.* **2011**, *133*, 10062 – 10065.

[6] a) H. Sohn, R. R. Huddleston, D. R. Powell, R. West, K. Oka, X. Yonghua, *J. Am. Chem. Soc.* **1999**, *121*, 2935 – 2936; b) R. Haga, M. Saito, M. Yoshioka, *Chem. Eur. J.* **2008**, *14*, 4068 – 4073; c) S. J. Toal, H. Sohn, L. N. Zakarov, W. S. Kassel, J. A. Golen, A. L. Rheingold, W. C. Trogler, *Organometallics* **2005**, *24*, 3081 – 3087.

[7] See, for example: a) I. Nagao, M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2009**, *48*, 7573 – 7576; *Angew. Chem.* **2009**, *121*, 7709 – 7712; b) M. Saito, M. Shimosawa, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* **2006**, *35*, 940 – 941; c) K. Geramita, J. McBee, T. D. Tilley, *J. Org. Chem.* **2008**, *74*, 820 – 829; d) P. A. Chase, W. E. Piers, B. O. Patrick, *J. Am. Chem. Soc.* **2000**, *122*, 12911 – 12912.

[8] a) M. Saito, R. Haga, M. Yoshioka, *Eur. J. Inorg. Chem.* **2005**, 3750 – 3755; b) J. Krause, K.-J. Haack, K.-R. Pörschke, B. Gabor, R. Goddard, C. Pluta, K. Seevogel, *J. Am. Chem. Soc.* **1996**, *118*, 804 – 821; c) M. Saito, T. Kuwabara, C. Kambayashi, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* **2010**, *39*, 700 – 701; d) B. Wrackmeyer, P. Thoma, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, 1469 – 1476; e) M. Saito, R. Haga, M. Yoshioka, K. Ishimura, S. Nagase, *Angew. Chem. Int. Ed.* **2005**, *44*, 6553 – 6556; *Angew. Chem.* **2005**, *117*, 6711 – 6714; f) B. Wrackmeyer, G. Kehr, S. Willbold, S. Ali, *J. Organomet. Chem.* **2002**, *646*, 125 – 133; g) B. Wrackmeyer, K. H. von Locquenghien, S. Kundler, *J. Organomet. Chem.* **1995**, *503*, 289 – 295.

[9] see Ref. [7a]

[10] a) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **1999**, *38*, 2411 – 2413; *Angew. Chem.* **1999**, *111*, 2568 – 2570; b) W. Su, S. Urgaonkar, J. G. Verkade, *Org. Lett.* **2004**, *6*, 1421 – 1424; c) D. R. McKean, G. Parrinello, A. F. Renaldo, J. K. Stille, *J. Org. Chem.* **1987**, *52*, 422 – 424.

[11] a) A. M. Echavarren, J. K. Stille, *J. Am. Chem. Soc.* **1987**, *109*, 5478 – 5486; b) A. Kamimura, M. So, S. Ishikawa, H. Uno, *Org. Lett.* **2013**, *15*, 1402 – 1405.

[12] B. Kumar, C. E. Strasser, B. T. King, *J. Org. Chem.* **2012**, *77*, 311 – 316.

[13] a) A. J. Ashe III, S. Mahmoud, *Organometallics* **1988**, *7*, 1878 – 1880; b) M. Saito, M. Nakamura, T. Tajima, *Heterocycles* **2009**, *78*, 657 – 668; c) E. H. Braye, W. Huebel, I. Caplier, *J. Am. Chem. Soc.* **1961**, *83*, 4406 – 4413.

[14] a) C. Fan, W. E. Piers, M. Parvez, *Angew. Chem. Int. Ed.* **2009**, *48*, 2955 – 2958; *Angew. Chem.* **2009**, *121*, 2999 – 3002; b) Y. Ura, Y. Li, F.-Y. Tsai, K. Nakajima, M. Kotora, T. Takahashi, *Heterocycles* **2000**, *52*, 1171 – 1189; c) Y. Ura, L. Yanzhong, X. Zhenfeng, T. Takahashi, *Tetrahedron Lett.* **1998**, *39*, 2787 – 2790; d) S. Kim, K. H. Kim, *Tetrahedron Lett.* **1995**, *36*, 3725 – 3728; e) P. J. Fagan, W. A. Nugent, *J. Am. Chem. Soc.* **1988**, *110*, 2310 – 2312.

[15] For Reviews on this topic, see: a) B. Wrackmeyer, *Coord. Chem. Rev.* **1995**, *145*, 125 – 156; b) B. Wrackmeyer, *Heteroat. Chem.* **2006**, *17*, 188 – 208; c) G. Kehr, G. Erker, *Chem. Commun.* **2012**, *48*, 1839 – 1850.

[16] a) B. Wrackmeyer, P. Thoma, S. Marx, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2014**, 2103 – 2112; b) B. Wrackmeyer, P. Thoma, S. Marx, G. Glatz, R. Kempe, *Z. Anorg. Allg. Chem.* **2013**, *639*, 1205 – 1213; c) B. Wrackmeyer, U. Klaus, W. Milius, E. Klaus, T. Schaller, *J. Organomet. Chem.* **1996**, *517*, 235 – 242; d) B. Wrackmeyer, *J. Organomet. Chem.* **1989**, *364*, 331 – 342; e) L. Killian, B. Wrackmeyer, *J. Organomet. Chem.* **1977**, *132*, 213 – 221.
[17] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457 – 2483.
[18] E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson, T. Takahashi, *J. Am. Chem. Soc.* **1989**, *111*, 3336 – 3346.
[19] C. F. Harris, D. Ravindranathan, S. Huo, *Tetrahedron Lett.* **2012**, *53*, 5389 – 5392.
[20] a) J. R. Nitschke, S. Zürcher, T. D. Tilley, *J. Am. Chem. Soc.* **2000**, *122*, 10345 – 10352; b) U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, H. Görls, V. V. Burlakov, V. B. Shur, *Z. Anorg. Allg. Chem.* **1995**, *621*, 77 – 83.
[21] C. Lin, T. Endo, M. Takase, M. Iyoda, T. Nishinaga, *J. Am. Chem. Soc.* **2011**, *133*, 11339 – 11350.
[22] It was not possible to identify the formed products.
[23] J. Ferman, J. P. Kakareka, W. T. Klooster, J. L. Mullin, J. Quattrucci, J. S. Ricci, H. J. Tracy, W. J. Vining, S. Wallace, *Inorg. Chem.* **1999**, *38*, 2464 – 2472.
[24] T. Kuwabara, J.-D. Guo, S. Nagase, M. Minoura, R. H. Herber, M. Saito, *Organometallics* **2014**, *33*, 2910 – 2913.
[25] See the Supporting Information.
[26] T.-A. Chen, X. Wu, R. D. Rieke, *J. Am. Chem. Soc.* **1995**, *117*, 233 – 244.

