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Selective and Mild Synthesis of Mono- and Diarylated Group 13−15 Halides Using [CuMes]$_n$, a Readily Available, Thermally Stable Organocopper(I) Reagent

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The use of mesitylcopper, a soluble, thermally stable arylcopper compound, was investigated as an alternative to less selective organolithium and Grignard reagents or toxic mercury, tin, and organozinc compounds. $[CuMes]_5 \cdot$toluene (**1**) was found to readily react with various main group metal halides MX_n and RMX_n (M = B, Sn; X = Cl, Br; R = *n*Bu, Ph, 1,1′-fc) to give, depending on the stoichiometry of the reactions, monoarylated, diarylated, or mixed substituted species $MesMX_{n-1}$, Mes_2MX_{n-2}, and $MesRMX_{n-1}$ (**2**−**5**) in high yields.

Introduction

Organocopper compounds have attracted considerable attention during the past 20 years as a result of their important role in carbon−carbon bond forming reactions in organic syntheses.[1,2] In most cases the organocopper reagents have been reacted in situ without isolation of the active copper species. This is not surprising in view of the air and moisture sensitivity and the thermal lability of many alkylcopper compounds. Arylcopper compounds on the other hand show much higher thermal stability, being perfectly stable at ambient temperature under an inert atmosphere.[3] Their thermal stability strongly depends on the substitution pattern at the aryl group. It has been shown in many cases that in particular bulky substituents and heteroatom donors in *ortho* position such as ethers, amines, or phosphines lead to increased stability. As a consequence, a large variety of thermally stable, well-defined aryl- and even alkylcopper compounds have recently been synthesized and structurally characterized.[3−5] These studies have shown that organocopper compounds either assemble to small, soluble aggregates or form (insoluble) polymeric species. The formation of smaller aggregates is favored by bulky substituents,[5−13] chelating donor substituents,[14−21] and the presence of external donor molecules, respectively.[12,22−26] Even mononuclear species have been isolated when stabilized with phosphine, sulfide, and alkyne donors.[4,22,27−29] Despite extensive studies on structural aspects, the unique bonding situation in organocopper compounds, and their use in organic synthesis for C−C bond formation via organocopper intermediates, the use of copper reagents as alkyl or aryl transfer reagents in organometallic synthesis has been reported only for very few specific cases.[30]

The most commonly used reagents for the introduction of organic substituents to metal halides are orga-

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(1) Taylor, R. J. K., Ed. *Organocopper Reagents: A Practical Approach*; Oxford University Press: Oxford, 1994.

(2) Lipshutz, B. H. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, Chapter 3.2.

(3) van Koten, G.; James, S. L.; Jastrzebski, J. T. B. H. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 3, Chapter 2.

(4) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817, and references therein.

(5) Niemeyer, M. *Organometallics* **1998**, *17*, 4649, and references therein.

(6) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39.

(7) Jarvis, J. A. J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999.

(8) Lingnau, R.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 436.

(9) Haaland, A.; Rypdal, K.; Verne, H. P.; Scherer, W.; Thiel, W. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2443.

(10) Nobel, D.; van Koten, G.; Spek, A. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 208.

(11) Eriksson, H.; Örtendahl, M.; Håkansson, M. *Organometallics* **1996**, *15*, 4823.

(12) Eriksson, H.; Håkansson, M. *Organometallics* **1997**, *16*, 4243.

(13) Eriksson, H.; Håkansson, M. *Inorg. Chim. Acta* **1998**, *277*, 233.

(14) Guss, J. M.; Mason, R.; Søtofte, I.; van Koten, G.; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* **1972**, 446.

(15) Van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 129.

(16) Van Koten, G.; Leusink, A. J.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 117.

(17) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1979**, *174*, 121.

(18) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1419.

(19) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 3085.

(20) Wehman, E.; van Koten, G.; Knotter, M.; Spelten, H.; Heijdenrijk, D.; Mak, A. N. S.; Stam, C. H. *J. Organomet. Chem.* **1987**, *325*, 293.

(21) Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Rotteveel, M. A.; Stam, C. H. *Organometallics* **1988**, *7*, 1477.

(22) Coan, P. S.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1989**, *8*, 2724.

(23) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156.

(24) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

(25) Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1990**, *112*, 5895.

(26) Lenders, B.; Grove, D. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L.; van Koten, G. *Organometallics* **1991**, *10*, 786.

(27) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1984**, *3*, 1444.

(28) He, X.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 9668.

(29) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

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nolithium and Grignard reagents. However, these highly reactive species are often not selective enough to exclusively produce mono- and disubstituted metal complexes, respectively. Furthermore, their preparation in ether solvents can lead to side reactions of the metal halide with the solvent, particularly in the case of group 13 halides. Organomercury, zinc, or tin reagents on the other hand are generally less reactive and more selective and are therefore widely used. However, in view of their toxicity alternative alkyl and aryl group transfer reagents are highly desirable. As part of our ongoing interest in alkyl- and aryl-substituted main group halides as precursors for the synthesis of [1]ferrocenophanes,[31−33] we report in this paper on the general applicability of thermally stable, isolable arylcopper reagents for metathesis reactions with various main group metal halides. To demonstrate the scope of organocopper compounds as very selective and mild arylating reagents, we have chosen mesitylcopper, which can be prepared easily and on a large scale from the respective Grignard species.[12,23,24,34]

Experimental Section

The compounds Me_3SnCl, Me_2SnCl_2, nBuSnCl$_3$, $PhSnCl_3$, $SnCl_4$, BCl_3, and PCl_3 were purchased from Aldrich and were used without further purification. 1,1′-fc$(BBr_2)_2$ was synthesized from ferrocene and BBr_3 in hexanes according to a literature procedure.[35] $[CuMes]_5 \cdot$toluene (**1**) was synthesized from MesMgBr and CuCl in THF and recrystallized from toluene according to a literature procedure.[12] Compound **1** is also commercially available from Alfa AESAR. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres). Solvents were dried over sodium/benzophenone and freshly distilled prior to use. ^1H NMR spectra of 200, 300, or 400 MHz and 50.3, 75.5, or 100.5 MHz ^{13}C NMR spectra were recorded on either a Varian XL200, a Varian XL300, or a Unity 400 spectrometer, respectively. ^{119}Sn (111.8 MHz) and ^{11}B (160.4 MHz) NMR spectra were recorded on a Varian XL 300 and a Unity 500 spectrometer, respectively. All solution ^1H and ^{13}C NMR spectra were referenced externally to TMS. ^{119}Sn and ^{11}B NMR spectra were referenced externally to $SnMe_4$ and to $BF_3 \cdot Et_2O$, respectively. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in an electron impact (EI) mode. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

General Synthetic Procedure. A solution of the chosen element halide in toluene was added slowly to a freshly prepared solution of **1** in toluene at −30 °C (tin halides) and −78 °C (boron halides), respectively. The reaction mixture was slowly warmed to room temperature, stirred for 12 h, and heated to 50 °C for 1 h. An amber-orange precipitate formed initially, which gradually turned white (exception: in the reaction of **1** with PCl_3 an orange solid was not observed, but a white precipitate formed slowly). The copper halide was separated by filtration through a fritted glass disk and washed with toluene. All volatile material was removed under high vacuum, and the resulting crude product was analyzed by ^1H NMR spectroscopy. The *ortho*-methyl groups of the mesityl moiety are very sensitive to the substitution pattern and allow for facile distinction between mono-, di-, or trisubstituted species.

Reaction of $SnCl_4$ with 1: Synthesis of $MesSnCl_3$ (2a). Compound **2a** was obtained from **1** (1.00 g, 4.97 mmol CuMes) in toluene (30 mL) and $SnCl_4$ (1.36 g, 5.22 mmol) in toluene (10 mL) as a white solid in ca. 97% purity according to ^1H NMR spectroscopy. Recrystallization from hexanes at −55 °C gave colorless needles of spectroscopically pure **2a** (1.57 g, 92%). Spectroscopic data for **2a** are given in the literature.[36,37]

Reaction of $SnCl_4$ with 2 equiv of 1: Synthesis of Mes_2SnCl_2 (2b). Compound **2b** was obtained from **1** (10.08 g, 50.1 mmol CuMes) in toluene (200 mL) and $SnCl_4$ (6.51 g, 25.0 mmol) in toluene (50 mL) as a white solid in greater than 97% purity according to ^1H NMR spectroscopy. Recrystallization from hot toluene gave colorless needles of spectroscopically pure **2b** (9.30 g, 87%). Spectroscopic data for **2b** are given in the literature.[36,37]

Reaction of *n*BuSnCl$_3$ with 1: Synthesis of Mes*n*BuSnCl$_2$ (3a). Compound **3a** was obtained from **1** (0.81 g, 4.03 mmol CuMes) in toluene (30 mL) and *n*BuSnCl$_3$ (1.20 g, 4.25 mmol) in toluene (10 mL) as a white solid in ca. 97% purity according to ^1H NMR spectroscopy. Recrystallization from hot hexanes gave colorless needles of analytically pure **3a** (1.31 g, 89%). For **3a**: ^1H NMR (300 MHz, $CDCl_3$, 20 °C) $\delta = 6.95$ (s/d, $J(^{117/119}Sn, H) = 34$ Hz, 2 H, *meta*-Mes), 2.56 (s/d, $J(^{117/119}Sn, H) = 9$ Hz, 6 H, *ortho*-Me), 2.30 (s/d, $J(^{117/119}Sn, H) = 5$ Hz, 3 H, *para*-Me), 2.0−1.8, 1.51 (m, m, 4 H, 2H, CH_2-CH_2CH_2), 0.98 (t, $J(H, H) = 7.1$ Hz, 3 H, Me); ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C) $\delta = 143.7$ (s/d, $J(^{117/119}Sn, ^{13}C) = 59$, 62 Hz, *ortho*-Mes), 141.8 (s/d, $J(^{117/119}Sn, ^{13}C) = 14$ Hz, *para*-Mes), 137.1 (*ipso*-Mes), 129.2 (s/d, $J(^{117/119}Sn, ^{13}C) = 70$, 73 Hz, *meta*-Mes), 30.4 (s/d, $J(^{117/119}Sn, ^{13}C) = 469$, 491 Hz, Sn−$CH_2$), 26.7 (s/d, $J(^{117/119}Sn, ^{13}C) = 42$ Hz, CH_2), 26.0 (s/d, $J(^{117/119}Sn, ^{13}C) = 102$, 107 Hz, CH_2), 24.8 (s/d, $J(^{117/119}Sn, ^{13}C) = 45$ Hz, *ortho*-Me), 21.1 (*para*-Me), 13.5 (s, CH_3); ^{119}Sn NMR (111.8 MHz, $CDCl_3$, 20 °C) $\delta = 38.3$; *m/z* (%) 331 (65) $[M^+ - Cl]$, 309 (100) $[M^+ - n\text{Bu}]$, 274/273 (33) $[MesSnCl^+/MesSnCl^+ - H]$, 239/238 (34) $[MesSn^+/MesSn^+ - H]$; $C_{13}H_{20}Cl_2Sn$ (365.92) calcd C 42.67, H 5.51; found C 42.74, H 5.51.

Reaction of $PhSnCl_3$ with 1: Synthesis of $MesPhSnCl_2$ (3b). Compound **3b** was obtained from **1** (1.00 g, 4.97 mmol CuMes) in toluene (30 mL) and $PhSnCl_3$ (1.58 g, 5.22 mmol) in toluene (10 mL) as a colorless oil in ca. 95% purity according to ^1H NMR spectroscopy. Recrystallization from hot hexanes gave large colorless needles of analytically pure **3b** (1.63 g, 85%). For **3b**: ^1H NMR (400 MHz, $CDCl_3$, 20 °C) $\delta = 7.76$ (m, 2 H, *ortho*-Ph), 7.51 (m, 3 H, *meta*-Ph, *para*-Ph), 6.95 (s/d, $J(^{117/119}Sn, H) = 28$ Hz, 2 H, *meta*-Mes), 2.52 (s/d, $J(^{117/119}Sn, H) = 10$ Hz, 6 H, *ortho*-Me), 2.29 (s, 3 H, *para*-Me); ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C) $\delta = 144.2$ (s/d, $J(^{117/119}Sn, ^{13}C) = 60$, 62 Hz, *ortho*-Mes), 142.6 (*ipso*-Mes), 142.1 (s/d, $J(^{117/119}Sn, ^{13}C) = 15$ Hz, *para*-Mes), 135.2 (*ipso*-Ph), 134.3 (s/d, $J(^{117/119}Sn, ^{13}C) = 62$, 64 Hz, *ortho*-Ph), 131.1 (s/d, $J(^{117/119}Sn, ^{13}C) = 17$ Hz, *para*-Ph), 129.6 (s/d, $J(^{117/119}Sn, ^{13}C) = 81$, 84 Hz, *meta*-Ph), 129.4 (s/d, $J(^{117/119}Sn, ^{13}C) = 79$, 82 Hz, *meta*-Mes), 25.3 (s/d, $J(^{117/119}Sn, ^{13}C) = 48$ Hz, *ortho*-Me), 21.1 (s/d, $J(^{117/119}Sn, ^{13}C) = 9$ Hz, *para*-Me); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20 °C) $\delta = -40.9$; *m/z* (%) 386 (20) $[M^+]$, 351 (36) $[M^+ - Cl]$, 308 (100) $[M^+ - Ph - H]$; $C_{15}H_{16}Cl_2Sn$ (385.91) calcd C 46.69, H 4.18; found C 46.86, H 4.16.

Reaction of BCl_3 with 1: Synthesis of $MesBCl_2$ (4). Compound **4** was obtained from **1** (1.00 g, 4.97 mmol CuMes)

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(30) van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, Chapter 14.

(31) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Resendes, R.; Gates, D. P.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2338.

(32) Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1805.

(33) Jäkle, F.; Rulkens, R.; Zech, G.; Foucher, D. A.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 2117.

(34) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192.

(35) Ruf, W.; Renk, T.; Siebert, W. *Z. Naturforsch.* **1976**, *31b*, 1028.

(36) Berwe, H.; Haas, A. *Chem. Ber.* **1987**, *120*, 1175.

(37) Brown, P.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1992**, *435*, 265.

in toluene (30 mL) and BCl_3 (1 M in hexane, 5.2 mL, 5.2 mmol) as a colorless liquid in greater than 97% purity according to ^1H NMR spectroscopy. Distillation under reduced pressure gave **4** (0.88 g, 88%). For **4**: $C_9H_{11}BCl_2$ (200.90) calcd C 53.81, H 5.51; found C 54.54, H 5.70; spectroscopic data for **4** are given in the literature.[38]

Reaction of 1,1′-fc(BBr_2)$_2$ with 2 equiv of 1: Synthesis of 1,1′-fc(BBrMes)$_2$ (5). Compound **5** was obtained from **1** (1.53 g, 7.62 mmol CuMes) in toluene (50 mL) and 1,1′-fc-(BBr_2)$_2$ (2.00 g, 3.81 mmol) in toluene (50 mL) as a red oil in ca. 97% purity according to ^1H NMR spectroscopy. Recrystallization from hexanes gave red crystals of analytically pure **5** (1.66 g, 72%). For **5**: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ = 6.68 (s, 4 H, *meta*-Mes), 4.53 (m, 8 H, Cp), 2.25 (s, 12 H, *ortho*-Me), 2.13 (s, 6 H, *para*-Me); ^{13}C NMR (100.5 MHz, C_6D_6, 20 °C) δ = 138.9 (*para*-Mes), 138.4 (*ortho*-Mes), 128.4 (*meta*-Mes), 77.9, 77.5 (Cp), 23.0 (*ortho*-Me), 21.2 (*para*-Me), not observed (*ipso*-Me, *ipso*-Cp); ^{11}B NMR (160.4 MHz, C_6D_6, 20 °C) δ = 68.0 ($h_{1/2}$ = 1000 Hz); *m/z* (%) 604 (100) [M^+]; $C_{28}H_{30}B_2Br_2Fe$ (603.82) calcd C 55.70, H 5.01; found C 55.15, H 4.96.

Reaction of PCl_3 with 1: Synthesis of $MesPCl_2$ (6). (i) Equimolar reaction of **1** (1.00 g, 4.97 mmol CuMes) in toluene (30 mL) and PCl_3 (0.72 g, 5.24 mmol) in toluene (10 mL) gave ca. 60% **6** and 40% Mes_2PCl (**7**) according to ^1H NMR spectroscopy of the crude product. (ii) Reaction of **1** (1.00 g, 4.97 mmol CuMes) in toluene (30 mL) with 2 equiv of PCl_3 (1.37 g, 9.98 mmol) in toluene (10 mL) gave **6** in ca. 95% yield according to ^1H NMR spectroscopy of the crude product. Distillation under reduced pressure gave spectroscopically pure **6** (0.90 g, 82%).[39]

Attempts to Isolate an Intermediate [ArCu·CuX]$_n$. (a) Reaction of Me_2SnCl_2 with 2 equiv of 1: Synthesis of Me_2SnMes_2 (8a). A solution of Me_2SnCl_2 (0.30 g, 1.37 mmol) in toluene (10 mL) was added to a solution of **1** (0.55 g, 2.73 mmol CuMes) in toluene (30 mL) at −30 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. A slightly gray precipitate formed, which was separated from a colorless solution by filtration and washed with toluene (2 × 10 mL). The combined filtrates were analyzed by ^1H NMR spectroscopy, indicating the exclusive formation of disubstituted species **8a**. Column chromatography of the crude product (neutral alumina with toluene as eluent) followed by removal of all volatile material under vacuum gave spectroscopically pure **8a** as a colorless oil (0.40 g, 75%). For **8a**: ^1H NMR (300 MHz, C_6D_6, 20 °C) δ = 6.74 (s/d, $J(^{117/119}Sn, H)$ = 16 Hz, 4 H, *meta*-Mes), 2.32 (s/d, $J(^{117/119}Sn, H)$ = 6 Hz, 12 H, *ortho*-Me), 2.12 (s, 6 H, *para*-Me), 0.59 (s/d, $J(^{117/119}Sn, H)$ = 50, 53 Hz, 6 H, Sn−CH_3); ^{13}C NMR (75.5 MHz, C_6D_6, 20 °C) δ = 144.4 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 33 Hz, *ortho*-Mes), 139.9 (*ipso*-Mes), 138.0 (*para*-Mes), 128.5 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 42 Hz, *meta*-Mes), 25.5 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 32 Hz, *ortho*-Me), 21.1 (*para*-Me), −1.6 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 324, 338 Hz, Sn−CH_3); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20 °C) δ = −100.6; *m/z* (%) 387 (2) [M^+ − H], 373 (100) [M^+ − Me], 269/268 (41) [M^+ − Mes/M^+ − Mes − H], 274/273 (33) [$MesSnCl^+$/$MesSnCl^+$ − H], 239/238 (34) [$MesSn^+$/$MesSn^+$ − H]; $C_{20}H_{28}Sn$ (387.15) calcd C 62.05, H 7.29; found C 62.58, H 7.21.

(b) Reaction of Me_3SnCl with 2 equiv of 1. A solution of Me_3SnCl (0.25 g, 1.25 mmol) in toluene (10 mL) was added to a solution of **1** (0.50 g, 2.49 mmol CuMes) in toluene (30 mL) at −30 °C, slowly warmed to room temperature, and stirred for 2 days. An amber precipitate formed, which gradually turned gray-green. The solid material (ca. 100 mg) was separated from a yellow solution by filtration and was washed with toluene (2 × 10 mL). The combined filtrates were analyzed by ^1H and ^{119}Sn NMR spectroscopy, indicating the formation of **8b** and the presence of unreacted **1** (mixture of tetramer and pentamer) in equimolar amounts. One further species was identified in the reaction mixture. This compound showed broad signals in the ^1H NMR spectum and did not show a ^{119}Sn NMR signal. ^1H NMR (200 MHz, C_6D_6, 20 °C): δ = 6.59 (br, 2 H, *meta*-Mes), 2.71 (br, 6 H, *ortho*-Me), 1.94 (br, 3 H, *para*-Me); ^{13}C NMR (50.3 MHz, C_6D_6, 20 °C) δ = 154.9 (br, *ortho*-Mes), 141.9 (br, *para*-Mes), 126.9 (br, *meta*-Mes), 29.1 (*ortho*-Me), 21.3 (*para*-Me), not observed (*ipso*-Mes).

Table 1. NMR Spectroscopic and Isolated Yields for Reactions of 1 with Main Group Element Halides MX_n

MX_n (equiv)	product	yield (%)[a]	isolated yield (%)
$SnCl_4$ (1.05)	$MesSnCl_3$ (**2a**)	97	92
$SnCl_4$ (0.50)	Mes_2SnCl_2 (**2b**)	>97	87
n$BuSnCl_3$ (1.05)	Mes*n*$BuSnCl_2$ (**3a**)	97	89
$PhSnCl_3$ (1.05)	$MesPhSnCl_2$ (**3b**)	95	85
BCl_3 (1.05)	$MesBCl_2$ (**4**)	>97	88
1,1′-fc(BBr_2)$_2$ (0.50)	1,1′-fc(BBrMes)$_2$ (**5**)	97	72
PCl_3 (1.05)	$MesPCl_2$ (**6**)	60	
PCl_3 (2.00)	$MesPCl_2$ (**6**)	95	82

[a] Estimated yield from ^1H NMR spectroscopy.

(c) Reaction of Me_3SnCl with 1 equiv of 1: Synthesis of Me_3SnMes (8b). A solution of Me_3SnCl (0.25 g, 1.25 mmol) in toluene (10 mL) was added slowly to a solution of **1** (0.25 g, 1.24 mmol CuMes) in toluene (30 mL) at room temperature, stirred for 12 h, and heated to 50 °C for 1 h. A gray-green precipitate formed, which was separated from the colorless solution by filtration and washed with toluene (2 × 10 mL). The combined filtrates were passed through a column (neutral alumina with toluene as eluent), and all volatile material was removed under vacuum to give spectroscopically pure **8b** as a colorless oil (0.30 g, 86%). For **8b**: ^1H NMR (300 MHz, C_6D_6, 20 °C) δ = 6.77 (s/d, $J(^{117/119}Sn, H)$ = 16 Hz, 2 H, *meta*-Mes), 2.29 (s/d, $J(^{117/119}Sn, H)$ = 6 Hz, 6 H, *ortho*-Me), 2.15 (s, 3 H, *para*-Me), 0.31 (s/d, $J(^{117/119}Sn, H)$ = 51, 53 Hz, 9 H, Sn−CH_3); ^{13}C NMR (50.3 MHz, C_6D_6, 20 °C) δ = 144.8 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 34 Hz, *ortho*-Mes), 138.1 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 9 Hz, *para*-Mes), 137.6 (*ipso*-Mes), 128.2 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 43 Hz, *meta*-Mes), 25.7 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 32 Hz, *ortho*-Me), 21.1 (*para*-Me), −5.2 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 322, 337 Hz, Sn−CH_3); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20 °C) δ = −52.3; *m/z* (%) 284 (2) [M^+], 269 (100) [M^+ − Me], 239 (38) [$MesSn^+$]; $C_{12}H_{20}Sn$ (283.00) calcd C 50.93, H 7.12; found C 50.92, H 7.35.

Results and Discussion

In a general procedure, a freshly prepared solution of [CuMes]$_5$·toluene (**1**) was reacted with the chosen metal halide at −30 °C in toluene, and the reaction mixture was stirred for 12 h at room temperature and heated to 50 °C for 1 h. After filtration from the insoluble copper halide all volatile material was removed under vacuum. The crude product was analyzed by ^1H NMR spectroscopy prior to recrystallization or distillation. Results for the reaction of **1** with selected group 13−15 metal halides in toluene solution are summarized in Table 1. Both the yields as determined by ^1H NMR spectroscopy and the isolated yields after recrystallization or distillation of the compounds are given based on one unit of CuMes.

Alkyl or aryl groups are usually introduced to tin halides through reaction with Grignard reagents or lithium or aluminum organyls.[40] However, selective

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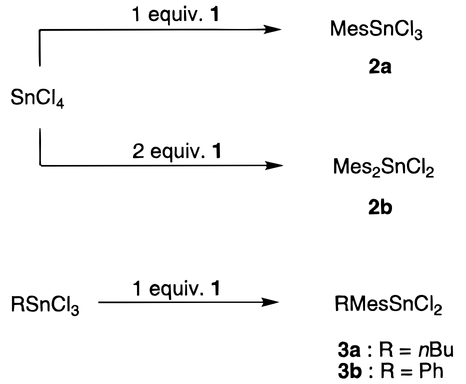
[38] Schacht, W.; Kaufmann, D. *Chem. Ber.* **1987**, *120*, 1331.

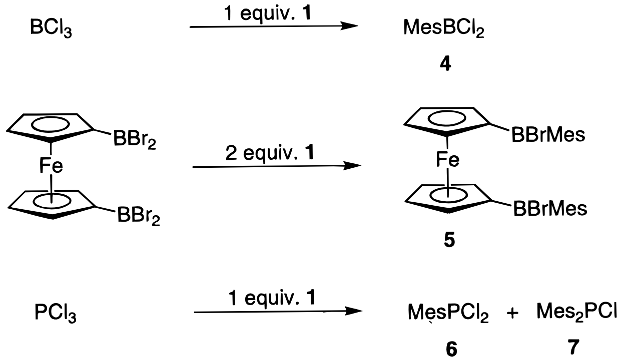
[39] **6** was previously synthesized from PCl_3 and MesMgBr in ca. 80% yield; see: Xie, Z.-M.; Neilson, R. H. *Organometallics* **1983**, *2*, 921.

[40] Davies, A. G., Ed. *Organotin Chemistry*; VCH: Weinheim, New York, Basel, Cambridge, Tokyo, 1997.

Scheme 1: Reaction of 1 with $SnCl_4$ and Organotintrichlorides $RSnCl_3$



Scheme 2: Reaction of 1 with MCl_3 (M = B, P) and 1,1′-fc$(BBr_2)_2$



partial substitution is in most cases difficult to achieve. An alternative route involves a two-step procedure of arylation to the tetraorganostannane and subsequent dearylation via selective cleavage of Sn−C bonds with halogens X_2, halogen acids HX, or tin halides (Kocheshkov disproportion reaction). Milder reagents with metals such as mercury, zinc, or copper allow for the use of functionalized substituents and provide more selective substitution. Organocopper reagents $[ArCu]_n$ (Ar = 2-$CHRNMe_2Ph$) with donor substituents in *ortho*-position were introduced by van Koten and co-workers for the preparation of pentacoordinate and hexacoordinate organotin compounds $ArRSnX_2$ and Ar_2SnX_2,[41,42] including chiral compounds ArRR′SnX.[43,44] Furthermore, formation of the trisubstituted stannanes Ph_3SnX and Me_2PhSnX from phenylcopper was found to proceed very selectively.[41] Despite these encouraging initial reports organocopper reagents were not further considered in the synthesis of organotin compounds.

Mesityltin trichloride (**2a**) was previously synthesized by two different synthetic pathways. Reaction of mesityllithium and tin tetrachloride gave 40% of **2a** after fractionational distillation.[45] In another attempt **2a** was prepared via redistribution between dimesityltin dichloride (**2b**) and tin tetrachloride in 62% yield after distillation.[36] Compound **2b** on the other hand was synthesized from dimesitylmercury and tin(II) chloride in 53% yield after recrystallization.[36] Preparation of **2b** from mesityllithium and tin tetrachloride gave this compound in only 21% yield.[37] We found that if **1** is used as the arylating agent, spectroscopically pure **2a** and **2b** are obtained in 92 and 87% yield, respectively, after a single recrystallization step (Scheme 1, Table 1). The same synthetic method can be applied to synthesize diorganodichlorostannanes with two different substituents (Scheme 1). Reaction of **1** with $nBuSnCl_3$ and $PhSnCl_3$ gave **3a** and **3b** in 89 and 85% isolated yield, respectively. A small excess of the tin species (1.05 equiv) avoids formation of any trisubstituted compound, whereas the tin reagent can easily be removed in high vacuum or by one recrystallization step from hexanes.

We were interested to see whether the use of **1** would also be advantageous for the introduction of mesityl groups to group 13 and group 15 halides. Reaction of **1** with BCl_3 gave **4** as the only NMR spectroscopically detectable product, which was isolated in 88% yield after distillation (Scheme 2).[46,47] Compound **1** can also be used for the synthesis of mixed diorganohaloboranes, as shown for the reaction of 1,1′-fc$(BBr_2)_2$ (fc = Fe(η-C_5H_4)$_2$) with 2 equiv of the copper reagent. ^1H NMR spectroscopy revealed the formation of 1,1′-fc$(BBrMes)_2$ (**5**) in ca. 97% yield. However, the isolated yield after recrystallization from hexanes (72%) was significantly lower due to the high solubility of **5**. Surprisingly, reaction of **1** with one equiv PCl_3 did not proceed with similar chemoselectively and gave substantial amounts of Mes_2PCl (**7**; 40%) in addition to $MesPCl_2$ (**6**; 60%) (Scheme 2). However, when an excess of PCl_3 was used (2 equiv), **6** was formed almost exclusively and was isolated in 82% yield after distillation.[39]

Van Koten and co-workers previously reported the initial formation of a red precipitate for the reaction of R_2SnX_2 (R = Me, Ph; X = Cl, Br) with donor-substituted phenylcopper derivatives $[ArCu]_n$.[41] This precipitate was found to be a 1/1 complex of the organocopper compound with cuprous halide ($[ArCu{\cdot}CuX]_n$).[41,48] The high selectivity in these arylation reactions was therefore ascribed not only to the steric bulk of the aryl group but also to the formation of such an aggregate lowering the reactivity of the Cu−C bond toward the Sn−X bonds.[41] Reaction of **1** with tin and boron halides initially led to the formation of an orange-amber precipitate, which gradually turned white upon stirring at room temperature. With $SnCl_4$, BCl_3, and 1,1′-fc$(BBr_2)_2$ formation of a precipitate was observed at the addition temperature, whereas with $RSnCl_3$ precipitation occurred at higher temperatures, but still below 25 °C. Complete conversion as evidenced by a color change to white required prolonged reaction times or even slight heating (50 °C). These observations prompted us to elucidate the possible formation of an aggregate $[MesCu{\cdot}CuX]_n$ as reaction intermediate in analogy with van Koten's results.

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[41] Van Koten, G.; Schaap, C. A.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *99*, 157.

[42] Van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Organomet. Chem.* **1979**, *177*, 283.

[43] van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393.

[44] van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

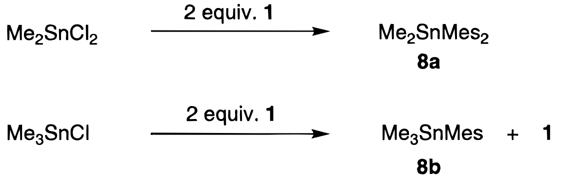
[45] Weidenbruch, M.; Schäfers, K.; Schlaefke, J.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1991**, *415*, 343.

[46] The synthesis of $MesBCl_2$ was previously described from tris(2,4,6-trimethylphenyl)boroxin and BCl_3 in 22% yield; see ref 38.

[47] Organomercury compounds are the most commonly used reagents for the selective arylation of boron halides; see: Niedenzu, K. *Organomet. Chem. Rev.* **1966**, *1*, 305.

[48] van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 419.

Scheme 3: Reaction of Me_2SnCl_2 and Me_3SnCl with 2 equiv of 1



When Me_2SnCl_2 was treated with 2 equiv of CuMes under similar conditions as applied by van Koten and co-workers,[41] quantitative formation of Me_2SnMes_2 (**8a**) was observed and a reaction intermediate could not be isolated (Scheme 3). Treatment of Me_3SnCl with 2 equiv of CuMes resulted in the formation of Me_3SnMes (**8b**) and a gray precipitate (Scheme 3). However, ^{1}H NMR spectroscopy indicated that only 1 equiv CuMes was used, and the soluble part of the reaction mixture contained a 1/1 mixture of **8b** and **1**. We conclude that, even though it may initially form, a complex $[MesCu\cdot CuCl]_n$ is not a stable intermediate in the described metathesis reactions.[49] The presence of donor substituents on the aryl group seems to be essential in order to stabilize such an aggregate.[41] The observed high chemoselectivity of **1** in reactions with tin and boron halides may therefore primarily be attributed to the steric bulk of the mesityl substituent and to the high degree of aggregation of **1** in solution (tetrameric and pentameric structure).

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(49) The observed orange color of the precipitate in reactions with **1** may possibly be due to the presence of trace amounts of oxygen resulting in an orange-red cluster compound $[Cu_{10}O_2(Mes)_6]$: Håkansson, M.; Örtendahl, M.; Jagner, S.; Sigalas, M. P.; Eisenstein, O. *Inorg. Chem.* **1993**, *32*, 2018.