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Trans-Selective hydrogermylation of alkynes promoted by methyliron and bis(germyl)hydridoiron complexes as catalyst precursor

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All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. A methyliron complex $CpFe(CO)_2(Me)$ was prepared according to the literature method.[1] The other chemicals used were purchased. Spectroscopic data of (*Z*)-vinylgermyl products obtained in this work, **1a**, **1j**, **1k**, **1l**, agreed with those in the literature.[2] NMR spectra (^1H and $^{13}C\{^1H\}$) were recorded on a JNM-AL-400 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR data were referred to the residual peaks of the solvent. IR spectra were recorded on a Perkin Elmer FTIR-Spectrum one. Photo-irradiation was performed with a 400 W medium-pressure mercury arc lamp at 5 ºC.

General method for hydrogermylation of alkynes: The mixture of phenylacetylene (0.52 mmol, 57 μL), tributylgermane (0.63 mmol, 153 μL), and $CpFe(CO)_2(Me)$ (7 mol%, 0.04 mmol, 7 mg) were stirred at 80 ºC in nitrogen atmosphere. After 18 h, the reaction mixture was purified directly by flash chromatography (silica gel, hexane). Evaporation of volatile materials led to the formation of (*Z*)-tributyl(2-phentyethenyl)germane (171 mg, 95%) as a colorless oil.

1b: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 6.35 (d, J_{HH} = 15 Hz, 1H, *H*C=CH), 6.78–6.80 (m, 3H, Ph) 7.08–7.12 (m, 9H, GePh), 7.26 (d, J_{HH} = 7 Hz, 2H, Ph), 7.59 (d, J_{HH} = 7 Hz, 6H, GePh), 7.61 (d, J_{HH} = 15 Hz, 1H, HC=C*H*). $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 25 °C): δ 126.66 (s, Ph),

128.55 (s, GePh), 128.83 (s, GePh), 129.13 (s, GePh), 135.22 (s, GePh), 135.55 (s, Ph), 135.80 (s, Ph), 137.69 (s, HC=*C*H), 138.41 (s, Ph), 148.63 (s, H*C*=CH). Elemental analysis $C_{20}H_{34}Ge$, Calculated: C, 76.71; H, 5.45%. Found: C, 76.36; H, 5.42%.

1c: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.84–0.89 (m, 15H, CH_2CH$_2$CH$_2$CH_3), 1.25–1.44 (m, 12H, CH$_2$CH_2CH_2CH$_3$), 6.03 (d, J_{HH} = 15 Hz, 1H, *H*C=CH), 7.05 (t, J_{HH} = 7 Hz, 1H, Ph), 7.13 (t, J_{HH} = 7 Hz, 2H, Ph), 7.32 (d, J_{HH} = 7 Hz, 2H, Ph) 7.49 (d, J_{HH} = 15 Hz, 1H, HC=C*H*). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.00 (s, Bu), 14.89 (s, Bu), 26.90 (s, Bu), 27.95 (s, Bu), 127.64 (s, Ph), 128.16 (s, Ph), 128.30 (s, Ph), 131.98 (s, HC=*C*H), 140.87 (s, Ph), 146.09 (s, H*C*=CH). Elemental analysis $C_{20}H_{34}Ge$, Calculated: C, 69.20; H, 9.87%. Found: C, 69.10; H, 9.87%.

1d: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.80–0.88 (m, 15H, CH_2CH$_2$CH$_2$CH_3), 1.24–1.40 (m, 12H, CH$_2$CH_2CH_2CH$_3$), 5.96 (d, J_{HH} = 14 Hz, 1H, *H*C=CH), 6.75-6.80 (m, 2H, Ph-*o*), 7.07–7.11 (m, 2H, Ph-*m*) 7.33 (d, J_{HH} = 14 Hz, 1H, HC=C*H*). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.05 (s, Bu), 14.88 (s, Bu), 26.94 (s, Bu), 27.96 (s, Bu), 115.00 (d, J_{CF} = 22 Hz, Ph-*m*), 129.66 (d, J_{CF} = 9 Hz, Ph-*o*), 131.97 (s, HC=*C*H), 136.81 (d, J_{CF} = 2 Hz, Ph-*ipso*), 144.66 (s, H*C*=CH), 162.61 (d, J_{CF} = 246 Hz, Ph-*p*). Elemental analysis $C_{20}H_{33}FGe$, Calculated: C, 65.79; H, 9.11%. Found: C, 65.74; H, 9.06%.

1e: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.86–0.93 (m, 15H, CH_2CH$_2$CH$_2$CH_3), 1.28–1.45 (m, 12H, CH$_2$CH_2CH_2CH$_3$), 2.09 (s, 3H, CH$_3$), 5.99 (d, J_{HH} = 14 Hz, 1H, *H*C=CH), 6.97 (d, J_{HH} = 8 Hz, 2H, Ph), 7.26 (d, J_{HH} = 8 Hz, 2H, Ph) 7.50 (d, J_{HH} = 14 Hz, 1H, HC=C*H*). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.09 (s, Bu), 15.04 (s, Bu), 27.00 (s, Bu), 28.06 (s, Bu), 21.25 (s, CH$_3$), 128.12 (s, Ph), 128.98 (s, Ph), 130.87 (s, HC=*C*H), 137.16 (s, Ph), 138.01 (s, Ph), 146.00 (s, H*C*=CH). Elemental analysis $C_{21}H_{36}Ge$, Calculated: C, 69.84; H, 10.05%. Found: C, 70.11;

H, 10.11%.

1f: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.88-0.96 (m, 15H, C*H*$_2$CH$_2$CH$_2$C*H*$_3$), 1.31–1.47 (m, 12 H, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 3.29 (s, 3H, OCH$_3$), 5.97 (d, J_{HH} = 14 Hz, 1H, *H*C=CH), 6.79 (d, J_{HH} = 9 Hz, 2H, Ph), 7.30 (d, J_{HH} = 9 Hz, 2H, Ph) 7.50 (d, J_{HH} = 14 Hz, 1H, HC=C*H*). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.10 (s, Bu), 15.05 (s, Bu), 27.00 (s, Bu), 28.07 (s, Bu), 54.84 (OCH$_3$), 113.80 (s, Ph), 129.37 (s, Ph), 129.80 (s, HC=*C*H), 133.33 (s, Ph), 145.59 (s, H*C*=CH), 159.69 (s, Ph). Elemental analysis $C_{21}H_{36}OGe$, Calculated: C, 66.88; H, 9.62%. Found: C, 66.97; H, 9.42%.

1g: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.87–0.99 (m, 15H, C*H*$_2$CH$_2$CH$_2$C*H*$_3$), 1.29–1.50 (m, 12H, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 2.79 (s, 2H, NH$_2$), 5.88 (d, J_{HH} = 14 Hz, 1H, *H*C=CH), 6.28 (d, J_{HH} = 9 Hz, 2H, Ph), 7.21 (d, J_{HH} = 9 Hz, 2H, Ph) 7.49 (d, J_{HH} = 14 Hz, 1H, HC=C*H*). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.14 (s, Bu), 15.12 (s, Bu), 27.03 (s, Bu), 28.12 (s, Bu), 114.42 (s, Ph), 127.39 (s, HC=*C*H), 129.26 (s, Ph), 130.70 (s, Ph), 146.12 (s, H*C*=CH), 146.63 (s, Ph). Elemental analysis $C_{21}H_{35}NGe$, Calculated: C, 66.33; H, 9.74; N, 3.87%. Found: C, 66.05; H, 9.88; N, 3.83%.

1h: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.87-1.27 (m, 18H, GeC*H*$_2$CH$_2$CH$_2$C*H*$_3$, CH$_3$ in Hex), 1.31–1.54 (m, 20H, GeCH$_2$C*H*$_2$C*H*$_2$CH$_3$, CH$_2$ in Hex), 2.16 (q, J_{HH} = 7 Hz, 2H, CH$_2$ in Hex), 5.77 (d, J_{HH} = 13 Hz, 1H, *H*C=CH), 6.46 (dt, J_{HH} = 13, 7 Hz, 1H, HC=C*H*). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.16 (s, Bu), 14.42 (s, Hex), 14.84 (s, Bu), 23.14 (s, Hex), 27.11 (s, Bu), 28.17 (s, Bu), 29.67 (s, Hex), 30.38 (s, Hex), 32.35 (s, Hex), 34.92 (s, Hex), 127.47 (s, HC=*C*H), 147.75 (s, H*C*=CH). Elemental analysis $C_{20}H_{42}Ge$, Calculated: C, 67.63; H, 11.92%. Found: C, 67.25; H, 11.77%.

1i: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.94–1.00 (m, 15H, GeC*H*$_2$CH$_2$CH$_2$C*H*$_3$), 1.08–1.34 (m, 4H, CH$_2$ in ^{c}Hex), 1.35–1.60 (m, 14H, GeCH$_2$C*H*$_2$C*H*$_2$CH$_3$, CH$_2$ in ^{c}Hex), 1.67-1.73 (m, 4H, CH$_2$ in ^{c}Hex), 2.08–2.18 (m, 1H, CH in ^{c}Hex), 5.65 (d, J_{HH} = 13 Hz, 1H, HC=C*H*), 6.29 (dd, J_{HH} = 8, 13 Hz, 1H, *H*C=CH). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.18 (s, Bu), 14.97 (s, Bu), 26.38 (s, ^{c}Hex), 26.47 (s, ^{c}Hex), 27.17 (s, Bu), 28.19 (s, Bu), 33.77 (s, ^{c}Hex), 44.33 (s, ^{c}Hex), 125.34 (s, HC=*C*H), 153.20 (s, H*C*=CH). Elemental analysis $C_{20}H_{40}Ge$, Calculated: C, 68.02; H, 11.42%. Found: C, 68.30; H, 11.56%.

1m: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.78–0.90 (m, 15H, C*H*$_2$CH$_2$CH$_2$C*H*$_3$), 1.18–1.36 (m, 12H, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 7.09 (t, J_{HH} = 7 Hz, 2H, Ph), 7.15 (d, J_{HH} = 7 Hz, 2H, Ph), 7.17 (t, J_{HH} = 7 Hz, 1H, Ph), 7.21 (t, J_{HH} = 7 Hz, 1H, Ph), 7.26 (t, J_{HH} = 7 Hz, 2H, Ph), 7.33 (d, J_{HH} = 7 Hz, 2H, Ph), 7.40 (s, 1H, HC=C). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 13.85 (s, Bu), 14.85 (s, Bu), 26.62 (s, Bu), 27.52 (s, Bu), 125.70 (s, Ph), 127.10 (s, Ph), 127.20 (s, Ph), 127.91 (s, Ph), 127.94 (s, Ph), 128.39 (s, Ph), 140.02 (s, H*C*=C), 143.06 (s, HC=*C*), 147.36 (s, Ph), 147.59 (s, Ph). Elemental analysis $C_{26}H_{38}Ge$, Calculated: C, 73.79; H, 9.05%. Found: C, 73.41; H, 9.12%.

1n: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.87–0.92 (m, 12H, GeC*H*$_2$CH$_3$, CH$_3$ in Pr), 1.09 (t, 7 Hz, 9H, GeCH$_2$C*H*$_3$), 1.33–1.43 (m, 4H, CH$_2$ in Pr), 2.03–2.13 (m, 4H, CH$_2$ in Pr), 5.99 (t, 1H, J_{HH} = 7 Hz, HC=C). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 5.91 (s, Et), 9.52 (s, Et), 14.15 (s, Pr), 14.21 (s, Pr), 23.87 (s, Pr), 24.20 (s, Pr), 34.88 (s, Pr), 41.64 (s, Pr), 139.05 (s, HC=*C*), 140.91 (s, H*C*=C). Elemental analysis $C_{14}H_{30}Ge$, Calculated: C, 62.04; H, 11.16 %. Found: C, 61.98; H, 11.26%.

1o: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.92–1.01 (m, 21H, GeC*H*$_2$CH$_2$CH$_2$C*H*$_3$, CH$_3$ in Pr), 1.36–1.52 (m, 16H, GeCH$_2$C*H*$_2$C*H*$_2$CH$_3$, CH$_2$ in Pr), 2.09–2.19 (m, 4H, CH$_2$ in Pr), 6.01 (t, 1H, J_{HH} = 7 Hz, HC=C). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.15 (s, Bu), 14.18 (s, Pr),

14.23 (s, Pr), 14.45 (s, Bu), 23.90 (s, Pr), 24.23 (s, Pr), 27.19 (s, Bu), 28.17 (s, Bu), 34.92 (s, Pr), 41.61 (s, Pr), 139.65 (s, HC=*C*), 140.68 (s, H*C*=C). Elemental analysis $C_{20}H_{42}Ge$, Calculated: C, 67.63; H, 11.92%. Found: C, 67.30; H, 11.86%.

1p: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.09-1.21 (m, 15H, C*H*$_2$C*H*$_3$), 3.24 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 6.85 (s, 1H, HC=C). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 5.93 (s, Et), 9.26 (s, Et), 51.32 (OCH_3), 51.44 (s, OCH_3), 134.55 (s, H*C*=C), 156.58 (s, HC=*C*), 166.54 (s, *C*$OOCH_3$), 171.23 (s, *C*$OOCH_3$). Elemental analysis $C_{18}H_{34}O_4Ge$, Calculated: C, 47.58; H, 7.32%. Found: C, 47.56; H, 7.36%.

1q: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.92 (t, 7 Hz, 9H, $CH_2CH_2CH_2CH_3$), 1.22–1.26 (m, 6H, $CH_2CH_2CH_2CH_3$), 1.34–1.43 (sext, 7 Hz, 6H, $CH_2CH_2CH_2CH_3$), 1.48–1.56 (m, 6H, $CH_2CH_2CH_2CH_3$), 3.27 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 6.87 (s, 1H, HC=C). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ 14.10 (s, Bu), 14.46 (s, Bu), 26.94 (s, Bu), 27.96 (s, Bu), 51.46 (OCH_3), 51.57 (s, OCH_3), 127.47 (s, H*C*=C), 157.24 (s, HC=*C*), 166.53 (*C*$OOCH_3$), 171.21 (s, *C*$OOCH_3$). Elemental analysis $C_{18}H_{34}O_4Ge$, Calculated: C, 55.85; H, 8.85%. Found: C, 56.05; H, 8.91%.

Synthesis of CpFe(CO)(H)(GeEt$_3$)$_2$ (2): A benzene solution (2 mL) containing $CpFe(CO)_2(Me)$ (0.18 mmol, 35 mg) and Et_3GeH (0.36 mmol, 59 μL) was stirred at 60 °C. After 12 h, removing volatile materials under reduced pressure led to the formation of a dark red oil, which was dissolved in hexane (2 mL). After the hexane solution was cooled at –60 °C for 24 h, the resulting colorless crystals were filtered off and dried in vacuo to give **2** (0.15 mmol, 69 mg, 81%). ^{1}H NMR (400 MHz, C_6D_6, 25°C): δ = –12.67 (s, 1H, FeH), 1.10 (q, J_{HH} = 7.3 Hz, 12H, C*H*$_2$CH$_3$), 1.21 (t, J_{HH} = 7.3 Hz, 18H, CH$_2$C*H*$_3$), 4.15 (s, 5H, Cp). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25 °C): δ = 10.61 (s, *C*H$_2$CH$_3$), 13.20 (s, CH$_2$*C*H$_3$), 81.64 (s, Cp), 214.86 (s, CO). IR (cm^{-}

^{1}, benzene): ν(CO) 1926 (s). Elemental analysis $C_{18}H_{36}FeGe_2O$, Calculated: C, 46.04; H, 7.73. Found: C, 46.11; H, 7.76%.

Synthesis of $CpFe(CO)(H)(GePh_3)_2$ (3): In a procedure analogous to that outlined above, $CpFe(CO)_2(Me)$ (0.18 mmol, 35 mg) and Ph_3GeH (0.37 mmol, 111 mg) in benzene solution gave an orange powder of **3** (92 mg, 0.12 mmol, 67%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = –10.38 (s, 1H, FeH), 4.11 (s, 5H, Cp), 7.11 (m, 18H, Ph), 7.65 (m, 12H, Ph). $^{13}C\{^{1}H\}$ NMR (100.4 MHz, C_6D_6, 25 °C): δ = 85.75 (s, Cp), 128.21 (s, Ph), 135.25 (s, Ph), 144.69 (s, Ph), 215.00 (s, CO), a signal of one phenyl carbon was not observed by overlapping solvent peak. IR (cm^{-1}, benzene): ν(CO) 1912 (s). Elemental analysis $C_{42}H_{36}FeGe_2O$, Calculated: C, 66.56; H, 4.79. Found: C, 66.46; H, 5.01%.

References

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