Supporting Information

Substituent Effects on Ditetrel Alkyne Analogues: Multiple vs Single Bonded Isomers

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Experimental Section

General Procedures. All reactions were performed with the use of modified Schlenk techniques under anaerobic and anhydrous conditions. The syntheses of most of the modified ligands have been already reported.[S1] These followed routes are already well established for related large terphenyl derivatives.[S2, S3] The synthesis of 4-Me_3Ge-Ar′MgBr is given in the Supporting Information. Derivatization to their lithium salts by means of their reaction with ^{n}BuLi also proceeded normally and in high yields.[S1-S5] The compounds $(Ar'SnCl)_2$, $(Ar^*SnCl)_{1,2}$, $(Ar'GeCl)_2$ and $(Ar^*GeCl)_{1,2}$ were prepared as previously described.[S6, S7-S10] ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Varian Mercury 300MHz spectrometer (75.5MHz, respectively) and referenced internally to residual protio hexane, benzene or toluene in deuterated solvent. Solution ^{119}Sn NMR spectra were recorded on a Varian Inova 600 MHz spectrometer (224.2MHz, respectively) and referenced externally to neat Sn^nBu_4. UV-vis data were recorded on a Hitachi-1200 spectrometer, while infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 1430 instrument. Melting points were measured in sealed glass capillaries under nitrogen using a Mel-Temp II apparatus and are uncorrected.

4-Me_3Ge-Ar′MgBr: To a stirred solution of $Me_3Ge\text{-}C_6H_2Cl_2$[S11] (8.35 g, 0.0314 mol) in 150 mL of dry THF in a 500 mL two necked flask was added 15 mL 2.5M ^{n}BuLi (0.0370 mol) over a period of 10 min with cooling to ca. -78°C. After stirring for 1 h, a freshly prepared solution of 2,6-$^i Pr_2$-H_3C_6-MgBr (34 g, 0.0691 mol) in 150 ml THF was added dropwise with stirring over a period of 2h, after which time the mixture was warmed to room temperature and the solvents were removed to a ca. 20 mL volume under reduced pressure. Then, ca. 100 mL of dry hexane was then added to afford a white precipitate. The resultant mixture was filtered and the white precipitate was dried under the reduced pressure to afford 4-Me_3Ge-Ar′MgBr·$(THF)_3$ (16.8g, 70%). ^{1}H NMR (C_6D_6, 300.08MHz, 25°C): δ 7.31 (s, 2H), 7.22 (t, 2H, $^3J_{HH}$ = 6.8Hz), 7.15 (d, 4H, $^3J_{HH}$ = 6.8Hz), 3.66 (br, 12H, THF), 3.39 (sept, 4H, $^3J_{HH}$ = 6.9Hz), 1.42 (d, 12H, $^3J_{HH}$ = 6.9MHz), 1.27 (br, 12H, THF), 1.20 (d, 12H, $^3J_{HH}$ = 6.9MHz), 0.44 (s, 9H, -Ge(CH_3)$_3$).^{13}C {^{1}H} NMR (C_6D_6, 150.8MHz, 25°C): δ 154.6, 148.2, 144.3, 140.1, 136.7, 132.6, 128.4, 124.6, 31.2 (o-$CH(CH_3)_2$), 27.8 (o-$CH(CH_3)_2$), 24.5 (o-$CH(CH_3)_2$), -2.0 (($CH_3)_3$Ge).

Aryl germanium(II) and tin(II) halides.

[4-Cl-Ar′GeCl]$_2$: A solution of 4-Cl-Ar′Li·$(OEt_2)_2$ (2.50 g, 4.26 mmol) in diethyl ether (30 mL) was added to a cooled (ca. -78°C) rapidly stirred suspension of 0.986 g (5.00 mmol) of $GeCl_2$·dioxane in diethyl ether (15 mL). After complete addition, the reaction mixture was allowed to warm slowly to room temperature and stirring was continued for an additional 12 h to produce a bright yellow solution. All volatile materials were removed under reduced pressure and the remaining solid was extracted with ca. 40 mL of hexanes. The precipitate was allowed to settle and the reaction mixture was filtered through a filter tipped cannula. Concentration to incipient crystallization and storage at ca.-20°C yielded 1.37 g (1.27 mmol, 59.6 % yield) of yellow crystals of [4-Cl-Ar′GeCl]$_2$. m.p.: 162-163°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 358 (2550). ^{1}H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.28 (s, 2H), 7.20 (t, 2H, $^3J_{HH}$ = 6.6 Hz), 7.11 (d, 4H, $^3J_{HH}$ = 6.6 Hz), 2.95 (sept, 4H, $^3J_{HH}$ = 5.1 Hz), 1.33 (d, 12H, $^3J_{HH}$ = 5.1 Hz), 0.93 (d, 12H, $^3J_{HH}$ = 5.1 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 75.45 MHz, 25°C): δ (*i*-C_6H_2ClGe) not obs., 147.36 (*i*-Dipp), 138.11 (*o*-Dipp), 134.79 (*o*-C_6H_2ClGe), 131.13 (*p*-C_6H_2ClGe), 129.42 (*p*-Dipp), 128.61 (*m*-C_6H_2ClGe), 123.82 (*m*-Dipp), 31.10 (*o*-$CH(CH_3)_2$), 25.56 (*o*-$CH(CH_3)_2$), 23.20 (*o*-$CH(CH_3)_2$).

[4-Me_3Si-Ar′GeCl]$_2$: By a procedure similar to that for [4-Cl-Ar′GeCl]$_2$, [4-Me_3Si-Ar′GeCl]$_2$ was prepared by using 0.875 g (3.78 mmol) of $GeCl_2$·dioxane and 1.50 g (3.15 mmol) of 4-Me_3Si-Ar′Li to afford 1.33 g (72.9 %

yield) of [4-Me$_3$Si-Ar′GeCl]$_2$ which was obtained as yellow crystals after filtration, concentration under reduced pressure and storage at ca. -20°C. m.p.: 138-141°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 379 (2700). ^{1}H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.52 (s, 2H), 7.40 (t, 2H, $^3J_{HH}$ = 6.8 Hz), 7.29 (d, 4H, $^3J_{HH}$ = 6.8 Hz), 3.01 (sept, 4H, $^3J_{HH}$ = 6.9 Hz), 1.33 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.02 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 0.23 (s, 9H). ^{13}C{^{1}H} NMR (C_6D_6, 100.53 MHz, 25°C): δ 167.90 (*ipso*-$C_6H_2SiMe_3$), 147.63 (*o*-Dipp), 144.08 (*i*-Dipp), 143.96 (*o*-$C_6H_2SiMe_3$), 137.66 (*p*-$C_6H_2SiMe_3$), 136.74 (*m*-$C_6H_2SiMe_3$), 129.83 (*p*-Dipp), 123.54 (*m*-Dipp), 31.40 (*o*-*C*H(CH_3)$_2$), 25.60 (*o*-CH(*C*H$_3$)$_2$), 22.89 (*o*-CH(*C*H$_3$)$_2$), -1.93 ((*C*H$_3$)$_3$Si). ^{29}Si{^{1}H} NMR ($CDCl_3$, 119.163 MHz, 25°C): δ -3.67.

3,5-^{i}Pr$_2$-Ar*GeI: By a procedure similar to that of [4-Cl-Ar′GeCl]$_2$, 3,5-^{i}Pr$_2$-Ar*GeI was prepared using 1.5 g (6.48 mmol) of GeCl$_2$·dioxane and 3.40 g (5.26 mmol) of 3,5-^{i}Pr$_2$-Ar*Li to afford 1.45 g (36.9 % yield) of 3,5-^{i}Pr$_2$-Ar*GeI which was obtained as yellow crystals after filtration, concentration under reduced pressure and storage at ca. -20°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 388 (800). ^{1}H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.54 (s, 1H), 7.23 (s, 4H), 3.01 (sept, 4H, $^3J_{HH}$ = 6.7 Hz), 2.87 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 2.75 (sept, 2H, $^3J_{HH}$ = 6.9 Hz), 1.30 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.26 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.18 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.14 (d, 12H, $^3J_{HH}$ = 6.9 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 100.53 MHz, 25°C): δ 184.4 (*o*-C$_6$H$_2$^{i}Pr$_2$), 155.0 (*p*-Dipp), 148.5 (*o*-Dipp), 146.3 (*i*-Dipp), 136.0 (*m*-C$_6$H$_2$^{i}Pr$_2$), 125.0 (*p*-C$_6$H$_2$^{i}Pr$_2$), 120.8 (*m*-Dipp), *i*-C$_6$H$_2$^{i}Pr$_2$ was not observed. 35.6 (*p*-*C*H(CH_3)$_2$), 34.7 (*o*-*C*H(CH_3)$_2$), 30.5 (*m*-*C*H(CH_3)$_2$), 27.6 (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$).

[4-F-Ar′SnCl]$_2$: A solution of 4-F-Ar′Li/LiI (2.00 g, 3.59 mmol) in diethyl ether (40 mL) was added to a cooled (ca. -78°C) rapidly stirred suspension of 1.04 g (5.50 mmol) of SnCl$_2$ in diethyl ether (20 mL). After complete addition the reaction mixture was allowed to slowly warm to room temperature and stirring was continued for additional 12 h. After concentrating the resulting orange solution under reduced pressure to about 5 mL, 60 mL of hexanes were added. The resultant precipitates were allowed to settle and the reaction mixture was filtered through a filter tipped cannula. Due to chloride/iodide exchange reactions, the product was obtained as a 4:1 mixture of [4-F-Ar′SnCl]$_2$ and the4-F-Ar′SnI. m.p: 183-184°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 395 (2200). ^{1}H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.40 (s, 2H), 7.14 (t, 2H, $^3J_{HH}$ = 6.0 Hz), 7.07 (d, 2H, $^3J_{HF}$ = 10.3 Hz), 7.03 (d, 4H, $^3J_{HH}$ = 6.0 Hz), 2.95 (sept, 4H, $^3J_{HH}$ = 5.1 Hz), 1.21 (d, 12H, $^3J_{HH}$ = 5.1 Hz), 0.93 (d, 12H, $^3J_{HH}$ = 5.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.45 MHz, 25°C): δ 176.9 (*i*-C_6H_2F, $^4J_{FC}$ = not res.), 162.6 (*p*-C_6H_2F, $^1J_{FC}$ = 248 Hz), 147.8 (*o*-C_6H_2FI, $^3J_{FC}$ = 6.8 Hz), 147.3 (*o*-Dipp), 136.3 (*i*-Dipp), 129.5 (*p*-Dipp), 123.7 (*m*-Dipp), 117.6 (*m*-C_6H_2FI, $^2J_{FC}$ = 19.1 Hz), 30.9 (*o*-*C*H(CH_3)$_2$), 26.0 (*o*-CH(*C*H$_3$)$_2$), 22.8 (*o*-CH(*C*H$_3$)$_2$). ^{19}F{^{1}H} NMR (C_6D_6, 282.33 MHz, 25°C): δ -113.2 (t, $^3J_{HF}$ = 10.3 Hz). ^{119}Sn{^{1}H} NMR (C_6D_6, 224.192 MHz, 25°C): δ 719.5

[4-Cl-Ar′SnCl]$_2$: By a procedure similar to that for [4-F-Ar′SnCl]$_2$, [4-Cl-Ar′SnCl]$_2$ was prepared using 4-Cl-Ar′Li·(OEt$_2$)$_2$ (2.35 g, 4.00 mmol) and 1.14 g (6.00 mmol) of SnCl$_2$ in diethyl ether (60 mL). This afforded 1.47 g (62.6%) of [4-Cl-Ar′SnCl]$_2$ as yellow crystals from toluene at ca. -20°C. m.p: 177-179°C (decomp.). UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 394 (2600). ^{1}H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.41 (s, 2H), 7.13 (t, 2H, $^3J_{HH}$ = 6.6 Hz), 7.06 (d, 4H, $^3J_{HH}$ = 6.6 Hz), 2.94 (sept, 4H, $^3J_{HH}$ = 5.1 Hz), 1.22 (d, 12H, $^3J_{HH}$ = 5.1 Hz), 0.91 (d, 12H, $^3J_{HH}$ = 5.1 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 75.45 MHz, 25°C): δ 180.58 (*i*-C_6H_2ClSn), 147.57 (*i*-Dipp), 144.79 (*o*-Dipp), 136.65 (*o*-C_6H_2ClSn), 131.78 (*p*-C_6H_2ClSn), 129.18 (*p*-Dipp), 125.54 (*m*-C_6H_2ClSn), 123.82 (*m*-Dipp), 30.88 (*o*-*C*H(CH_3)$_2$), 26.24 (*o*-CH(*C*H$_3$)$_2$), 22.84 (*o*-CH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C_6D_6, 224.192 MHz, 25°C): δ 443.4.

[4-MeO-Ar′SnCl]$_2$: In a manner similar to that described for [4-F-Ar′SnCl]$_2$, [4-MeO-Ar′SnCl]$_2$ was prepared from a solution of 4- MeO-Ar′Li (1.5g, 3.45 mmol) and 0.78 g (4.11mmol) of SnCl$_2$. Work up afforded 0.8g (40%) of [4-MeO-Ar′SnCl]$_2$ as large orange crystals. m. p: 187-190°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 402(730). ^{1}H NMR (C_6D_6, 300.08MHz, 25°C): δ 7.18 (t, 2H, $^3J_{HH}$ = 6.8Hz), 7.13 (d, 4H, $^3J_{HH}$ = 6.8Hz), 6.99 (s, 2H), 3.36(s, 9H), 3.18 (sept, 4H, $^3J_{HH}$ = 6.9Hz), 1.34 (d, 12H, $^3J_{HH}$ = 6.9MHz), 1.04 (d, 12H, $^3J_{HH}$ = 6.9MHz). ^{13}C{^{1}H} NMR (C_6D_6, 150.8MHz, 25°C): δ *i*-C_6H_2MeO (not observed) 160.5 (*o*-Dipp), 148.3 (*i*-Dipp), 147.5 (*p*-Dipp), 138.5 (*o*-C_6H_2MeO), 129.9 (*p*- C_6H_2MeO), 124.6 (*m*-Dipp), 117.3 (*m*- C_6H_2MeO), 55.3 (-

O*C*H$_3$), 31.7 (o-*C*H(CH$_3$)$_2$), 27.2 (o-CH(*C*H$_3$)$_2$), 23.7 (o-CH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H}NMR (C$_6$D$_6$, 224.19MHz, 25°C): δ 1115.

[4-^{t}Bu-Ar′SnCl]$_2$: In a manner similar to that described for [4-F-Ar′SnCl]$_2$, [4-^{t}Bu-Ar′SnCl]$_2$ was prepared from a solution of 4-^{t}Bu-Ar′Li (4.00 g, 8.66 mmol) with SnCl$_2$ (1.93 g, 10.2 mmol). Work up gave 2.39 g of yellow microcrystalline [4-^{t}Bu-Ar′SnCl]$_2$ (45%) after 1 week. m.p: 216-218°C. UV-vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 402 (1240). ^{1}H NMR (C$_6$D$_6$, 300.08MHz, 25°C): δ 7.38 (s, 2H, Ar*H*), 7.18-7.25 (m, 6H, Ar*H*), 3.12 (septet, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.33 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.32 (s, 9H, C(C*H*$_3$)$_3$), 1.05 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{13}C {^{1}H} NMR (C$_6$D$_6$, 150.8MHz, 25°C): δ 150.3, 147.7, 144.4, 129.3, 125.5, 123.7 and 122.8 (Ar*C*), 34.5 (*C*(CH$_3$)$_3$), 31.2 (*C*H(CH$_3$)$_2$), 30.9 (C(*C*H$_3$)$_3$), 26.1 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 224.19MHz, 25°C): δ 1001.0.

[4-Me$_3$Si-Ar′SnCl]$_2$: In a manner similar to that described for [4-F-Ar′SnCl]$_2$, [4-Me$_3$Si-Ar′SnCl]$_2$ was prepared from a solution of 4-Me$_3$Si-Ar′Li (2.00g, 4.20 mmol) with (1.20 g, 6.3 mmol) of SnCl$_2$. Work up afforded 1.65 g (63.1%) of [4-Me$_3$Si-Ar′SnCl]$_2$ which contained minor traces of the respective iodide as a side product. m.p: 154-155°C, UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 406 (2400). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.54 (s, 2H), 7.22 (t, 2H, $^3J_{HH}$ = 6.8 Hz), 7.11 (d, 4H, $^3J_{HH}$ = 6.8 Hz), 3.06 (sept, 4H, $^3J_{HH}$ = 6.9 Hz), 1.27 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.00 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 0.24 (s, 9H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.53 MHz, 25°C): δ 183.5 (*ipso*-C$_6$H$_2$SiMe$_3$), 148.3 (*o*-Dipp), 144.6 (*i*-Dipp), 134.0 (*o*-C$_6$H$_2$SiMe$_3$), 137.7 (*p*-C$_6$H$_2$SiMe$_3$), 135.9 (*m*-C$_6$H$_2$SiMe$_3$), 129.9 (*p*-Dipp), 124.3 (*m*-Dipp), 31.6 (*o*-*C*H(CH$_3$)$_2$), 26.7 (*o*-CH(*C*H$_3$)$_2$), 23.4 (*o*-CH(*C*H$_3$)$_2$), -1.37 ((*C*H$_3$)$_3$Si). ^{29}Si{^{1}H} NMR (CDCl$_3$, 119.163 MHz, 25°C): -4.3. ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 224.192 MHz, 25°C): δ 904.1.

[4-Me$_3$Ge-Ar′SnCl]$_2$: A solution of 4-Me$_3$Ge-Ar′MgBr (see supporting information) (3g, 3.58 mmol) in diethyl ether (40 mL) was added dropwise to a dispersion of 1.2g (6.32 mmol) of SnCl$_2$ in ether (30 mL) with cooling in an ice bath. The reaction mixture became orange. Stirring was maintained for 12h, after which time the solvents were removed under reduced pressure. The resultant orange powder was extracted into toluene and filtered. Concentration to incipient crystallization and storage of the solution at ca. -30°C for 12 h afforded 1.0 g (42%) of [4-Me$_3$Ge-Ar′SnCl]$_2$ as orange crystals which contained minor traces of the respective iodide as a side product. m. p: 180-182°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 408 (740). ^{1}H NMR (C$_6$D$_6$, 300.08MHz, 25°C): δ 7.60 (s, 2H), 7.19 (t, 2H, ^{3}J$_{HH}$ = 6.8Hz), 7.15 (d, 4H, ^{3}J$_{HH}$ = 6.8Hz), 3.16 (sept, 4H, ^{3}J$_{HH}$ = 6.9Hz), 1.34 (d, 12H, ^{3}J$_{HH}$ = 6.9MHz), 1.04 (d, 12H, ^{3}J$_{HH}$ = 6.9MHz), 0.40 (s, 9H, -Ge(C*H*$_3$)$_3$). ^{13}C {^{1}H} NMR (C$_6$D$_6$, 150.8MHz, 25°C): δ *i*- C$_6$H$_2$GeMe$_3$ (not observed), 147.8 (*o*-Dipp), 144.3 (*i*-Dipp), 135.3 (*o*-C$_6$H$_2$GeMe$_3$), 132.7 (*p*- C$_6$H$_2$GeMe$_3$), 129.6 (*m*- C$_6$H$_2$GeMe$_3$), 123.9 (*p*-Dipp), 123.0 (*m*-Dipp), 31.1 (o-*C*H(CH$_3$)$_2$), 26.3(o-CH(*C*H$_3$)$_2$), 23.0 (o-CH(*C*H$_3$)$_2$), -1.9 ((*C*H$_3$)$_3$Ge). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 224.19MHz, 25°C): δ 805.7.

[3,5-^{i}Pr$_2$-Ar′SnCl]$_2$: In a manner similar to that described for [4-F-ArSnCl]$_2$, [3,5-^{i}Pr$_2$-Ar′SnCl]$_2$ was prepared from a solution of 3,5-^{i}Pr$_2$-Ar′Li (1.25 g, 2.56 mmol) with SnCl$_2$ (0.76 g, 4.00 mmol). Work up yielded 1.18 g (72.3%) of [3,5-^{i}Pr$_2$-Ar′SnCl]$_2$ as orange needles. m.p: 187-189°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 399 (2200). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.49 (s, 1H), 7.27 (t, 2H, $^3J_{HH}$ = 6.8 Hz), 7.15 (d, 4H, $^3J_{HH}$ = 6.8 Hz), 2.91 (sept, 2H, $^3J_{HH}$ = 7.4 Hz), 2.80 (sept, 4H, $^3J_{HH}$ = 6.9 Hz), 1.39 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.14 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.07 (d, 12H, $^3J_{HH}$ = 7.4 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.53 MHz, 25°C): δ *i*-C$_6$H$_2$^{i}Pr$_2$ not observed, 149.1 (*i*-Dipp), 148.5 (*o*-Dipp), 148.0 (*m*-C$_6$H$_2$^{i}Pr$_2$), 140.3 (*o*-C$_6$H$_2$^{i}Pr$_2$), 129.6 (*p*-Dipp), 125.5 (*i*-C$_6$H$_2$^{i}Pr$_2$), 123.5 (*m*-Dipp), 30.9 (*o*-*C*H(CH$_3$)$_2$), 30.3 (*m*-*C*H(CH$_3$)$_2$), 30.0 (CH(*C*H$_3$)$_2$), 25.7 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 224.192 MHz, 25°C): δ 748.8.

3,5-^{i}Pr$_2$-Ar*SnCl: In a manner similar to that described for [4-F-ArSnCl]$_2$, 3,5-^{i}Pr$_2$-Ar*SnCl was prepared from a solution of 3,5-^{i}Pr$_2$-Ar*Li·2(Et$_2$O) (3.0 g, 4.16 mmol) with 1.18 g of SnCl$_2$ (6.2 mmol). Work up yielded 1.67 g (55.7%) of 3,5-^{i}Pr$_2$-Ar*SnCl as orange crystals. m.p: 149-151°C (decomp.) UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 416 (2700). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.47 (s, 1H), 7.22 (s, 4H), 2.98 (sept, 4H, $^3J_{HH}$ = 6.7 Hz), 2.84 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 2.75 (sept, 2H, $^3J_{HH}$ = 6.9 Hz), 1.43 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.25 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.16 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.12 (d, 12H, $^3J_{HH}$ = 6.9 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.53 MHz, 25°C): δ 221.3 (*i*-C$_6$H$_2$^{i}Pr$_2$), 149.9 (*o*-C$_6$H$_2$^{i}Pr$_2$), 148.5 (*p*-Dipp), 148.1 (*o*-Dipp), 140.5 (*i*-Dipp), 134.0 (*m*-

C$_6$H$_2$^{i}Pr$_2$), 123.6 (*p*-C$_6$H$_2$^{i}Pr$_2$), 123.4 (*m*-Dipp), 35.0 (*p*-*C*H(CH$_3$)$_2$), 31.0 (*o*-*C*H(CH$_3$)$_2$), 30.1 (*m*-*C*H(CH$_3$)$_2$), 26.8 (CH(*C*H$_3$)$_2$), 25.7 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 224.192 MHz, 25°C): δ 1256.0.

Digermynes and Distannynes.

4-Cl-Ar′GeGeAr′-4-Cl: To a cooled (ca. -78°C) solution of 0.75 g (0.694 mmol) of [4-Cl-Ar′GeCl]$_2$ in diethyl ether, 1.40 ml (1.40 mmol) of a 1.0 molar solution of di-*iso*-butylaluminum hydride were added with stirring. Stirring at ca. -78°C was continued for additional 45 minutes after which time the reaction mixture was allowed to warm slowly to room temperature to give a dark red reaction mixture. Stirring was continued for 8 h whereupon filtration through a filter tipped cannula and concentration under reduced pressure to incipient crystallization and storage at -20°C yielded 0.313 g (0.310 mmol, 44.7 % yield) of orange-red crystals of 4-Cl-Ar′GeGeAr′-4-Cl. m.p.: 159-162°C (decomp.) UV-Vis λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 324 (sh, 5100) 438 (1800). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.24 (s, 2H), 7.15 (t, 2H, $^3J_{HH}$ = 6.6 Hz), 7.01 (d. 4H, $^3J_{HH}$ = 6.6 Hz), 2.68 (sept, 4H, $^3J_{HH}$ = 5.1 Hz), 1.08 (d, 12H, $^3J_{HH}$ = 5.1 Hz), 0.96 (d, 12H, $^3J_{HH}$ = 5.1 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.45 MHz, 25°C): δ (*i*-C$_6$H$_2$Ge) not obs., 147.49 (*i*-Dipp), 145.84 (*o*-Dipp), 139.09 (*o*-C$_6$H$_2$Ge), 129.03 (*p*-C$_6$H$_2$Ge), 128.10 (*p*-Dipp), 123.82 (*m*-Dipp), 123.71 (*m*-C$_6$H$_2$Ge), 31.10 (*o*-*C*H(CH$_3$)$_2$), 25.56 (*o*-CH(*C*H$_3$)$_2$), 23.20 (*o*-CH(*C*H$_3$)$_2$).

4-Me$_3$Si-Ar′GeGeAr′-4-SiMe$_3$: At ca. 0°C a solution of 0.65 g (1.12 mmol) of [4-Me$_3$Si-Ar′GeCl]$_2$ in diethyl ether (30 mL) was added to a stirred suspension of 0.162 g (1.20 mmol) KC$_8$ in diethyl ether (20 mL). The reaction mixture slowly became a dark-red color and after stirring for further 36 h at ca. 25°C. The precipitated salts and graphite were seperated via a cannula to produce a dark red solution which was concentrated *in vacuo* to incipient crystallization and stored at ca. -20°C to give 0.265 g (43.7 % yield) of 4-Me$_3$Si-Ar′GeGeAr′-4-SiMe$_3$ as dark red crystals. m.p.: 161-163°C (decomp.) UV-Vis λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 380 (5600) 510 (1050). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.31 (t, 2H, $^3J_{HH}$ = 6.8 Hz), 7.24 (s, 2H), 7.12 (d, 4H, $^3J_{HH}$ = 6.8 Hz), 2.74 (sept, 4H, $^3J_{HH}$ = 6.9 Hz), 1.32 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 1.06 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 0.29 (s, 9H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.53 MHz, 25°C): δ 158.72 (*ipso*-C$_6$H$_2$Ge), 146.47 (*o*-Dipp), 141.10 (*i*-Dipp), 140.48 (*o*-C$_6$H$_2$Ge), 137.98 (*p*-C$_6$H$_2$Ge), 132.65 (*m*-C$_6$H$_2$Ge), 127.96 (*p*-Dipp), 123.84 (*m*-Dipp), 30.95 (*o*-*C*H(CH$_3$)$_2$), 25.55 (*o*-CH(*C*H$_3$)$_2$), 24.72 (*o*-CH(*C*H$_3$)$_2$), -1.20 ((*C*H$_3$)$_3$Si). ^{29}Si{^{1}H} NMR (CDCl$_3$, 119.163 MHz, 25°C): δ -5.24.

3,5-^{i}Pr$_2$-Ar*GeGeAr*-3,5-^{i}Pr$_2$: 2.2 g (2.94 mmol) of 3,5-^{i}Pr$_2$-Ar*GeI in THF (30 mL) was added to a stirred suspension of 0.406 g (3.22 mmol) of KC$_8$. The reaction mixture slowly became dark-red, and after stirring the reaction for 24 h at ca. 25°C, the precipitated salts and graphite were filtered off via a cannula to produce a dark red solution which was concentrated *in vacuo* to incipient crystallization and stored at -20°C to give 1.50 g (36.0 % yield) of 3,5-^{i}Pr$_2$-Ar*GeGeAr*-3,5-^{i}Pr$_2$ as dark red crystals. UV-Vis λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 378 (3033), 496 (407). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.54 (s, 1H), 6.83 (s, 4H), 3.07 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 2.92 (sept, 4H, $^3J_{HH}$ = 6.7 Hz), 2.80 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 1.34 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.28 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.20 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.16 (d, 12H, $^3J_{HH}$ = 6.7 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.53 MHz, 25°C): δ *i*-C$_6$H$_2$^{i}Pr$_2$ not observed, 176.9 (*m*-C$_6$H$_2$^{i}Pr$_2$), 148.4 (*o*-Dipp), 147.5 (*p*-Dipp), 146.9 (*i*-Dipp), 130.8 (*o*-C$_6$H$_2$^{i}Pr$_2$), 122.3 (*p*-C$_6$H$_2$^{i}Pr$_2$), 121.0 (*m*-Dipp), 34.8 (*p*-*C*H(CH$_3$)$_2$), 30.7 (*o*-*C*H(CH$_3$)$_2$), 29.9 (*m*-*C*H(CH$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$).

4-F-Ar′SnSnAr′-4-F: A solution of [4-F-Ar′SnCl]$_2$ (1.10 g, 0.935 mmol) in diethyl ether (ca. 20 mL) were added to a precooled (ca. 0°C) and rapidly stirred suspension of 0.078 g (2.00 mmol) finely dispersed potassium. The cooling bath was removed after complete addition and stirring was continued at room temperature for 96 h. During this time the reaction mixture acquired an intense dark blue-green color. The precipitates were then allowed to settle overnight and the reaction mixture was filtered through a filter-tipped cannula and was concentrated to incipient crystallization. Storage at ca.-20°C afforded 0.56 g (56.1%) of microcrystalline, dark green 4-F-Ar′SnSnAr′-4-F. m.p: 167-169°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 425 (4200), 592 (3100). ^{1}H NMR (C$_6$D$_6$, 300.08 MHz, 25°C): δ 7.81 (d, 2H, $^3J_{HF}$ = 9.8 Hz), 7.13 (t, 2H, $^3J_{HH}$ = 6.0 Hz), 7.05 (d. 4H, $^3J_{HH}$ = 6.0 Hz), 2.82 (sept, 4H, $^3J_{HH}$ = 5.1 Hz), 1.41 (d, 12H, $^3J_{HH}$ = 5.1 Hz), 1.01 (d, 12H, $^3J_{HH}$ = 5.1 Hz).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.45 MHz, 25°C): δ *i*-C_6H_2FSn (not observed) 173.9 (*p*-C_6H_2FSn, $^1J_{FC}$ = 282 Hz), 153.4 (*o*-Dipp), 147.0 (*i*-Dipp), 142.1 (*o*-C_6H_2FSn, $^3J_{FC}$ = <2 Hz), 131.6 (*p*-Dipp), 123.3 (*m*-Dipp), 107.6 (*m*-C_6H_2FSn, $^2J_{FC}$ = 18.2 Hz), 33.5 (*o*-$\mathit{C}H(CH_3)_2$), 28.2 (*o*-$CH(\mathit{C}H_3)_2$), 24.5 (*o*-$CH(\mathit{C}H_3)_2$). ^{19}F NMR (C_6D_6, 282.33 MHz, 25°C): δ -111.40 (t, $^3J_{HF}$ = 9.8 Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.192 MHz, 25°C): not observed.

4-Cl-Ar′SnSnAr′-4-Cl: A solution of [4-Cl-Ar′SnCl]$_2$ (0.8 g, 0.682 mmol) in diethyl ether (ca. 20 mL) was added to a precooled (ca. -78°C) and rapidly stirred suspension of 0.06 g (1.53 mmol) finely dispersed potassium. The cooling bath was removed after complete addition and stirring was continued at room temperature for 48 h. During this time the reaction mixture acquired a teal color. Workup as above afforded 0.335 g (44.6%) of dichroic orange-green crystals of 4-Cl-Ar′SnSnAr′-4-Cl. m.p: 154-157°C (decomp.) UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 406 (4300), 592 (1550). ^1H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.98 (s, 2H), 7.22 (t, 2H, $^3J_{HH}$ = 6.6 Hz), 7.08 (d. 4H, $^3J_{HH}$ = 6.6 Hz), 2.92 (sept, 4H, $^3J_{HH}$ = 5.1 Hz), 1.38 (d, 12H, $^3J_{HH}$ = 5.1 Hz), 1.17 (d, 12H, $^3J_{HH}$ = 5.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.45 MHz, 25°C): δ 161.5 (*i*-C_6H_2Sn), 150.9 (*i*-Dipp), 147.6 (*o*-Dipp), 146.6 (*o*-C_6H_2Sn), 143.2 (*p*-C_6H_2Sn), 141.2 (*p*-Dipp), 127.7 (*m*-C_6H_2ClSn), 125.3 (*m*-Dipp), 36.0 (*o*-$\mathit{C}H(CH_3)_2$), 32.4 (*o*-$CH(\mathit{C}H_3)_2$), 26.9 (*o*-$CH(\mathit{C}H_3)_2$).$^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.192 MHz, 25°C): not observed.

4-MeO-Ar′SnSnAr′-4-OMe : A solution of [4-MeO-Ar′SnCl]$_2$ (0.62 g, 1.07 mmol) in toluene (ca. 50 mL) was added dropwise to a suspension of 0.041g (1.05 mmol) of finely dispersed potassium with rapid stirring at room temperature. The reaction mixture quickly became a deep green color and stirring was continued for 12h after which time the precipitated material and unreacted potassium was allowed to settle. The solution was filleted through a filter tipped cannula and concentrated under reduced pressure to incipient crystallization (ca. 10 mL). Storage at ca. -20°C yielded 0.4g (34%) of 4- MeO-Ar′SnSnAr′-4-OMe. m.p: 182-184°C. UV-Vis (hexanes) λ_{max} nm (ε [Lmol^{-1}cm^{-1}]): 586 (1050), 402 (3960). ^1H NMR (C_6D_6, 300.08MHz, 25°C): δ 7.87 (s, 2H), 7.06 (d, 4H, $^3J_{HH}$ = 6.8Hz), 3.56 (s, 9H), 2.91 (sept, 4H, $^3J_{HH}$ = 6.9Hz), 1.50 (d, 12H, $^3J_{HH}$ = 6.9MHz), 1.21 (d, 12H, $^3J_{HH}$ = 6.9MHz). ^{13}C $\{^1H\}$ NMR (C_6D_6, 150.8MHz, 25°C): δ *i*- C_6H_2MeO (not observed), 154.9 (*o*-Dipp), 137.9 (*i*-Dipp), 131.4 (*o*-C_6H_2MeO), 129.3 (*p*- C_6H_2MeO), 125.5 (*m*- C_6H_2MeO), 125.7 (*p*-Dipp), 122.9 (*m*-Dipp), 33.5 (o-$\mathit{C}H(CH_3)_2$), 28.7 (o-$CH(\mathit{C}H_3)_2$), 23.7 (o-$CH(\mathit{C}H_3)_2$), 1.44 (-$O\mathit{CH_3}$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.19MHz, 25°C): not observed.

4-^{t}Bu-Ar′SnSnAr′-4-^{t}Bu: To a mixture of [4-^{t}Bu-Ar′SnCl]$_2$ (0.608 g, 1 mmol) and K shavings (0.040 g, 1 mmol) was added toluene (ca. 60 mL). The mixture was sonicated and heated briefly to *ca.* 75 °C to dissolve all the [4-^{t}Bu-Ar′SnCl]$_2$, and was then stirred for 4 d at *ca.* 25 °C. The resulting dark green solution was filtered through Celite on a fine frit, and *ca.* ¼ of the solvent was removed under reduced pressure. Storage at *ca.* -13 °C afforded 0.1 g (17%) small dark green block-shaped crystals (4-^{t}Bu-Ar′)SnSn(Ar′-4-^{t}Bu), which also contained a small amount of yellow and red crystals also visible (possibly unreacted starting material (yellow) or overreduced anionic speices, (red). m.p: 217°C. UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 406 (10600), 592 (2230). ^1H NMR (C_6D_6 , 300.08, 25 °C): δ 8.21 (s, likely Sn-H hydride impurity), 7.16 (s, solvent, ArH), 7.09 (s, ArH), 2.90 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, $C\mathit{H}(CH_3)_2$), 1.44 (d, 12H , $^3J_{HH}$ = 6.9 Hz, $CH(C\mathit{H}_3)_2$), 1.34 (s, 9H, $C(C\mathit{H}_3)_3$), 1.21 (d, 12H , $^3J_{HH}$ = 6.9 Hz, $CH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6 , 25 °C): δ 173.8, 160.2, 153.6, 143.3, 130.7, 125.7, 116.8 (Ar*C*), 43.5 ($\mathit{C}(CH_3)_3$), 35.1 ($\mathit{C}H(CH_3)_2$), 33.6 ($C(\mathit{C}H_3)_3$), 30.8 ($CH(\mathit{C}H_3)_2$), 27.9 ($CH(\mathit{C}H_3)_2$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.19MHz, 25°C): not observed.

4-Me$_3$Si-Ar′SnSnAr′-4-SiMe$_3$: In a similar manner, a solution of [4-Me$_3$Si-Ar′SnCl]$_2$ (0.850 g, 1.36 mmol) in diethyl ether (25 mL) was added to a diethyl ether suspension of 0.059 g (1.51 mmol) of finely dispersed potassium with rapid stirring. The reaction mixture quickly adopted a deep green colour and stirring was continued for 24 h. Workup as above afforded 0.41 g (48%) of dichroic green-dark orange crystals of 4-Me$_3$Si-Ar′SnSnAr′-4-SiMe$_3$. The identical product was obtained when the reaction was carried out with KC_8 instead of potassium as the reducing agent. m.p. 183-185 (decomp.) UV-Vis (hexanes) λ_{max} nm (ε [L mol^{-1}cm^{-1}]): 416 (4700), 608 (1200). ^1H NMR (C_6D_6, 599.814 MHz, 25 °C) *δ* 7.98 (s, 2H, *m*-$C_6H_2Si(CH_3)_3$), 7.17 (t, 2H, $^3J_{HH}$ = 6.7 Hz, *p*-Dipp), 7.07 (d, 4H, $^3J_{HH}$ = 6.7 Hz, *m*-Dipp), 2.94 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, $C\mathit{H}(CH_3)_2$), 1.38 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(C\mathit{H}_3)_2$), 1.16 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(C\mathit{H}_3)_2$), 0.28 (s, 9H, $\mathit{(CH_3)}_3Si$). $^{13}C\{^1H\}$ (C_6D_6, 150.823 MHz, 25°C) *δ* 174.6 (*i*-C_6H_2), 161.4 (*o*-C_6H_2), 151.1 (*i*-Dipp), 143.2 (*p*-C_6H_2), 141.2 (*o*-Dipp), 138.0

(*m*-C_6H_2), 127.9 (*m*-Dipp), 125.2 (*p*-Dipp), 35.9 ($\mathit{C}H(CH_3)_2$), 32.5 ($CH(\mathit{C}H_3)_2$), 26.9 ($CH(\mathit{C}H_3)_2$), -0.6 ($(H_3C)_3Si$). $^{29}Si\{^1H\}$ NMR (C_6D_6, 119.165 MHz, 25°C): δ -4.9. $^{119}Sn\{^1H\}$ NMR (C_6D_6, 223.671 MHz, 25°C): not observed.

4- Me_3Ge-Ar′SnSnAr′-4-$GeMe_3$: A solution of $[4\text{-}Me_3Ge\text{-}Ar'SnCl]_2$ (3 g, 4.49 mmol) in toluene (ca. 50mL) was added dropwise to freshly prepared KC_8 (0.66 g, 4.87 mmol) in toluene at room temperature. The reaction mixture quickly adopted a deep green color and stirring was continued for 12h after which the precipitated material and unreacted potassium was allowed to settle. The solution was filtered through a filter tipped cannula and concentrated under reduced pressure to incipient crystallization (ca. 10 mL). Storage at ca. -20°C yielded 0.60 g (10.7%) of 4- Me_3Ge-Ar′SnSnAr′-4- $GeMe_3$. m.p: 175-177°C. UV-Vis (hexanes) λ_{max} nm (ε [L $mol^{-1}cm^{-1}$]): 602 (2200), 430 (4450). ^1H NMR (C_6D_6, 300.08MHz, 25°C): δ 8.03 (s, 2H), 7.09 (t, 2H, $^3J_{HH}$ = 6.8Hz), 7.06(d, 4H, $^3J_{HH}$ = 6.8Hz), 2.91 (sept, 4H, $^3J_{HH}$ = 6.9Hz), 1.39 (d, 12H, $^3J_{HH}$ = 6.9MHz), 1.17 (d, 12H, $^3J_{HH}$ = 6.9MHz), 0.34 (s, 9H). ^{13}C $\{^1H\}$ NMR (C_6D_6, 150.8MHz, 25°C): δ *i*- $C_6H_2GeMe_3$ (not observed), 146.9 (*o*-Dipp), 137.9 (*i*-Dipp), 129.4 (*o*-$C_6H_2GeMe_3$), 128.8 (*p*- $C_6H_2GeMe_3$), 127.9 (*m*- $C_6H_2GeMe_3$), 125.5 (*p*-Dipp), 123.0 (*m*-Dipp), 32.8 (o-$\mathit{C}H(CH_3)_2$), 27.3 (o-$CH(\mathit{C}H_3)_2$), 24.5 (o-$CH(\mathit{C}H_3)_2$), -1.78 ($(\mathit{C}H_3)_3Ge$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.19MHz, 25°C): not observed.

3,5-$^iPr_2$-Ar′SnSnAr′-3,5-$^iPr_2$: A solution of 3,5-$^iPr_2$-Ar′SnCl (0.90 g, 0.71 mmol) in diethyl ether (30 mL) was slowly added to a suspension of KC_8 (0.20 mg, 1.50 mmol) in diethyl ether (20 mL) at 0°C. The reaction mixture quickly became a dark green. The reaction mixture was kept at 0°C for 30 minutes and was then allowed to warm to the room temperature where it was stirred for 8 h. Filtration through a filter tipped cannula, followed by concentration to approximately 5 mL and storage at ca. -20°C yielded 0.192 g (22.6% yield) of 3,5-$^iPr_2$-Ar′SnSnAr′-3,5-$^iPr_2$ as dichroic orange-green crystals. m.p.: 221-225°C (decomp.) UV-Vis (hexanes) λ_{max} nm (ε [L $mol^{-1}cm^{-1}$]): 414 (4600), 608 (1200). ^1H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.43 (s, 1H), 7.20 (t, 2H, $^3J_{HH}$ = 6.8 Hz), 7.07 (d, 4H, $^3J_{HH}$ = 6.8 Hz), 2.73 (sept, 4H, $^3J_{HH}$ = 6.3 Hz), 2.65 (sept, 2H, $^3J_{HH}$ = 7.4 Hz), 1.08 (d, 12H, $^3J_{HH}$ = 6.3 Hz), 1.06 (d, 12H, $^3J_{HH}$ = 6.3 Hz), 1.02 (d, 12H, $^3J_{HH}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.53 MHz, 25°C): δ *i*-$C_6H_2{}^iPr_2$ (not observed), 148.4 (*i*-Dipp), 147.9 (*o*-Dipp), 147.2 (*m*-$C_6H_2{}^iPr_2$), 131.8 (*o*-$C_6H_2{}^iPr_2$), 128.7 (*p*-Dipp), 125.7 (*i*-$C_6H_2{}^iPr_2$), 123.5 (*m*-Dipp), 31.0 (*o*-$\mathit{C}H(CH_3)_2$), 30.3 (*m*-$\mathit{C}H(CH_3)_2$), 26.5 ($CH(\mathit{C}H_3)_2$), 25.0 ($CH(\mathit{C}H_3)_2$), 24.3 ($CH(\mathit{C}H_3)_2$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.192 MHz, 25°C): not observed.

3,5-$^iPr_2$-Ar*SnSnAr*-3,5-$^iPr_2$: A solution of 3,5-$^iPr_2$-Ar*SnCl (0.80 g, 1.11 mmol) in diethyl ether (30 mL) was added dropwise to a suspension of KC_8 (0.170 g, 1.25 mmol) in diethyl ether (20 mL). The reaction mixture rapidly developed an intense dark green color. Stirring was maintained for 12 h after which all precipitates were allowed to settle. The dark green solution was filtered through a filter tipped cannula, concentrated at reduced pressure to incipient crystallizaiton (ca. 10 mL) and storage at ca. -20°C yielded 0.364 g (47.9 %) of dichroic, orange/green crystals of 3,5-$^iPr_2$-Ar*SnSnAr*-3,5-$^iPr_2$. m.p: 201-203°C. UV-Vis (hexanes) λ_{max} nm (ε [L $mol^{-1}cm^{-1}$]): 292 (3400), 424 (4900), 612 (550). ^1H NMR (C_6D_6, 300.08 MHz, 25°C): δ 7.27 (s, 1H), 7.18 (s, 4H), 3.09 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 2.98 (sept, 4H, $^3J_{HH}$ = 6.7 Hz), 2.55 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 1.48 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.45 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.30 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.18 (d, 12H, $^3J_{HH}$ = 6.7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.53 MHz, 25°C): δ *i*-$C_6H_2{}^iPr_2$ not observed, 148.7 (*m*-$C_6H_2{}^iPr_2$), 148.1 (*o*-Dipp), 145.8 (*p*-Dipp), 142.6 (*i*-Dipp), 136.0 (*o*-$C_6H_2{}^iPr_2$), 128.1 (*p*-$C_6H_2{}^iPr_2$), 122.6 (*m*-Dipp), 33.8 (*p*-$\mathit{C}H(CH_3)_2$), 30.7 (*o*-$\mathit{C}H(CH_3)_2$), 29.9 (*m*-$\mathit{C}H(CH_3)_2$), 25.8 ($CH(\mathit{C}H_3)_2$), 24.8 ($CH(\mathit{C}H_3)_2$), 24.1 ($CH(\mathit{C}H_3)_2$), 24.0 ($CH(\mathit{C}H_3)_2$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 224.192 MHz, 25°C): not observed.

^{119}Sn Mössbauer Effect Spectroscopy. Temperature-dependent Mössbauer experiments were carried out in transmission mode[S12] using a 2.5 mCi $^{119m}Sn/BaSnO_3$ source at room temperature. Spectrometer calibration was accomplished by using a 20 mg·cm^{-2} α-Fe absorber. Isomer shifts are reported with respect to the centroid of the room-temperature $BaSnO_3$ spectrum. The as-received samples were transferred in an inert atmosphere glovebox to O-ring sealed plastic sample holders and immediately cooled to liquid nitrogen temperature. These cooled sample holders then were transferred to a pre-cooled cryostat and examined in transmission geometry. All temperature-dependent Mössbauer data were obtained in both warming and cooling mode, and no evidence of hysteresis was observed. Rapidly cooled green samples of (4-^tBu-Ar′)SnSn(Ar′-4-^tBu) and (4-Me_3Si-

Ar′)SnSn(Ar′-4-SiMe$_3$) were examined by Mössbauer spectroscopy at 90K and the spectra are shown in Figure S1.

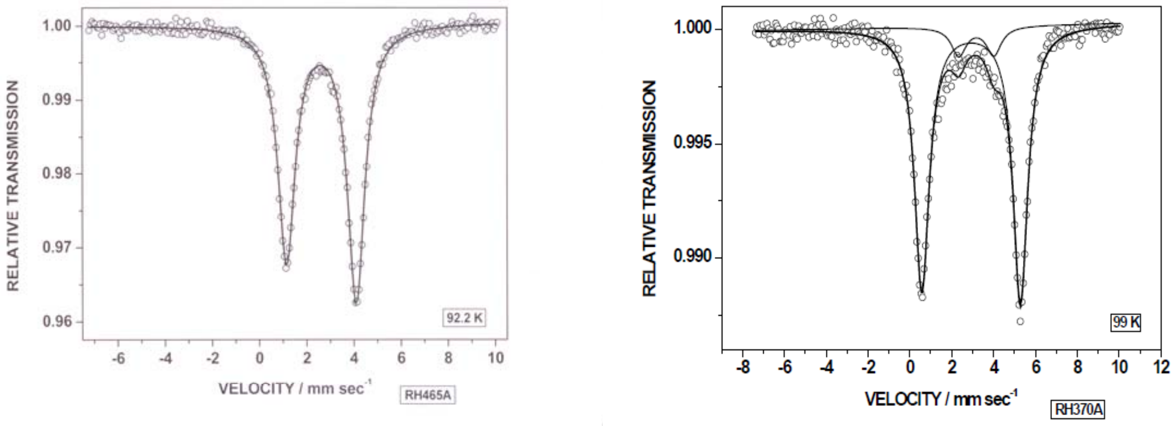

Figure S1. Mössbauer spectra for (4-^{t}Bu-Ar′Sn)$_2$ (left) and (4-Me$_3$Si-Ar′Sn)$_2$ (right).

X-ray crystallographic Studies. Crystals of 3,5-^{i}Pr$_2$-Ar*GeI, (4-Cl-Ar′SnCl)$_2$, (4-MeO-Ar′SnCl)$_2$, (4-Me$_3$Si-Ar′SnCl)$_2$, 3,5-^{i}Pr$_2$-Ar*SnCl, (4-Cl-Ar′Ge)$_2$, (4-Me$_3$Si-Ar′Ge)$_2$, (3,5-^{i}Pr$_2$-Ar*Ge)$_2$, (4-Cl-Ar′Sn)$_2$, (4-MeO-Ar′Sn)$_2$, (4-^{t}Bu-Ar′Sn)$_2$, (4-Me$_3$Si-Ar′Sn)$_2$, (4-Me$_3$Ge-Ar′Sn)$_2$ and (3,5-^{i}Pr$_2$-Ar*Sn)$_2$ were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber on a copper pin, and quickly placed in a N$_2$ cold stream on the diffractometer. Data for (4-MeO-Ar′SnCl)$_2$, (4-Me$_3$Si-Ar′SnCl)$_2$, (4-Me$_3$Ge-Ar′SnCl)$_2$, 3,5-^{i}Pr$_2$-Ar*SnCl, (4-Cl-Ar′Ge)$_2$, (4-Me$_3$Si-Ar′Ge)$_2$, (3,5-^{i}Pr$_2$-Ar*Ge)$_2$, (4-Cl-Ar′Sn)$_2$, (4-^{t}Bu-Ar′Sn)$_2$, (4-Me$_3$Si-Ar′Sn)$_2$ and (4-Me$_3$Ge-Ar′Sn)$_2$ were collected at 90 K on a Bruker APEX instrument with use of Mo Kα (λ = 0.710 73Å) radiation and a CCD area detector. Data for 3,5-^{i}Pr$_2$-Ar*GeI, (4-Cl-Ar′SnCl)$_2$, (4-MeO-Ar′Sn)$_2$, (4-Me$_3$Ge-Ar′SnCl)$_2$ and (3,5-^{i}Pr$_2$-Ar*Sn)$_2$ were collected at 90 K on a Bruker SMART 1000 diffractometer with use of Mo Kα (λ = 0.710 73Å) radiation and a CCD area detector. The SHELX version 6.1 program package was used for the structure solutions and refinements.[S13] Absorption corrections were applied using the SADABS program.[S14] Crystals of (4-Cl-Ar′Ge)$_2$, (4-MeO-Ar′SnCl)$_2$, (4-Cl-Ar′Sn)$_2$ and (4-MeO-Ar′Sn)$_2$ and were determined to be twinned, and the “de-twin” procedure was used to afford a solution. The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-H atoms were refined anisotropically. All carbon-bound H atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Some details of the data collection and refinement are given in Tables S1 and S2.

Table S1. Selected crystallographic data for aryl M(II) halide (M = Ge, Sn)

	3,5-^{i}Pr$_2$-Ar*GeI	**(4-Cl-Ar'SnCl)$_2$**	**(4-MeO-Ar'SnCl)$_2$**	**(4-Me$_3$Si-Ar'SnCl)$_2$**	**(4-Me$_3$Ge-Ar'SnCl)$_2$**	**3,5-^{i}Pr$_2$-Ar*SnCl**
Formula	$C_{84}H_{122}Cl_{0.13}Ge_2I_{1.87}$	$C_{60}H_{72}Cl_4Sn_2$	$C_{76}H_{94}Cl_2O_2Sn_2$	$C_{80}H_{106}Si_2Cl_2Sn_2$	$C_{80}H_{106}Cl_2Ge_2Sn_2$	$C_{42}H_{60}ClSn$
Fw	1518.91	1172.36	1347.79	1432.11	1899.2	719.06
Color, habit	Orange, block	Yellow, block	Yellow, plate	Orange, block	Orange, block	Orange, block
Cryst syst	Triclinic	Orthorthombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	Pccn	C2/c	P-1	P-1	C2/c
a, Å	11.9294(5)	20.3965(16)	23.035(4)	11.3422(6)	11.4346(13)	16.5041(5)
b, Å	18.4084(8)	15.7884(13)	10.8053(17)	12.9163(6)	12.9085(15)	9.4880(3)
c, Å	20.7414(9)	17.1574(14)	27.610(4)	15.1478(11)	15.1952(17)	26.2185(8)
α, deg	114.657(2)	90	90	112.0530(10)	111.709(2)	90
β, deg	105.431(2)	90	98.801(2)	103.2470(10)	103.674(2)	108.442(4)
γ, deg	90.806(2)	90	90	103.1560(10)	103.032(2)	90
V, Å^3	3949.4(3)	5525.2(8)	6791.2(19)	1877.17(19)	1899.2(4)	3894.7(2)
Z	2	4	4	1	1	4
Cryst dims, mm^3	0.24× 0.11× 0.06	0.17× 0.16× 0.09	0.33× 0.28× 0.12	0.51× 0.30 × 0.21	0.32× 0.21×0.10	0.31× 0.22× 0.15
μ, mm^{-1}	1.537	1.134	0.858	0.809	1.544	0.751
No. of reflns	35270	37024	29098	16959	8693	3993
No. of obsd reflns	18059	4136	24901	8096	400	3262
R, obsd reflns(I >2σ(I))	0.0542	0.0568	0.0534	0.0295	0.0584	0.0855
wR$_2$, all	0.1423	0.1304	0.1463	0.0813	0.1746	0.2373

Table S2. Selected crystallographic data for neutral ArMMAr (M = Ge, Sn)

	(4-Cl-Ar'Ge)$_2$	**(4-SiMe$_3$-Ar'Ge)$_2$**	**(3,5-^{i}Pr$_2$-Ar*Ge)$_2$**	**(4-Cl-Ar'Sn)$_2$**	**(4-MeO-Ar'Sn)$_2$**	**(4-^{t}BuAr'Sn)$_2$**	**(4-Me$_3$Si Ar'Sn)$_2$**	**(4-Me$_3$Ge Ar'Sn)$_2$**	**(3,5-^{i}Pr$_2$-Ar*Sn)$_2$**
Formula	$C_{69.55}H_{84.37}Cl_2Ge_2$	$C_{67}H_{92.50}Ge_2O_{0.25}Si_2$	$C_{203}H_{284}Ge_4$	$C_{72}H_{84}Cl_2Sn_2$	$C_{76}H_{94}O_2Sn_2$	$C_{82}H_{106}Sn_2$	$C_{80}H_{106}Si_2Sn_2$	$C_{78}H_{102}Ge_2Sn_2$	$C_{254}H_{371}O_{0.5}Sn_6$
Fw	1136.414	1103.27	3014.76	1257.67	1276.89	1329.05	1361.21	1422.24	4144.65
Color, habit	Orange, Plate	Red, block	Red, plate	Blue, plate	Green, plate	Green, plate	Brown, block	Brown, block	Green, block
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	I2/m	$P2_1/c$	$P2_1/c$	I2/m	P-1	P-1	$P2_1/c$	$P2_1/c$	P-1
a, Å	14.3831(17)	12.9150(8)	15.153(4)	14.908(4)	10.851(2)	10.5215(6)	12.7007(4)	12.762(4)	15.1577(10)
b, Å	10.9750(13)	45.098(3)	22.600(6)	11.003(3)	12.507(2)	12.0825(7)	11.7079(4)	11.675(3)	22.7946(15)
c, Å	19.628(2)	22.5681(14)	26.212(7)	19.380(5)	13.880(3)	15.3370(9)	24.3198(8)	23.975(7)	36.174(3)
α, deg	90	90	90	90	96.444(3)	103.2180(10)	90	90	75.1150(10)
β, deg	95.579(2)	98.6700(10)	100.842(4)	98.493(4)	97.785(3)	107.0010(10)	90.138(1)	90.303(4)	84.2180(10)
γ, deg	90	90	90	90	114.634(3)	91.5410(10)	90	90	78.7320(10)
V, Å^3	3083.8(6)	12994.3(14)	8816(4)	3144.1(13)	1666.5(6)	1805.90(18)	3616.3	3572.2(8)	11829.4(14)
Z	2	8	2	2	1	1	2	4	2
Cryst dims, mm^3	0.54×0.38×0.24	0.28×0.24×0.24	0.20×0.18×0.12	0.19× 0.09×0.01	0.64×0.32×0.12	0.28×0.10×0.06	0.52×0.24×0.17	0.43×0.28×0.11	0.61×0.21×0.19
μ, mm^{-1}	1.101	0.998	0.727	0.920	0.793	0.733	0.765	1.564	0.673
No. of reflns	3731	23543	15965	2920	7273	10013	39562	6418	42862
No. of obsd reflns	2672	12403	8634	2110	373	8407	9249	381	21641
R,(I> 2σ(I))obsd reflns	0.0760 II)	0.0787	0.0974	0.0792	0.0622	0.0328	0.0240	0.0827	0.0716
wR$_2$, all	0.2288	0.1932	0.2985	0.2419	0.1695	0.1041	0.0660	0.2243	0.1980

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