The (Butadiene)metallocene/$B(C_6F_5)_3$ Pathway to Catalyst Systems for Stereoselective Methylmetacrylate Polymerization – Evidence for an Anion Dependent Metallocene Catalyzed Polymerization Process

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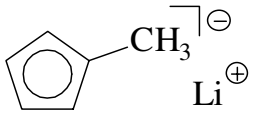
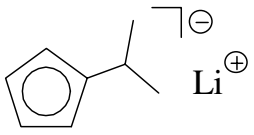
Supporting Material

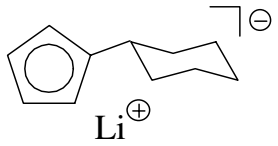


Yield 33.6g (90 %). **^{1}H-NMR** (200.1 MHz, [D_6]-benzene : [D_8]-thf ≈ 10 : 1, 300 K): δ = 5.97, 5.89 (each pt, each 2H, Cp-H), 2.40 (s, 3H, CH_3).

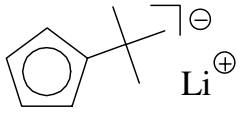


Yield 4.04g (77 %). **^{1}H-NMR** (200.1 MHz, [D_8]-thf, 300 K): δ = 5.41 (broad s, 4H, Cp), 2.72 (sept, 1H, $^3J_{HH}$ = 7.2 Hz, CH), 1.13 (d, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3).

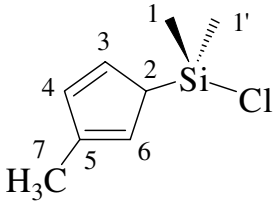
^{13}C{^{1}H}-NMR (50.1 MHz, [D_8]-thf, 300 K): δ = 128.3, 102.5, 101.4 (Cp), 30.0 (CH), 26.3 (CH_3).



Yield 3.76 g (72 %). **^{1}H-NMR** (200.1 MHz, [D_8]-thf, 300 K): δ = 5.47 (broad s, Cp), 2.39-1.25 (11H, cy-H). **^{13}C{^{1}H}-NMR** (50.1 MHz, [D_8]-thf, 300 K): δ = 129.5, 106.2, 103.6 (Cp), 42.7, 39.7, 30.9, 30.4 (cy).

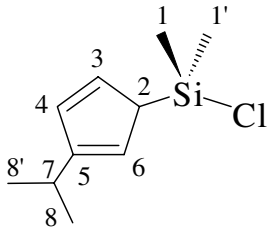


Yield 3.41 g (71 %). **^{1}H-NMR** (599.9 MHz, [D_8]-thf, 298 K): δ = 5.45, 5.38 (each pt, each 2H, Cp), 1.20 (s, 9H, tBu). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_8]-thf, 298 K): δ = 130.9 (ipso-Cp), 101.9, 100.4 (each Cp), 33.7 (tBu-*C*H_3), 32.3 (tBu-*C*$(CH_3)_3$).

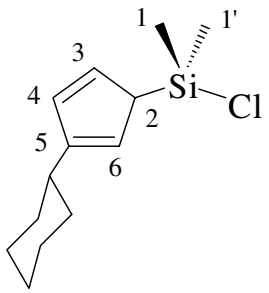


(4b) Yield (3.55 g, 88 %, yellow oil). **^{1}H-NMR** (599.9 MHz, [D_6]-benzene, 298 K): δ = 6.40 (br, 1H, 3-H), 6.37 (br, 1H, 4-H), 5.99 (br, 1H, 6-H), 3.43 (br, 1H, 2-H), 1.89 (s, 3H, 7-H), 0.09, 0.05 (each s, each 3H, 1'-H, 1-H). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_6]-benzene, 298 K): δ = 148.5 (C5), 135.8 (C3), 132.7 (C4), 128.5 (C6), 52.3 (C2), 15.0 (C7), 0.1 (C1'), -0.3 (C1). **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.40 / 6.37 (3-H / 4-H), 6.37 / 5.99 (4-H / 6-H), 5.99 / 3.43 (6-H / 2-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^{1}H = 135.8 / 6.40 (C3 / 3-H), 132.7 / 6.37 (C4 / 4-H), 128.5 / 5.99

(C6 / 6-H), 52.3 / 3.43 (C2 / 2-H), 15.0 / 1.89 (C7 / 7-H), 0.1 / 0.09 (C1' / 1'-H), -0.3 / 0.05 (C1 / 1-H).

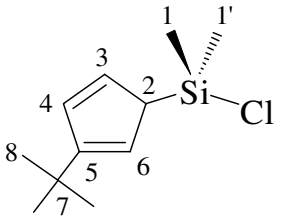


(4d) Yield 2.36 g (78 %, yellow oil). **^{1}H-NMR** (599.9 MHz, [D_6]-benzene, 298 K): δ = 6.52 (br, 1H, 3-H), 6.40 (br, 1H, 4-H), 6.03 (br, 1H, 6-H), 3.37 (br, 1H, 2-H), 2.59 (sept, 1H, $^{3}J_{HH}$ = 6.9 Hz, 7-H), 1.08, 1.07 (each d, each 3H, $^{3}J_{HH}$ = 6.9 Hz, 8'-H, 8-H), 0.09, 0.06 (each s, each 3H, 1'-H, 1-H). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_6]-benzene, 298 K): δ = 145.4 (C5), 133.6 (C3), 132.6 (C4), 123.2 (C6), 51.8 (C2), 29.2 (C7), 23.0 (C8'), 22.5 (C8), 0.1 (C1'), -0.2 (C1). **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.52 / 6.40 (3-H / 4-H), 6.40 / 6.03 (4-H / 6-H), 6.03 / 3.37 (6-H / 2-H), 2.59 / 1.08 (7-H, 8'-H, 8-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^{1}H = 133.6 / 6.52 (C3 / 3-H), 132.6 / 6.40 (C4 / 4-H), 123.2 / 6.03 (C6 / 6-H), 51.8 / 3.37 (C2 / 2-H), 29.2 / 2.59 (C7 / 7-H), 23.0 / 1.08 (C8' / 8'-H), 22.5 / 1.07 (C8 / 8-H), 0.1 / 0.09 (C1' / 1'-H), -0.2 / 0.06 (C1 / 1-H).

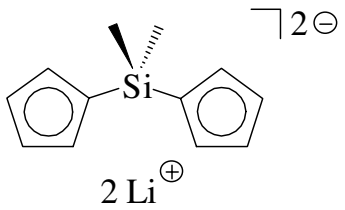


(4c) Yield (2.43 g, 74 %, yellow oil). **^{1}H-NMR** (599.9 MHz, [D_6]-benzene, 298 K): δ = 6.55 (br, 1H, 3-H), 6.41 (br, 1H, 4-H), 6.05 (br, 1H, 6H), 3.40 (br, 1H, 2-H), 2.26 (m, 1H, cy-CH), 1.82, 1.64, 1.61, 1.23, 1.11 (each m, each 2H, cy-CH_2), 0.10, 0.08 (each s, each 3H, 1'-H, 1-H). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_6]-benzene, 298 K): δ = 145.5 (C5), 133.8 (C3), 132.3 (C4), 123.5 (C6), 51.9 (C2), 39.0 (cyclohexyl-CH), 33.8, 33.6, 33.4, 26.7, 26.5, (cy-CH_2), 0.0,

-0.1 (C1', C1). **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 6.55 / 6.41 (3-H / 4-H), 6.41 / 6.05 (4-H / 6-H), 6.05 / 3.40 (6-H / 2-H), 2.26 / 1.82, 1.23 (each cy-CH / cy-CH_2), 1.82 / 1.64; 1.64 / 1.61, 1.64, 1.11; 1.61 / 1.23; 1.23 / 1.11 (each cy-CH_2 / cy-CH_2). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 133.8 / 6.55 (C3 / 3-H), 132.3 / 6.41 (C4 / 4-H), 123.5 / 6.05 (C6 / 6-H), 51.9 / 3.40 (C2 / 2-H), 39.0 / 2.26 (cy-CH / cy-CH), 33.8 / 1.82, 33.6. / 1.23, 33.4 / 1.61, 26.7 / 1.64, 26.5 / 1.11 (each cy-CH_2 / cy-CH_2), 0.0 / 0.08, -0.1 / 0.10 (C1' / 1'-H, C1 / 1-H).

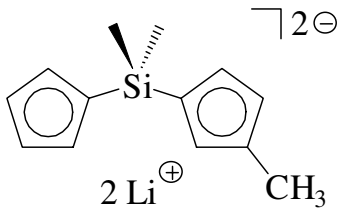


(4e) Yield (4.41 g, 88 %, yellow oil). **^{1}H-NMR** (599.9 MHz, [D_6]-benzene, 298 K): δ = 6.62 (br, 1H, 3-H), 6.40 (br, 1H, 4-H), 6.05 (br, 1H, 6-H), 3.38 (br, 1H, 2-H), 1.12 (s, 9H, 8-H), 0.09, 0.06 (each s, each 3H, 1'-H, 1-H). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_6]-benzene, 298 K): δ = 157.8 (C5), 132.5 (C3), 132.3 (C4), 121.9 (C6), 51.3 (C2), 32.0 (C7), 29.9 (C8), -0.3 (C1'), -0.5 (C1). **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 6.62 / 6.40 (3-H / 4-H), 6.40 / 6.05 (4-H / 6-H), 6.08 / 3.38 (6-H / 2-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 132.5 / 6.62 (C3 / 3-H), 132.3 / 6.40 (C4 / 4-H), 121.9 / 6.05 (C6 / 6-H), 51.3 / 3.38 (C2 / 2-H), 29.9 / 1.12 (C8 / 8-H), -0.3 / 0.09 (C1' / 1'-H), -0.5 / 0.06 (C1 / 1-H).

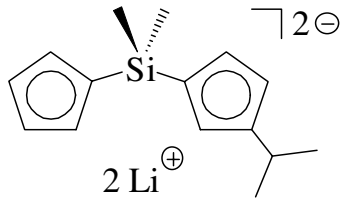


(6a) Yield 5.72 g (94 %). **^{1}H-NMR** (200.1 MHz, [D_6]-benzene : [D_8]-thf =10 :1, 298 K): δ = 6.08, 5.96 (each pt, each 4H, C_5H_4), 0.51 (s, 6H, Si(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (50.3 MHz, [D_6]-

benzene : [D_8]-thf =10 : 1, 298 K): δ = 113.9 (ipso-C_5H_4), 111.2, 106.2 (C_5H_4), 1.3 (Si(CH_3)$_2$).

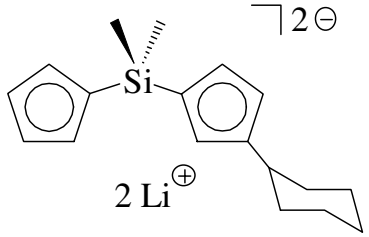


(6b) Yield 2.56 g (80 %). **Mp** 244 °C. **IR** (KBr): $\tilde{\nu}$ = 3076 (vs), 2953 (vs), 1439 (m), 1406 (m), 1355 (m), 1248 (vs), 1182 (s), 1096 (vs), 1038 (vs), 823 (vs), 764 (vs) cm^{-1}. **^{1}H-NMR** (599.9 MHz, [D_8]-thf, 298 K): δ = 5.87, 5.75 (each pt, each 2H, Cp), 5.70, 5.61, 5.50 (each m, each 1H, MeCp), 2.08 (s, 3H, MeCp-CH_3), 0.32 (s, 6H, Si(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_8]-thf, 298 K): δ = 117.0 (quart. MeCp), 114.5 (quart. Cp-CSi), 113.3 (quart. MeCp-CSi), 111.8, 111.0, 107.5 (each MeCp), 111.5, 106.4 (each Cp), 15.5 (MeCp-CH_3), 1.8 (Si(CH_3)$_2$). **GCOSY** (599.9 MHz / 599.9 MHz, [D_8]-thf, 298 K): δ^{1}H / δ^{1}H = 5.87 / 5.75 (Cp / Cp), 5.70 / 5.61, 5.50; 5.61 / 5.50 (MeCp / MeCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-thf, 298 K): δ^{13}C / δ^{1}H = 111.8 / 5.61, 111.0 / 5.70, 107.5 / 5.50 (MeCp / MeCp), 111.5 / 5.87, 106.4 / 5.75 (Cp / Cp), 15.5 / 2.08 (MeCp-CH_3 / MeCp-CH_3), 1.7 / 0.32 (Si(CH_3)$_2$ / Si(CH_3)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-thf, 298 K): δ^{13}C / δ^{1}H = 117.0 / 5.70, 5.61, 5.50 (quart. MeCp-C / MeCp), 114.5 / 5.70, 5.61, 5.50, 0.32 (quart. MeCp-CSi / MeCp, Si(CH_3)$_2$), 113.3 / 5.87, 5.75, 0.32 (quart. Cp-CSi / Cp, Si(CH_3)$_2$). **Anal. Calcd** for $C_{13}H_{16}SiLi_2$ (207.3): C 72.88, H 7.53; found C 72.88, H 7.23.



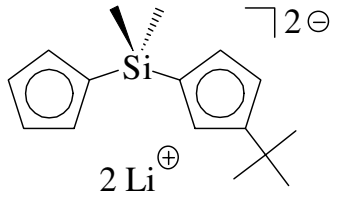
(6d) Yield 1.53 g, (77 %). **Mp** 249 °C. **IR** (KBr): $\tilde{\nu}$ = 3077 (vs), 2960 (vs), 2871 (s), 1466 (m), 1443 (m), 1408 (m), 1356 (m), 1249 (vs), 1178 (s), 1037 (vs), 955 (m), 813 (vs), 781 (vs) cm^{-1}. **^{1}H-NMR** (599.9 MHz, [D_8]-thf, 298 K): δ = 5.96, 5.79 (each pt, each 2H, Cp), 5.82, 5.79, 5.67 (each m, each 1H, iPrCp), 2.81 (sept, 1H, $^3J_{HH}$ = 7.2 Hz, iPr-CH), 1.16 (d, 6H, $^3J_{HH}$

= 7.2 Hz, iPr-CH_3), 0.30 (s, 6H, Si(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D$_8$]-thf, 298 K): δ = 130.4 (quart. iPrCp), 114.4 (quart. iPrCp-CSi), 112.2 (quart. Cp-CSi), 111.5, 106.0 (each Cp), 110.7, 108.6, 103.9 (each iPrCp), 29.9 (iPr-*C*H), 26.4 (iPr-*C*H$_3$), 2.0 (Si(*C*H$_3$)$_2$). **GCOSY** (599.9 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{1}H / δ^{1}H = 5.96 / 5.79 (Cp / Cp), 5.82 / 5.79, 5.67; 5.79 / 5.67 (each iPrCp / iPrCp), 2.81 / 1.16 (iPr-C*H* / iPr-CH_3). **GHSQC** (50.1 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{13}C / δ^{1}H = 111.5 / 5.96, 106.0 / 5.79 (each Cp / Cp), 110.7 / 5.82, 108.6 / 5.79, 103.9 / 5.67 (each iPrCp / iPrCp), 29.9 / 2.81 (iPr-*C*H / iPr-C*H*), 26.4 / 1.16 (iPr-*C*H$_3$ / iPr-CH_3), 2.0 / 0.30 (Si(CH_3)$_2$ / Si(*C*H$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{13}C / δ^{1}H = 130.4 / 5.82, 5.79, 5.67 (quart. iPrCp / each iPrCp), 114.4 / 5.82, 5.79, 5.67, 0.30 (quart. iPrCp-CSi / each iPrCp, Si(CH_3)$_2$), 112.2 / 5.96, 5.79, 0.30 (quart. Cp-CSi / each Cp-C*H*, Si(CH_3)$_2$). **Anal. Calcd** for $C_{15}H_{20}SiLi_2$ (242.3): C 74.36, H 8.32; found C 74.71, H 8.61.

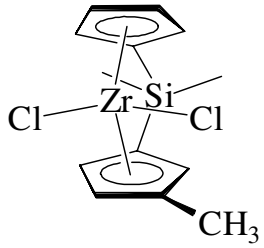


(6c) Yield 3.81 g (89 %). **Mp** 274 °C. **IR** (KBr): $\tilde{\nu}$ = 3076 (w), 2926 (vs), 2846 (s), 1458 (m), 1407 (s), 1355 (w), 1251 (s), 1171 (m), 1101 (w), 1033 (s), 833 (vs) cm^{-1}. **^{1}H-NMR** (599.9 MHz, [D$_8$]-thf, 298 K): δ = 5.95, 5.79 (each pt, each 2H, Cp), 5.81, 5.77, 5.65 (each pt, each 1H, cyCp), 2.41 (m, 1H, cy-C*H*), 1.91, 1.74, 1.33, 1.28 (each m, each 2H, cy-CH_2), 1.66, 1.20 (each m, each 1H, cy-CH_2), 0.30 (s, 6H, Si(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D$_8$]-thf, 298 K): δ = 129.5 (quart. cyCp), 114.2 (quart. cyCp-CSi), 111.7 (quart.Cp-CSi), 111.3, 105.8 (each Cp), 110.3, 108.3, 103.7 (each cyCp), 40.2 (cy-*C*H), 37.2, 28.2, 27.7 (each cy-*C*H$_2$), 1.7 (Si(*C*H$_3$)$_2$). **GCOSY** (599.9 MHz / 599.9 MHz, [D$_8$]-thf, 298 K) : δ^{1}H / δ^{1}H = 5.95 / 5.79 (Cp / Cp), 5.81 / 5.77, 5.77 / 5.65 (each cyCp / cyCp). (The cyclohexyl cross resonanzes are not listed). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{13}C / δ^{1}H = 111.3 / 5.95, 105.8 / 5.79 (each Cp / Cp), 110.3 / 5.81, 108.3 / 5.77, 103.7 / 5.65 (each cyCp / cyCp), 40.2 / 2.41 (cy-*C*H / cy-C*H*), 37.2 / 1.91, 1.28; 28.2 / 1.74, 1.33; 27.7 / 1.66, 1.20 (cy-*C*H$_2$ / cy-CH_2), 1.7 / 0.30 (Si(*C*H$_3$)$_2$ / Si(CH_3)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{13}C / δ^{1}H = 129.5 / 5.81, 5.77, 5.65 (quart. cyCp / each cyCp-C*H*), 114.2 / 5.81, 5.77, 5.65, 0.18 (quart.

cyCp-CSi / each cyCp, Si(CH_3)$_2$), 111.7 / 5.95, 5.79, 0.18 (quart. Cp-CSi / each Cp, Si(CH_3)$_2$). **Anal. Calcd** for $C_{18}H_{24}SiLi_2$ (288.4): C 76.57, H 8.57; found C 76.85, H 8.83.

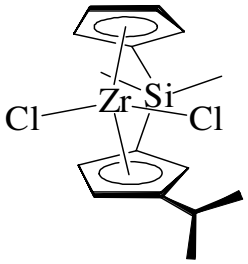


(6e) Yield 4.61 g (86 %). **Mp** 265 °C. **IR** (KBr): $\tilde{\nu}$ = 3080 (w), 2962 (vs), 2873 (s), 1465 (s), 1370 (s), 1352 (m), 1252 (vs), 1104 (vs), 1039 (vs), 956 (s), 814 (vs) cm^{-1}. **^{1}H-NMR** (599.9 MHz, [D$_8$]-thf, 298 K): δ = 5.96, 5.79 (each pt, each 2H, Cp-C*H*), 5.83 (m, 2H, tBuCp), 5.73 (m, 1H, tBuCp), 1.21 (s, 9H, tBu-CH_3), 0.31 (s, 6H, Si(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D$_8$]-thf, 298 K): δ = 133.5 (quart. tBuCp), 114.2 (quart. tBuCp-CSi), 111.4 (quart. Cp-CSi), 111.5, 105.8 (each Cp), 110.6, 107.2, 103.6 (each tBuCp), 33.9 (tBu-*C*H$_3$), 32.4 (*C*(CH$_3$)$_3$), 1.9 (Si(*C*H$_3$)$_2$). **GCOSY** (599.9 MHz / 599.9 MHz, [D$_8$]-thf, 298 K) : δ^{1}H / δ^{1}H = 5.96 / 5.79 (Cp / Cp), 5.83 / 5.73 (tBuCp / tBuCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{13}C / δ^{1}H = 111.4 / 5.96, 105.8 / 5.79 (each Cp / Cp), 110.6 / 5.83, 107.2 / 5.83, 103.9 / 5.73 (each tBuCp / tBuCp), 33.9 / 1.21 (tBu-*C*H$_3$ / tBu-CH_3), 1.9 / 0.31 (Si(*C*H$_3$)$_2$ / Si(CH_3)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-thf, 298 K): δ^{13}C / δ^{1}H = 133.5 / 5.83, 5.73 (quart. tBuCp / each tBuCp), 114.2 / 5.83, 5.73, 0.31 (quart. tBuCp-CSi / each tBuCp, Si(CH_3)$_2$), 111.4 / 5.96, 5.79, 0.32 (quart. Cp-CSi / each Cp, Si(CH_3)$_2$). **Anal. Calcd** for $C_{16}H_{22}SiLi_2$ (256.5): C 74.98, H 8.65; found C 75.69, H 9.08.



(7b) IR (KBr): $\tilde{\nu}$ = 3062 (w), 2951 (s), 2919 (s), 1454 (s), 1397 (vs), 1258 (vs), 1182 (vs), 1050 (vs), 993 (s), 923 (vs), 828 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.87 / 6.75, 5.35; 6.75 / 5.58, 5.58 / 5.35 (each Cp / Cp) 6.44 / 5.54, 5.06

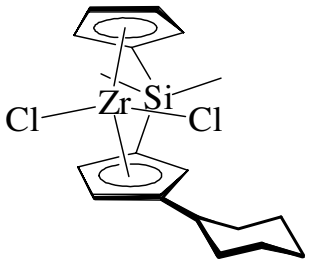
(MeCp / MeCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K) : δ^{13}C / δ^{1}H = 128.2 / 6.44, 115.5 / 5.54, 114.0 / 5.06 (MeCp / MeCp), 127.9 / 6.87, 127.1 / 6.75, 114.2 / 5.58, 113.0 / 5.35 (each Cp / Cp), 15.5 / 2.21 (MeCp-*C*H_3 / MeCp-C*H*$_3$), -5.6 / 0.12, -6.0 / 0.14 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^{1}H = 138.9 / 6.44, 5.54, 5.06 (quart. MeCp / each MeCp), 107.6 / 6.44, 5.54, 5.06, 0.14, 0.12 (quart. MeCp-CSi / each MeCp, each Si(C*H*$_3$)$_2$), 107.5 / 6.87, 6.75, 5.58, 5.35, 0.14, 0.12 (quart. Cp-CSi / each Cp, each Si(C*H*$_3$)$_2$).



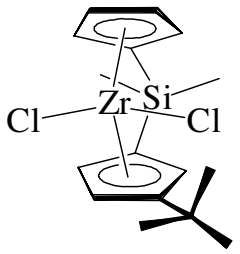
(7d) IR (KBr): $\tilde{\nu}$ = 3075 (m), 2964 (vs), 2873 (s), 1461 (s), 1402 (m), 1363 (s), 1298 (m), 1264 (vs), 1167 (vs), 1114 (s), 1043 (vs), 918 (s), 820 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.83 / 6.80, 5.45; 6.80 / 5.54; 5.54 / 5.45 (each Cp / Cp), 6.67 / 5.53, 6.67 / 5.29, 5.53 / 5.29 (each iPrCp / iPrCp), 3.29 / 1.32, 3.29 / 1.09 (each iPr-C*H* / iPr-C*H*$_3$). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^{1}H = 128.8 / 6.80, 126.6 / 6.83, 114.3 / 5.45, 112.9 / 5.54 (each Cp / Cp), 126.4 / 6.67, 113.9 / 5.53, 113.1 / 5.29 (each iPrCp / iPrCp), 29.0 / 3.29 (iPr-*C*H / iPr-C*H*), 24.8 / 1.09, 21.4 / 1.32 (iPr-*C*H$_3$ / iPr-C*H*$_3$), -5.5 / 0.17, -6.0 / 0.09 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^{1}H = 148.8 / 6.67, 5.53, 5.29 (quart. iPrCp / each iPrCp), 107.7 / 6.67, 5.53, 5.29, 0.17, 0.09 (quart. iPrCp-CSi / each iPrCp, each Si(C*H*$_3$)$_2$), 107.5 / 6.83, 6.80, 5.54, 5.45, 0.17, 0.09 (quart. Cp-CSi / each Cp, each Si(C*H*$_3$)$_2$).

X-ray crystal structure analysis of **7d**: formula $C_{15}H_{20}Cl_2SiZr$, M = 390.52, colourless crystal 0.20 x 0.20 x 0.15 mm, a = 7.946(1), b = 9.841(1), c = 12.337(1) Å, α = 73.36(1), β = 77.47(1), γ = 68.24(1)°, V = 851.8(2) Å^3, ρ_{calc} = 1.523 g cm^{-3}, μ = 10.15 cm^{-1}, empirical absorption correction (0.823 ≤ T ≤ 0.863), Z = 2, triclinic, space group P1bar (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 9237 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 4025 independent (R_{int} = 0.036) and 3279 observed reflections [$I \geq 2\,\sigma(I)$], 176 refined

parameters, R = 0.033, wR^2 = 0.059, max. residual electron density 0.34 (-0.37) e $Å^{-3}$, hydrogens calculated and refined as riding atoms.



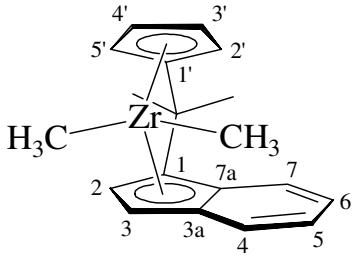
(7c) IR (KBr): $\tilde{\nu}$ = 3078 (s), 2923 (vs), 2843 (s), 1449 (vs), 1400 (s), 1308 (m), 1258 (vs), 1167 (vs), 1107 (vs), 1053 (vs), 920 (s), 830 (broad), 677 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 6.83 / 6.81, 5.47; 6.81 / 5.55, 5.55 / 5.47 (each Cp / Cp), 6.69 / 5.54, 5.30; 5.54 / 5.30 (each cyCp / cyCp). (no assignment of the cyclohexyl fragment) **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 128.9 / 6.81, 126.5 / 6.84, 114.2 / 5.47, 113.2 / 5.55 (each Cp / Cp), 126.6 / 6.69, 113.9 / 5.54, 112.8 / 5.30 (cyCp / cyCp-C*H*), 38.6 / 2.99 (cy-*C*H / cy-C*H*), 35.9 / 1.89, 35.9 / 1.14, 31.8 / 2.32, 31.8 / 1.32, 26.9 / 1.67, 26.9 / 1.43, 26.5 / 1.70, 26.5 / 1.38, 26.4 / 1.60, 26.4 / 1.06 (cy-*C*H_2 / cy-C*H*$_2$), -5.5 / 0.18, -6.0 / 0.11 (Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 147.8 / 6.69, 5.54, 5.30 (quart. cyCp / each cyCp), 107.6 / 6.69, 5.54, 5.30, 0.18, 0.11 (quart. cyCp-CSi / each cyCp, each Si(C*H*$_3$)$_2$), 107.3 / 6.83, 6.81, 5.55, 5.47, 0.18, 0.11 (quart. Cp-CSi / each Cp, each Si(C*H*$_3$)$_2$).



(7e) IR (KBr): $\tilde{\nu}$ = 3072 (vs), 2950 (vs), 2870 (s), 1490 (s), 1460 (vs), 1398 (vs), 1362 (vs), 1270 (vs), 1184 (vs), 1087 (vs), 1050 (vs), 909 (vs), 836 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 6.84 / 6.65, 5.45; 6.65 / 5.65, 5.65 / 5.45 (each

Cp / Cp), 6.82 / 5.72, 5.54; 5.72 / 5.54 (tBuCp / tBuCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 130.9 / 6.84, 124.9 / 6.65, 117.5 / 5.65, 111.4 / 5.45 (each Cp / Cp), 129.5 / 6.82, 113.8 / 5.45, 113.7 / 5.54 (each tBuCp / tBuCp), 30.9 / 1.42 (tBu-*C*H_3 / tBu-C*H*$_3$), -4.5 / 0.22, -6.6 / 0.09 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 150.4 / 6.82, 5.72, 5.54 (quart. tBuCp / each tBuCp), 107.9 / 6.82, 5.72, 5.54, 0.22, 0.09 (quart. tBuCp-CSi / each tBuCp, each Si(C*H*$_3$)$_2$), 105.7 / 6.84, 6.65, 5.65, 5.45, 0.22, 0.09 (quart. Cp-CSi / each Cp, each Si(C*H*$_3$)$_2$).

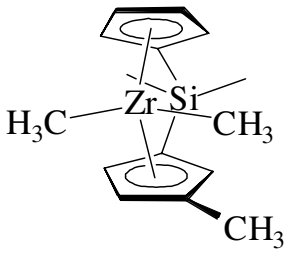
X-ray crystal structure analysis of **7e**: formula $C_{16}H_{22}Cl_2SiZr$, M = 404.55, light-yellow crystal 0.35 x 0.15 x 0.10 mm, a = 9.939(1), b = 12.730(1), c = 15.109(1) Å, β = 106.39(1)°, V = 1834.0(3) Å^3, ρ_{calc} = 1.465 g cm^{-3}, μ = 9.45 cm^{-1}, empirical absorption correction (0.733 ≤ T ≤ 0.911), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 7698 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.68 Å^{-1}, 4518 independent (R_{int} = 0.031) and 3404 observed reflections [$I \geq 2\ \sigma(I)$], 269 refined parameters, R = 0.071, wR^2 = 0.166, max. residual electron density 0.66 (-1.00) e Å^{-3}, asymmetric unit contains both enantiomers in a ratio of 0.72(1) to 0.28, refined with the PART command, carbon atoms of the minor enantiomer are treated with isotropic thermal displacement parameters, in addition geometrical restrains are used for the the Cp-rings (AFIX command) and the whole molecule (SAME command), hydrogens calculated and refined as riding atoms.



(2) ^{1}H-NMR (599.9 MHz, [D_6]-benzene, 298 K): δ = 7.42 (d, 1H, $^3J_{HH}$ = 8.6, 4-H), 7.20 (d, 1H, $^3J_{HH}$ = 8.9 Hz, 7-H), 7.07 (dd, 1H, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.5 Hz, 5-H), 6.73 (dd, 1H, $^3J_{HH}$ = 8.9, $^3J_{HH}$ = 7.5 Hz, 6-H), 6.59 (dd, 1H, ^3J = 3.5 Hz, ^4J = 0.9 Hz, 3-H), 6.25 (m, 1H, 4'-H), 6.18 (m, 1H, 3'-H), 5.50 (d, 1H, ^3J = 3.5 Hz, 2-H), 5.23 (m, 1H, 2'-H), 5.10 (m, 1H, 5'-H), 1.52 (s, 3H, C-C*H*$_3$(syn)), 1.29 (s, 3H, C-C*H*$_3$(anti)), 0.05 (s, 3H, Zr-C*H*$_3$(anti)), -1.01 (s, 3H, Zr-C*H*$_3$(syn)). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_6]-benzene, 298 K): δ = 127.1, 119.3 (C3a,

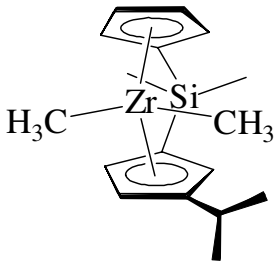
C7a), 125.9 (C4, $^1J_{CH}$ = 159.9 Hz), 124.1 (C6, $^1J_{CH}$ = 158.7 Hz), 123.8 (C7, $^1J_{CH}$ = 160.5 Hz), 123.7 (C5, $^1J_{CH}$ = 159.3 Hz), 114.7 (C4', $^1J_{CH}$ = 173.8 Hz), 113.8 (C1'), 113.4 (C3', $^1J_{CH}$ = 177.2 Hz), 113.0 (C2, $^1J_{CH}$ = 165.4 Hz), 104.6 (C3, $^1J_{CH}$ = 173.7 Hz), 103.9 (C5', $^1J_{CH}$ = 168.8 Hz), 103.6 (C2', $^1J_{CH}$ = 170.4 Hz), 98.0 (C1), 38.4 ($C(CH_3)_2$), 34.4 (Zr-CH_3(syn), $^1J_{CH}$ = 117.0 Hz), 30.7 (Zr-CH_3(anti) , $^1J_{CH}$ = 115.6 Hz), 26.2 (C-CH_3(anti) , $^1J_{CH}$ = 125.9 Hz), 25.3 (C-CH_3(syn) , $^1J_{CH}$ = 126.4 Hz). (The $^1J_{CH}$-coupling constants are obtained with a $^{13}C\{gated\}$ NMR experiment.)

X-ray crystal structure analysis of **2**: formula $C_{19}H_{22}Zr$, M = 341.59, yellow crystal 0.15 x 0.10 x 0.10 mm, a = 7.504(1), b = 7.611(1), c = 13.860(1) Å, α = 84.10(1), β = 88.18(1), γ = 80.42(1)°, V = 776.3(2) Å^3, ρ_{calc} = 1.461 g cm^{-3}, μ = 6.96 cm^{-1}, empirical absorption correction (0.903 ≤ T ≤ 0.934), Z = 2, triclinic, space group P1bar (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 5632 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.68 Å^{-1}, 3774 independent (R_{int} = 0.024) and 3276 observed reflections [$I \geq 2\,\sigma(I)$], 185 refined parameters, R = 0.035, wR^2 = 0.079, max. residual electron density 0.43 (-0.49) e Å^{-3}, hydrogens calculated and refined as riding atoms.

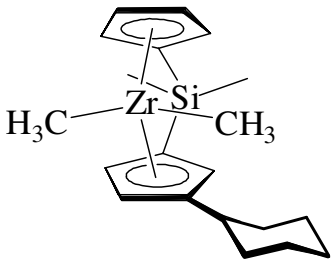


(8b) IR (KBr): $\tilde{\nu}$ = 2960 (s), 2923 (m), 1446 (w), 1409 (s), 1311 (m), 1257 (vs), 1196 (s), 1099 (vs), 1026 (vs), 916 (w), 812 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 6.74 / 6.70, 5.34; 6.70 / 5.49, 5.49 / 5.34 (each Cp / Cp), 6.37 / 5.39, 5.08; 5.39 / 5.08 (each MeCp / MeCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 121.4 / 6.37, 112.9 / 5.39, 112.6 / 5.08 (each MeCp / MeCp), 120.4 / 6.74, 120.3 / 5.34, 112.4 / 5.49, 112.0 / 5.34 (each Cp / Cp), 32.7 / -0.16, 29.0 / -0.08 (each Zr(CH_3)$_2$ / Zr(CH_3)$_2$), 14.8 / 2.16 (MeCp-CH_3 / MeCp-CH_3), -5.3 / 0.15, -5.5 / 0.14 (each Si(CH_3)$_2$ / Si(CH_3)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 130.1 / 6.37, 5.39, 5.08 (quart. MeCp / each MeCp), 100.2 / 6.37, 5.39, 5.08, 0.15, 0.14

(quart. MeCp-CSi / each MeCp-C*H*, each Si(CH_3)$_2$), 100.1 / 6.74, 6.70, 5.49, 0.15, 0.14 (quart. Cp-CSi / each Cp-C*H*, each Si(CH_3)$_2$).

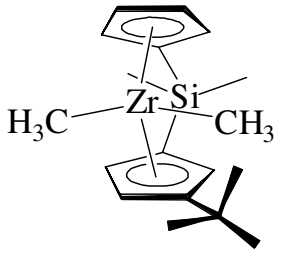


(8d) IR (KBr): $\tilde{\nu}$ = 2932 (vs), 2847 (vs), 1447 (vs), 1402 (s), 1381 (m), 1263 (vs), 1172 (s), 112 (vs), 1047 (vs), 955 (s), 915 (m), 817 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^1H / δ^1H = 6.74 / 6.70, 5.44; 6.70 / 5.42, 5.44 / 5.42 (each Cp / Cp), 6.57 / 5.36, 5.27, 5.36 / 5.27 (each iPrCp / iPrCp), 3.00 / 1.28, 1.20 (iPr-C*H* / iPr-CH_3). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{13}C / δ^1H = 121.3 / 6.74, 120.0 / 6.70, 112.7 / 5.44, 111.5 / 5.42 (Cp / Cp), 118.6 / 6.57, 117.7 / 5.36, 110.8 / 5.27 (each iPrCp / iPrCp), 32.1 / -0.13, 28.9 / -0.05 (each Zr(*C*H$_3$)$_2$ / Zr(CH_3)$_2$), 28.6 / 3.00 (iPr-*C*H / iPr-C*H*), 25.3 / 1.20, 22.4 / 1.28 (each iPr-*C*H$_3$ / iPr-CH_3), -5.1 / 0.18, -5.7 / 0.12 (Si(*C*H$_3$)$_2$ / Si(CH_3)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{13}C / δ^1H = 141.7 / 6.57, 5.36, 5.27 (quart. iPrCp / each iPrCp), 100.3 / 6.57, 5.36, 5.27, 0.18, 0.12 (quart. iPrCp-CSi / each iPrCp, each Si(CH_3)$_2$), 99.8 / 6.74, 6.70, 5.44, 5.42, 0.18, 0.12 (quart. Cp-CSi / each Cp, each Si(CH_3)$_2$).

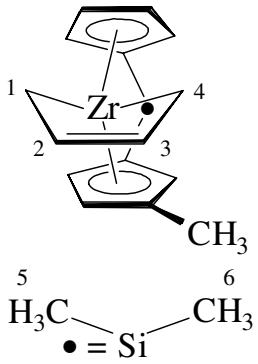


(8c) IR (KBr): $\tilde{\nu}$ = 2947 (w), 2864 (w), 1458 (m), 1406 (m), 1354 (s), 1149 (m), 1114 (s), 1044 (vs), 968 (w), 845 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^1H / δ^1H = 6.75 / 6.71, 5.45; 6.71 / 5.44, 5.45 / 5.44 (each Cp / Cp), 6.59 / 5.38, 5.25; 5.38 / 5.28 (each cyCp / cyCp). (no assignment of the cyclohexyl fragment). **GHSQC** (150.8 MHz /

599.9 MHz, [D_6]-benzene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 121.3 / 6.75, 120.0 / 6.71, 112.8 / 5.44, 111.4 / 5.45 (each Cp / Cp), 118.8 / 6.59, 111.6 / 5.38, 110.9 / 5.28 (each cyCp / cyCp), 38.5 / 2.71 (cy-*C*H / cy-C*H*), 32.1 / -0.12, 28.9 / -0.03 (each Zr(*C*H_3)$_2$ / Zr(C*H*$_3$)$_2$, 36.4 / 1.98, 36.4 / 1.31, 32.8 / 2.12, 32.8 / 1.47, 27.0 / 1.72, 27.0 / 1.38, 26.7 / 1.71, 26.7 / 1.36, 26.5 / 1.63, 26.5 / 1.15 (cy-*C*H_2 / cy-C*H*$_2$), -5.1 / 0.19, -5.7 / 0.14 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 140.7 / 6.59, 5.38, 5.28, 0.19, 0.14 (quart. cyCp / each cyCp), 100.3 / 6.59, 5.38, 5.28, 0.19, 0.14 (quart. cyCp-CSi / each cyCp-C*H*, each Si(C*H*$_3$)$_2$), 99.7 / 6.75, 6.71, 5.45, 5.44, 0.19, 0.14 (quart. Cp-CSi / each Cp-C*H*, each Si(C*H*$_3$)$_2$).



(8e) IR (KBr): $\tilde{\nu}$ = 2965 (w), 2877 (w), 1468 (m), 1407 (w), 1374 (m), 1252 (s), 1193 (s), 1089 (s), 1055 (s), 961 (w), 805 (vs) cm^{-1}. **GCOSY** (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): $\delta^{1}H$ / $\delta^{1}H$ = 6.74 / 6.56, 5.36, 6.56 / 5.58, 5.58 / 5.36 (each Cp / Cp), 6.67 / 5.62, 6.67 / 5.32, 5.58 / 5.32 (each tBuCp / tBuCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 121.2 / 6.74, 119.6 / 6.56, 114.4 / 5.58, 110.4 / 5.36 (each Cp / Cp), 120.1 / 6.67, 111.9 / 5.32, 110.2 / 5.62 (each tBuCp / tBuCp), 31.6 / 0.01, 28.2 / 0.00 (each Zr(*C*H_3)$_2$ / Zr(C*H*$_3$)$_2$), 31.3 / 1.37 (tBu-*C*H_3 / tBu-C*H*$_3$),-4.3 / 0.21, -6.1 / 0.12 (Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 145.1 / 6.67, 5.62, 5.32 (quart. tBuCp / each tBuCp), 100.5 / 6.67, 5.62, 5.32, 0.21, 0.12 (quart. tBuCp-CSi / each tBuCp-C*H*, each Si(C*H*$_3$)$_2$), 98.6 / 6.74, 6.56, 5.58, 5.36, 0.21, 0.12 (quart. Cp-CSi / each Cp, each Si(C*H*$_3$)$_2$).

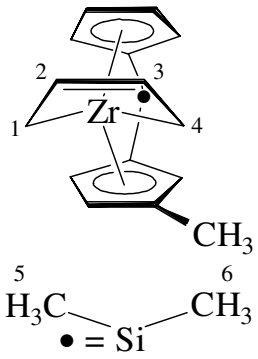


General

IR (KBr): $\tilde{\nu}$ = 2959 (s), 2896 (s), 1499 (m), 1441 (s), 1404 (s), 1303 (w), 1251 (vs), 1191 (s), 1094 (vs), 1031 (s), 822 (vs) cm^{-1}.

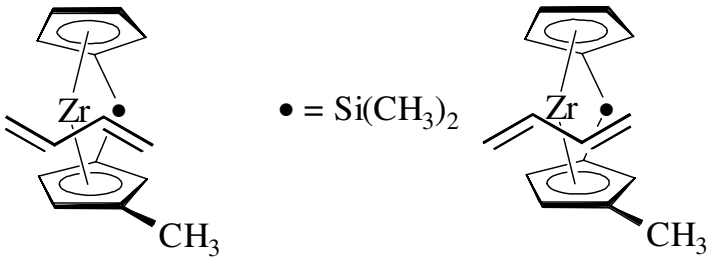
(*s-cis*-17b) Main *s-cis* isomer:

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 268 K): δ^1H / δ^1H = 5.92 / 5.42, 4.21; 5.42 / 4.21 (each MeCp / MeCp), 5.19 / 4.98, 4.91; 4.98 / 4.91 (each Cp / Cp), 4.79 / 4.69, 3.37, -1.50 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.69 / 3.36, -0.76 (2-H / 1_{syn}-H, 1_{anti}-H), 3.37 / -1.50 (4_{syn}-H / 4_{anti}-H), 3.36 / -0.76 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): δ^{13}C / δ^1H = 109.9 / 4.92 (Cp / Cp), 112.4 / 4.79 (C3 / 3-H), 110.1 / 4.69 (C2 / 2-H), 109.0 / 5.19 (Cp / Cp), 109.0 / 4.21 (MeCp / MeCp), 103.2 / 4.91 (Cp / Cp), 101.2 / 5.92 (MeCp / MeCp), 100.8 / 4.98 (Cp / Cp), 99.9 / 5.42 (MeCp / MeCp), 54.1 / 3.37, -1.50 (C4 / 4_{syn}-H, 4_{anti}-H), 49.5 / 3.36, -0.76 (C1 / 1_{syn}-H, 1_{anti}-H), 14.7 / 1.70 (MeCp-CH_3 / MeCp-CH_3), -3.6 / 0.42 (C6 / 6-H), -6.5 / 0.29 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): δ^{13}C / δ^1H = 142.8 / 5.92, 5.42, 4.21 (quart. MeCp / each MeCp), 99.7 / 5.92, 5.42, 4.21 (quart. MeCp-CSi / each MeCp), 94.1 / 5.25, 4.92, 4.88 (quart. Cp-CSi / each Cp), 102.9, 93.2, -3.6 / 0.42 (quart. MeCp-CSi, quart. Cp-CSi, C6 / 6-H), 102.9, 93.2, -6.5 / 0.29 (quart. MeCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 268 K): δ_{irr} / δ_{res} = 5.92 / 5.42, 4.21 (MeCp); 5.19 / 4.98, 4.91 (Cp); 4.79 / 4.69, 3.37, 3.36, -0.76, -1.50 (3-H / 2-H, 4_{syn}-H, 1_{syn}-H, 4_{anti}-H, 1_{anti}-H).



(*s-cis*-17'b) Second *s-cis* isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 268 K): δ^1H / δ^1H = 5.48 / 5.22, 4.56, 4.25; 5.22 / 4.56, 4.25; 4.56 / 4.25 (each Cp / Cp), 5.41 / 4.98, 3.75; 4.98 / 3.75 (each MeCp / MeCp), 4.80 / 4.71, 3.12, -0.88 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.71 / 3.4, -0.83 (2-H / 1_{syn}-H, 1_{anti}-H), 3.43 / -0.83 (1_{syn}-H / 1_{anti}-H), 3.12 / -0.88 (4_{syn}-H / 4_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): δ^{13}C / δ^1H = 112.7 / 4.80 (C3 / 3-H), 112.0 / 4.71 (C2 / 2-H), 111.2 / 4.25, 111.0 / 4.56, 95.5 /5.22, 95.0 / 5.48 (each Cp / Cp), 109.2 / 3.75, 97.3 / 4.98, 96.4 / 5.41 (each MeCp / MeCp), 51.9 / 3.12, -0.88 (C4 / 4_{syn}-H, 4_{anti}-H), 50.6 / 3.43, -0.83 (C1 / 1_{syn}-H, 1_{anti}-H), 13.8 / 1.26 (MeCp-CH_3 / MeCp-CH_3), -4.8 / 0.41 (C6 / 6-H), -6.0 / 0.20 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): δ^{13}C / δ^1H = 130.0 / 5.41, 4.98, 3.75 (quart. MeCp / each MeCp), 102.4 / 5.41, 4.98, 3.75 (quart. MeCp-CSi / each MeCp), 94.0 / 5.48, 5.22, 4.56, 4.25 (quart. Cp-CSi / each Cp), 102.4, 94.0, -4.8 / 0.44 (quart. MeCp-CSi, quart. Cp-CSi, C6 / 6-H), 102.4, 94.0, -6.0 / 0.28 (quart. MeCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 268 K): δ_{irr} / δ_{res} = 5.48 / 5.22, 4.56, 4.25 (Cp); 5.41 / 4.98, 3.75 (MeCp); 4.80 / 4.71, 3.43, 3.12, -0.83, -0.88, (3-H / 2-H, 1_{syn}-H, 4_{syn}-H, 1_{anti}-H, 4_{anti}-H).

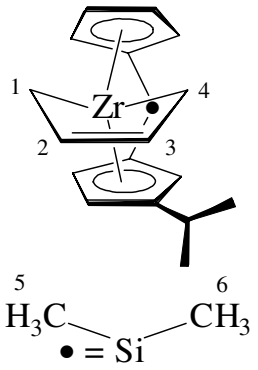


(*s-trans*-17b) Main *s-trans* isomer

GHSQC (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): $\delta^{13}C$ / $\delta^{1}H$ = 96.5 / 2.89, 95.0 / 2.35 (each Butadien-*C*H / Butadien-C*H*), 60.5 / 3.08, 1.23; 59.8 / 2.61, 1.30 (each Butadien-*C*H_2 / Butadien-C*H*$_2$). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 268 K): δ_{irr} / δ_{res} = 3.08 / 2.89, 2.61, 2.35, 1.30, 1.23 (H_{syn} / H_{meso}, H_{syn}, H_{meso}, H_{anti}, H_{anti}).

(*s-trans*-17'b) Second *s-trans* isomer

1D-TOCSY (599.9 MHz, [D_8]-toluene, 268 K): δ_{irr} / δ_{res} = 3.16 / 2.90, 2.77, 2.55, 1.33, 1.29 (H_{syn} / H_{meso}, H_{syn}, H_{meso}, H_{anti}, H_{anti}).



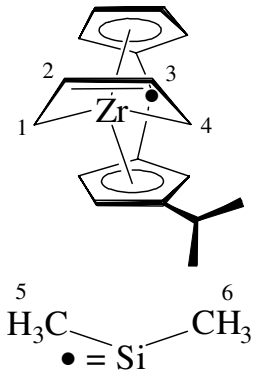
General

IR (KBr): $\tilde{\nu}$ = 2960 (s), 2865 (w), 1456 (w), 1420 (w), 1361 (w), 1260 (vs), 1164 (s), 1099 (m), 1033 (s), 967 (w), 916 (w), 807 (vs) cm^{-1}.

(*s-cis*-17d) Main *s-cis* isomer

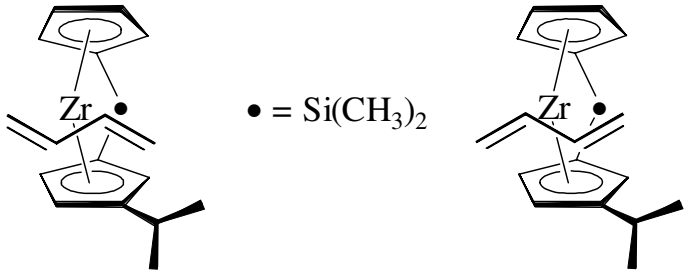
GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 248 K): $\delta^{1}H$ / $\delta^{1}H$ = 5.99 / 5.61, 4.10; 5.61 / 4.10 (each iPrCp / iPrCp), 5.25 / 4.92, 4.88; 4.92 / 4.88 (each Cp / Cp), 4.78 / 4.6, 3.40, -1.45 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.66 / 3.36, -0.78 (2-H / 1_{syn}-H, 1_{anti}-H), 3.40 / -1.45 (4_{syn}-H / 4_{anti}-H), 3.36 / -0.78 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 248 K): $\delta^{13}C$ / $\delta^{1}H$ = 112.7 / 4.78 (C3 / 3-H), 110.4 / 4.88, 109.1 / 5.25, 102.3 / 4.92, 100.1 / 4.92 (each Cp / Cp), 109.8 / 4.66 (C2 / 2-H), 105.9 / 4.10, 102.7 / 5.99, 96.1 / 5.61 (each iPrCp / iPrCp), 54.0 / 3.40, -1.45 (C4 / 4_{syn}-H, 4_{anti}-H), 50.1 / 3.36, -0.78 (C1 / 1_{syn}-H, 1_{anti}-H), 28.3 / 2.10 (iPr-C*H* / iPrCp-*C*H), 25.6 / 1.22, 22.1 / 0.90 (iPr-*C*H_3 / iPr-C*H*$_3$), -3.2 / 0.43 (C6 / 6-H), -6.6 / 0.30 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 248 K): $\delta^{13}C$ / $\delta^{1}H$ = 143.1

/ 5.99, 5.61, 4.10 (quart. iPrCp / each iPrCp), 101.4 / 5.99, 5.61, 4.10 (quart. iPrCp-CSi / each iPrCp), 94.1 / 5.25, 4.92, 4.88 (quart. Cp-CSi / each Cp), 101.4, 94.1, -3.2 / 0.43 (quart. iPrCp-CSi, quart. Cp-CSi, C6 / 6-H), 101.4, 94.1, -6.6 / 0.30 (quart. iPrCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 248 K): δ_{irr} / δ_{res} = 5.99 / 5.61, 4.10 (iPrCp); 5.25 / 4.92, 4.88 (Cp); 4.78 / 4.66, 3.40, 3.36, -0.78, -1.45 (3-H / 2-H, 4_{syn}-H, 1_{syn}-H, 1_{anti}-H, 4_{anti}-H).



(*s-cis*-17'd) Second *s-cis* isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 248 K): δ^1H / δ^1H = 5.48 / 5.22, 4.56, 4.25; 5.22, 4.25; 4.56 / 4.25 (each Cp / Cp), 5.41 / 4.98, 3.75; 4.98 / 3.75 (each iPrCp / iPrCp), 4.80 / 4.71, 3.12, -0.88 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.71 / 3.43, -0.83 (2-H / 1_{syn}-H, 1_{anti}-H), 3.43 / -0.83 (1_{syn}-H / 1_{anti}-H), 3.12 / -0.88 (4_{syn}-H / 4_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 248 K): δ^{13}C / δ^1H = 118.5 / 5.89, 105.0 / 4.24, 104.5 / 6.04, 99.0 / 5.67 (each Cp / Cp), 112.3 / 4.83 (C3 / 3-H), 111.5 / 4.77, 105.4 / 5.28, 98.7 / 4.87 (each iPrCp / iPrCp), 111.2 / 4.79 (C2 / 2-H), , 52.5 / 3.20, -0.91 (C4 / 4_{syn}-H, 4_{anti}-H), 50.6 / 3.41, -0.79 (C1 / 1_{syn}-H, 1_{anti}-H), 28.2 / 1.87, 26.5 / 1.02 (each iPr-CH_3 / iPr-CH_3), 21.9 / 0.86 (iPr-CH_3 / iPr-CH_3), -3.1 / 0.44 (C6 / 6-H), -6.7 / 0.29 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 248 K): δ^{13}C / δ^1H = 130.4 / 5.28, 4.87, 4.77 (quart. iPrCp / each iPrCp), 101.3 / 5.28, 4.87, 4.77 (quart. iPrCp-CSi / each iPrCp), 93.8 / 6.04, 5.89, 5.67, 4.24 (quart. Cp-CSi / each Cp), 101.3, 93.8, -3.1 / 0.44 (quart. iPrCp-CSi, quart. Cp-CSi, C6 / 6-H), 101.3, 93.8, -6.7 / 0.29 (quart. iPrCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 248 K): δ_{irr} / δ_{res} = 6.04 / 5.89, 5.67, 4.24 (Cp); 5.28 / 4.87, 4.77 (iPrCp); 4.83 / 4.79, 3.41, 3.20, -0.79, -0.91 (3-H / 2-H, 1_{syn}-H, 4_{syn}-H, 1_{anti}-H, 4_{anti}-H).

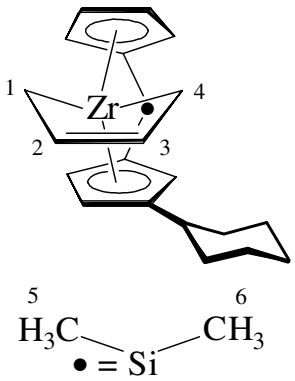


(*s-trans*-17d) Main *s-trans* isomer

GHSQC (150.8 MHz / 599.9 MHz, [D_8]-toluene, 248 K): δ^{13}C / δ^{1}H = 98.1 / 2.88, 97.9 / 2.55 (each Butadien-*C*H / Butadien-C*H*), 61.2 / 2.61, 1.38; 60.8 / 3.16, 1.23 (each Butadien-*C*H_2 / Butadien-C*H*$_2$). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 248 K): δ_{irr} / δ_{res} = 3.16 / 2.88, 2.61, 2.55, 1.38, 1.23 (H_{syn} / H_{meso}, H_{syn}, H_{meso}, H_{anti}, H_{anti}).

(*s-trans*-17'd) Second *s-trans* isomer

1D-TOCSY (599.9 MHz, [D_8]-toluene, 248 K): δ_{irr} / δ_{res} = 3.24 / 3.30, 2.97, 2.68, 1.43, 1.32 (H_{syn} / H_{meso}, H_{syn}, H_{meso}, H_{anti}, H_{anti}).

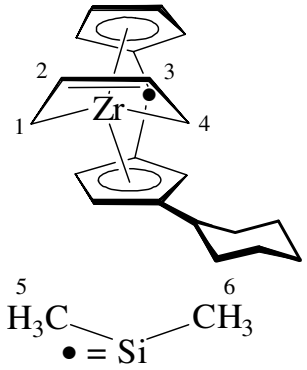


General

IR (KBr): $\tilde{\nu}$ = 2910 (s), 2853 (s), 1447 (s), 1408 (w), 1369 (w), 1251 (vs), 1178 (m), 1099 (m), 1047 (s), 955 (w), 922 (w), 817 (vs), 731 (m) cm^{-1}.

(*s-cis*-17c) Main *s-cis* isomer

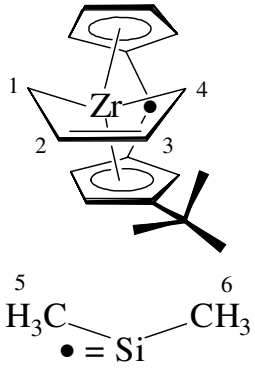
GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 228 K): δ^1H / δ^1H = 6.02 / 5.60, 4.02; 5.60 / 4.02 (each cyCp / cyCp), 5.28 / 4.92, 4.86; 4.92 / 4.86 (each Cp / Cp), 4.76 / 4.66, 3.44, -1.45 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.66 / 3.35, -0.73 (2-H / 1_{syn}-H, 1_{anti}-H), 3.44 / -1.45 (4_{syn}-H / 4_{anti}-H), 3.35 / -0.73 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 228 K): δ^{13}C / δ^1H = 112.3 / 4.76 (C3 / 3-H), 110.4 / 4.86, 109.1 / 5.28, 102.0 / 4.92, 99.8 / 4.92 (each Cp / Cp), 109.5 / 4.66 (C2 / 2-H), 105.2 / 4.02, 102.8 / 6.02, 96.3 / 5.60 (each cyCp / cyCp), 60.8 / 3.21 (cy-*C*H / cy-C*H*), 54.1 / 3.44, -1.45 (C4 / 4_{syn}-H, 4_{anti}-H), 50.1 / 3.35, -0.73 (C1 / 1_{syn}-H, 1_{anti}-H), 38.2, 36.7, 32.5, 26.9, 26.6 / 1.80-1.00 (cy-*C*H_2 / cy-C*H_2*), -3.2 / 0.48 (C6 / 6-H), -6.7 / 0.30 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 228 K): δ^{13}C / δ^1H = 143.4 / 6.02, 5.60, 4.02 (quart. cyCp / each cyCp), 101.4 / 6.02, 5.60, 4.02 (quart. cyCp-CSi / each cyCp), 95.4 / 5.28, 4.92, 4.86 (quart. Cp-CSi / each Cp), 101.4, 95.4, -3.2 / 0.48 (quart. cyCp-CSi, quart. Cp-CSi, C6 / 6-H), 101.4, 95.4, -6.7 / 0.30 (quart. cyCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 228 K): δ_{irr} / δ_{res} = 4.76 / 4.66, 3.44, 3.35, -0.73, -1.45 (3-H / 2-H, 4_{syn}-H, 1_{syn}-H, 1_{anti}-H, 4_{anti}-H); 6.02 / 5.60, 4.02 (cyCp); 5.28 / 4.92, 4.86 (Cp).



(*s-cis*-17'c) Second *s-cis* isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 253 K): δ^1H / δ^1H = 6.07 / 5.93, 5.69, 4.17; 5.69 / 4.17 (each Cp / Cp), 5.53 / 5.16, 4.08, 5.16 / 4.08 (each cyCp / cyCp), 4.83 / 4.70, 3.46, -0.88 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.70 / 3.22, -0.77 (2-H / 1_{syn}-H, 1_{anti}-H), 3.46 / -0.88 (4_{syn}-H / 4_{anti}-H), 3.22 / -0.77 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{13}C / δ^1H = 118.6 / 5.9, 104.9 / 6.07, 104.5 / 4.17, 99.1 / 5.69 (each Cp / Cp), 112.1 / 4.83 (C3 / 3-H), 111.6 / 4.70 (C2 / 2-H), 108.6 / 4.08, 95.5 / 5.53, 94.1 / 5.16 (each cyCp / cyCp),

61.1 / 2.61 (cy-*C*H / cy-C*H*), 52.3 / 3.4, -0.88 (C4 / 4_{syn}-H, 4_{anti}-H), 50.7 / 3.22, -0.77 (C1 / 1_{syn}-H, 1_{anti}-H), 37.7, 32.1, 26.7, 26.5, 26.4 / 1.80-1.00 (cy-*C*H_2 / cy-C*H*$_2$), -3.2 / 0.49 (C6 / 6-H), -6.8 / 0.29 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{13}C / δ^{1}H = 137.6 / 5.53, 5.16, 4.08 (quart. cyCp-C / each cyCp), 99.7 / 5.53, 5.16, 4.08 (quart. cyCp-CSi / each cyCp), 94.5 / 6.07, 5.93, 5.69, 4.17 (quart. Cp-CSi / each Cp), 99.7, 94.5, -3.0 / 0.49 (quart. cyCp-CSi, quart. Cp-CSi, C6 / 6-H), 99.7, 94.5, -6.8 / 0.29 (quart. cyCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 253 K): δ_{irr} / δ_{res} = 4.83 / 4.70, 3.46, 3.22, -0.77, -0.88 (3-H / 2-H, 4_{syn}-H, 1_{syn}-H, 1_{anti}-H, 4_{anti}-H); 5.53 / 5.16, 4.08 (cyCp); 6.07 / 5.93, 5.69, 4.17 (Cp).



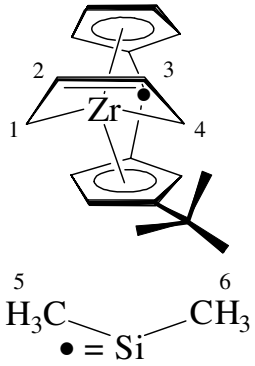
General

IR (KBr): $\tilde{\nu}$ = 2958 (vs), 2873 (vs), 1493 (m), 1467 (s), 1408 (s), 1369 (s), 1257 (vs), 1178 (vs), 1086 (vs), 1047 (vs), 942 (m), 923 (s), 810 (vs) cm^{-1}.

(*s-cis*-17e) Main *s-cis* isomer

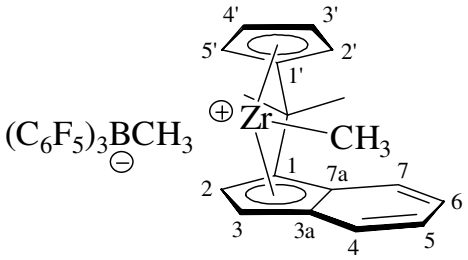
GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{1}H / δ^{1}H = 5.99 / 5.65, 4.41; 5.65 / 4.41 (each tBuCp / tBuCp), 5.31 / 4.99, 4.89, 4.81; 4.99 / 4.89, 4.81 (each Cp / Cp), 4.73 / 4.62, 3.27, -0.86 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.62 / 3.42, -0.72 (2-H / 1_{syn}-H, 1_{anti}-H), 3.42 / -0.72 (1_{syn}-H / 1_{anti}-H), 3.27 / -0.86 (4_{syn}-H / 4_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{13}C / δ^{1}H = 112.1 / 4.73 (C3 / 3-H), 110.9 / 4.89, 108.9 / 5.31, 101.7 / 4.99, 99.1 / 4.81 (each Cp / Cp), 110.1 / 4.62 (C2 / 2-H), 103.9 / 5.99, 103.3 / 4.41, 97.3 / 5.65 (each tBuCp / tBuCp), 51.6 / 3.27, -0.86 (C4 / 4_{syn}-H, 4_{anti}-H), 51.4 / 3.42, -0.72 (C1 / 1_{syn}-H, 1_{anti}-H), 32.1 / 1.09 (tBu-*C*H_3 / tBu-C*H*$_3$), -3.1 / 0.44 (C6 / 6-H), -6.6 / 0.29 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{13}C / δ^{1}H = 148.0 / 5.99, 5.65,

4.41 (quart. tBuCp / each tBuCp), 101.1 / 5.99, 5.65, 4.41 (quart. tBuCp-CSi / each tBuCp), 95.3 / 5.31, 4.99, 4.89, 4.81 (quart. Cp-CSi / each Cp), 101.1, 95.3, -3.1 / 0.44 (quart. tBuCp-CSi, quart. Cp-CSi, C6 / 6-H), 101.1, 95.3, -6.6 / 0.29 (quart. tBuCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 253 K): δ_{irr} / δ_{res} = 4.73 / 4.62, 3.42, 3.27, -0.72, -0.86 (3-H / 2-H, 1_{syn}-H, 4_{syn}-H, 1_{anti}-H, 4_{anti}-H); 5.99 / 5.65, 4.41 (tBuCp); 5.31 / 4.99, 4.89, 4.81 (Cp).



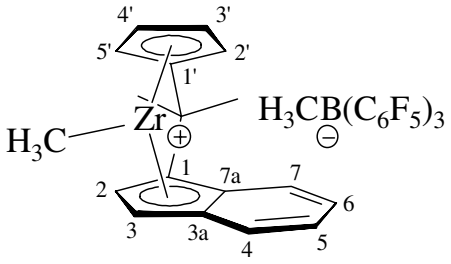
(*s-cis*-17e) Second *s-cis* isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 253 K): δ^1H / δ^1H = 6.19 / 6.10, 5.72, 4.00; 6.10 / 5.72, 4.00; 5.72 / 4.00 (each Cp / Cp), 5.32 / 4.90, 4.68; 4.90 / 4.68 (each tBuCp / tBuCp), 5.14 / 4.67, 3.47, -0.96 (3-H / 2-H, 4_{syn}-H, 4_{anti}-H), 4.67 / 3.25, -0.70 (2-H / 1_{syn}-H, 1_{anti}-H), 3.47 / -0.96 (4_{syn}-H / 4_{anti}-H), 3.25 / -0.70 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{13}C / δ^1H = 117.6 / 6.19, 110.7 / 6.10, 102.8 / 4.00, 101.4 / 5.72 (each Cp / Cp), 113.4 / 5.14 (C3 / 3-H), 109.1 / 4.67 (C2 / 2-H), 109.0 / 4.90, 106.1 / 5.32, 96.5 / 4.68 (each tBuCp / tBuCp), 52.1 / 3.47, -0.96 (C4 / 4_{syn}-H, 4_{anti}-H), 50.3 / 3.25, -0.70 (C1 / 1_{syn}-H, 1_{anti}-H), 31.4 / 0.96 (tBu-*C*H_3/ tBu-C*H*$_3$), -2.2 / 0.47 (C6 / 6-H), -6.9 / 0.28 (C5 / 5-H). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 253 K): δ^{13}C / δ^1H = 135.2 / 5.32, 4.90, 4.68 (quart. tBuCp / each tBuCp), 99.9 / 5.32, 4.90, 4.68 (quart. tBuCp-CSi / each tBuCp), 98.8 / 6.19, 6.10, 5.72, 4.00 (quart. Cp-CSi / each Cp), 99.9, 98.8, -2.2 / 0.47 (quart. tBuCp-CSi, quart. Cp-CSi, C6 / 6-H), 99.9, 98.8, -6.9 / 0.28 (quart. tBuCp-CSi, quart. Cp-CSi, C5 / 5-H). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 253 K): δ_{irr} / δ_{res} = 5.14 / 4.67, 3.47, 3.25, -0.70, -0.96 (3-H / 2-H, 4_{syn}-H, 1_{syn}-H, 1_{anti}-H, 4_{anti}-H); 5.32 / 4.90, 4.68 (tBuCp); 6.19 / 6.10, 5.72, 4.00 (Cp).



Main isomer (*anti*-betaine)

GCOSY (599.9 MHz / 599.9 MHz, [D_2]-dichloromethane, 253 K): δ^1H / δ^1H = 7.66 / 7.47 (4-H / 5-H), 7.47 / 7.10 (5-H / 6-H), 7.10 / 7.52 (6-H / 7-H), 6.52 / 6.27 (3-H / 2-H), 6.85 / 6.17 (5'-H / 4'-H), 6.17 / 5.82 (4'-H / 3'-H), 5.81 / 5.52 (3'-H / 2'-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_2]-dichloromethane, 253 K): δ^{13}C / δ^1H = 127.5 / 7.47 (C5 / 5-H), 127.0 / 7.10 (C-6 / 6-H), 126.4 / 7.66 (C4 / 4-H), 126.1 / 7.52 (C7 / 7-H), 119.8 / 6.85 (C5' / 5'-H), 115.3 / 6.17 (C4' / 4'-H), 113.2 / 6.27 (C2 / 2-H), 108.6 / 5.52 (C2' / 2'-H), 105.5 / 6.52 (C3 / 3-H), 104.2 / 5.81 (C3' / 3'-H), 42.7 / -0.75 (Zr-CH$_3$ / Zr-CH_3), 25.8 / 1.89 (C(CH$_3$)$_2$ / C(CH_3)$_2$-anti), 24.6 / 1.99 (C(CH$_3$)$_2$ / C(CH_3)$_2$-syn).

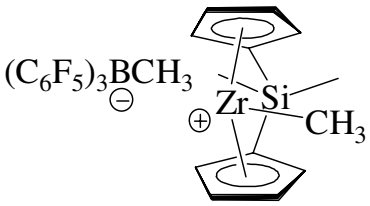


Minor isomer (*syn*-betaine)

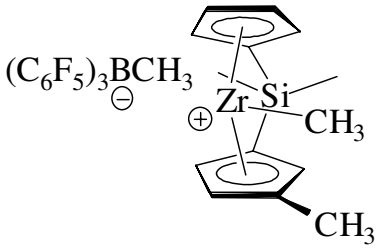
GCOSY (599.9 MHz / 599.9 MHz, [D_2]-dichloromethane, 253 K): δ^1H / δ^1H = 7.62 / 6.48 (4-H / 5-H), 6.48 / 6.73 (5-H / 6-H), 6.73 / 7.62 (6-H / 7-H), 5.80 / 7.32 (3-H / 2-H), 5.43 / 5.80, 5.80 / 5.87, 5.87 / 6.81 (each Cp' / Cp'). **GHSQC** (150.8 MHz / 599.9 MHz, [D_2]-dichloromethane, 253 K): δ^{13}C / δ^1H = 126.8 / 6.73, 125.7 / 6.48 (C6 / 6-H, C5 / 5-H), 124.8 / 7.62, 121.7 / 7.62 (C4 / 4-H, C7 / 7-H), 121.0 / 6.81 (Cp' / Cp'), 114.9 / 5.80 (C3 / 3-H), 113.4 / 5.80 (Cp' / Cp'), 112.3 / 7.32 (C2 / 2-H), 108.5 / 5.43, 104.0 / 5.87 (each Cp' / Cp'), 44.7 / 0.66 (Zr-CH$_3$ / Zr-CH_3), 25.9 / 1.78 (C(CH$_3$)$_2$-anti / C(CH_3)$_2$-anti), 24.8 / 2.07 (C(CH$_3$)$_2$-syn / C(CH_3)$_2$-syn).

Anion

^{1}H-NMR (599.9 MHz, [D_2]-dichloromethane, 253 K): δ = 0.61 (broad s, 3H, (C*H*$_3$)B(C_6F_5)$_3$). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_2]-dichloromethane, 253 K): δ = 147.5 (dm, $^{1}J_{CF}$ = 233 Hz, o-B(*C*$_6$F$_5$)$_3$), 138.5 (dm, $^{1}J_{CF}$ = 256 Hz, p- B(*C*$_6$F$_5$)$_3$), 136.7 (dm, $^{1}J_{CF}$ = 251 Hz, m- B(*C*$_6$F$_5$)$_3$), 129.2 (broad, ipso-B(*C*$_6$F$_5$)$_3$). (Me-[B] was not observed). **^{19}F-NMR** (563.7 MHz, [D_2]-dichloromethane, 253 K): δ = -133.9 (broad s, 6F, o-B(C$_6$*F*$_5$)$_3$), -160.0 (broad s, 3F, p-B(C$_6$*F*$_5$)$_3$), -164.8 (broad s, 6F, m-B(C$_6$*F*$_5$)$_3$).

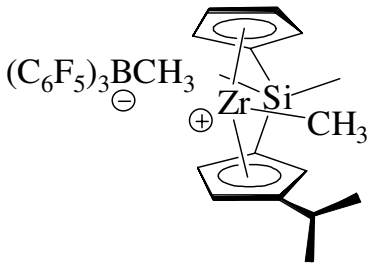


^{1}H-NMR (599.9 MHz, [D_6]-benzene, 298 K): δ = 6.34, 6.23, 5.28, 4.88 (each m, each 2H, Cp), 0.46 (br, 3H, (*H*$_3$C)B(C_6F_5)$_3$), 0.31 (s, 3H, Zr-C*H*$_3$), -0.02, -0.20 (each s, each 3H, Si(CH$_3$)$_2$).

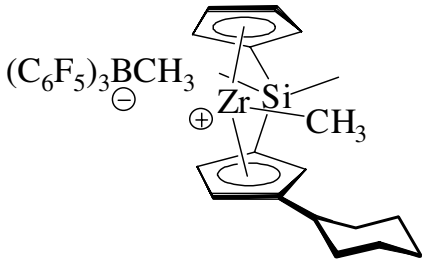


(9b) GCOSY (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.44 / 6.25, 4.80; 6.25 / 5.37, 5.37 / 4.80 (each Cp / Cp), 6.00 / 5.31, 4.57; 5.31 / 4.57 (each MeCp / MeCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^{1}H = 124.8 / 6.44, 121.9 / 6.25, 117.6 / 4.80, 111.5 / 5.37 (each Cp / Cp), 122.3 / 6.00, 118.2 / 4.57, 112.4 / 5.31 (each MeCp / MeCp), 42.1 / 0.23 (Zr-*C*H$_3$ / Zr-C*H*$_3$), 14.3 / 1.85 (MeCp-*C*H$_3$ / MeCp-C*H*$_3$), -5.5 /0.02, -6.6 / 0.18 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **^{19}F-NMR** (563.7 MHz, [D_6]-benzene, 298 K): δ

= -130.1 (broad, 6F, o-B(C_6F_5)$_3$), -161.6 (broad, 3F, p-B(C_6F_5)$_3$), -164.0 (broad, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_6$]-benzene, 298 K): δ = -14.2.

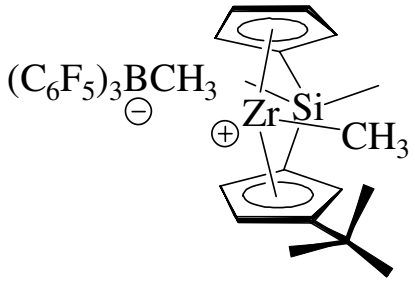


(9d) GCOSY (599.9 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.43 / 6.30, 4.82; 6.30 / 5.36, 5.36 / 4.82 (each Cp / Cp), 6.23 / 5.38, 4.78; 5.38 / 4.78 (each iPrCp / iPrCp), 2.66 / 0.90, 0.88 (iPr-C*H* / iPr-C*H*$_3$). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{13}C / δ^{1}H = 124.9 / 6.43, 122.2 / 6.30, 117.6 / 4.82, 111.1 / 5.36 (each Cp / Cp), 119.3 / 6.23, 115.9 / 4.78, 111.4 / 5.38 (iPrCp / iPrCp), 42.1 / 0.29 (Zr-*C*H$_3$ / Zr-C*H*$_3$), 28.5 / 2.66 (iPr-*C*H / iPr-C*H*), 24.8 / 0.90, 20.5 / 0.88 (each iPr-*C*H$_3$ / iPr-C*H*$_3$), -5.8 / 0.02, -6.8 / 0.21 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **^{19}F-NMR** (563.7 MHz, [D$_6$]-benzene, 298 K): δ = -130.6 (broad, 6F, o-B(C_6F_5)$_3$), -161.9 (broad, 3F, p-B(C_6F_5)$_3$), -164.9(broad, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_6$]-benzene, 298 K): δ = -14.1.

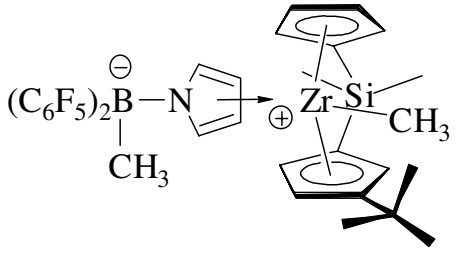


(9c) GCOSY (599.9 M,Hz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.42 / 6.34, 4.90; 6.40 / 5.33, 5.33 / 4.90 (each Cp / Cp), 6.30 / 5.40, 4.84; 5.40 / 5.33 (each cyCp / cyCp). (Die Kreuzsignale der cyclohexylgruppe wurden nicht gelistet.) **GHSQC** (150.8 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{13}C / δ^{1}H = 124.2 / 6.42, 122.6 / 6.34, 118.0 / 4.90, 110.8 / 5.33 (each Cp / Cp), 119.8 / 6.30, 116.4 / 4.84, 111.0 / 5.40 (each cyCp / cyCp), 40.8 / 0.32 (Zr-*C*H$_3$), 38.2 / 2.45 (cy-*C*H / cy-C*H*), 36.0 / 1.68, 0.98; 31.6 / 1.57, 1.13; 26.5 / 1.54, 1.21; 26.0 / 1.66, 1.18; 25.8 / 1.48, 0.95 (each cy-*C*H$_2$ / cy-C*H*$_2$), -5.6 / 0.04, -6.9 / -0.19 (each Si(*C*H$_3$)$_2$ /

Si(CH_3)$_2$). **^{19}F-NMR** (563.7 MHz, [D$_6$]-benzene, 298 K): δ = -129.7 (broad, 6F, o-B(C$_6F_5$)$_3$), -161.0 (broad, 3F, p-B(C$_6F_5$)$_3$), -163.9(broad, 6F, m-B(C$_6F_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_6$]-benzene, 298 K): δ = -14.3.



(9e) GCOSY (599.9 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{1}H = 6.40 / 5.37, 5.27; 5.37 / 5.27 (each tBuCp / tBuCp), 6.33 / 6.29, 5.20; 6.29 / 5.07, 5.27 / 5.07 (each Cp / Cp). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_6$]-benzene, 298 K): δ^{13}C / δ^{1}H = 123.3 / 6.33, 123.2 / 6.29, 119.7 / 5.07, 109.7 / 5.20 (each Cp / Cp), 121.4 / 6.40, 115.9 / 5.27, 111.1 / 5.37 (each tBuCp / tBuCp), 42.1 / 0.46 (Zr-*C*H$_3$ / Zr-C*H*$_3$), 30.5 / 0.98 (tBu-*C*H$_3$ / tBu-C*H*$_3$), -4.9 / 0.03, -7.4 / -0.24 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **^{19}F-NMR** (563.7 MHz, [D$_6$]-benzene, 298 K): δ = -130.4 (broad, 6F, o-B(C$_6F_5$)$_3$), -161.5 (broad, 3F, p-B(C$_6F_5$)$_3$), -164.2(broad, 6F, m-B(C$_6F_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_6$]-benzene, 298 K): δ = -14.5.

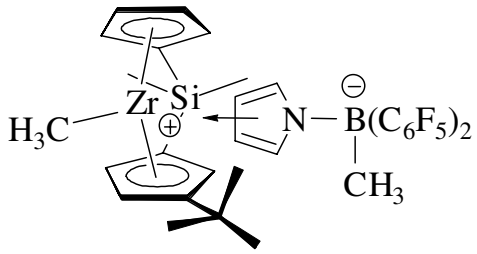


General

^{19}F-NMR (563.7 MHz, [D$_6$]-benzene, 298 K): δ = -132.0 (m, 6F, o-B(C$_6F_5$)$_3$), -159.2 (m, 3F, p-B(C$_6F_5$)$_3$), -164.4 (m, 6F, m-B(C$_6F_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_6$]-benzene, 298 K): δ = -7.4.

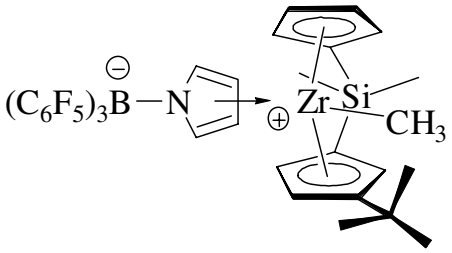
(*anti*-11e) Main isomer

GCOSY (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 7.40 / 7.32 (α-pyrrole / α-pyrrole), 7.40 / 5.91, 5.44; 7.32 / 5.91, 5.44 (each α-pyrrole / β-pyrrole), 5.91 / 5.44 (β-pyrrole / β-pyrrole), 6.29 / 4.95, 4.77; 4.95 / 4.77 (each Cp / Cp), 5.97 / 5.10, 5.03; 5.10 / 5.03 (each tBuCp / tBuCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 140.3 / 7.40, 136.3 / 7.32 (each α-pyrrole / α-pyrrole), 127.1 / 4.95, 124.1 / 6.29, 114.9 / 4.77, 109.0 / 4.95 (each Cp / Cp), 121.1 / 5.97, 112.6 / 5.03, 109.1 / 5.10 (each tBuCp / tBuCp), 103.8 / 5.91, 97.5 / 5.44 (β-pyrrole / β-pyrrole), 38.6 / 0.13 (Zr-*C*H_3 / Zr-C*H*$_3$), 30.9 / 1.13 (tBu-*C*H_3 / tBu-C*H*$_3$), -5.3 / 0.10, -7.0 / -0.15 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **^{1}D-TOCSY** (599.9 MHz, [D_6]-benzene, 298 K): δ_{irr} / δ_{res} = 7.40 / 7.32, 5.91, 5.44 (α-pyrrole / α-pyrrole, β-pyrrole, β-pyrrole); 6.29 / 4.95, 4.77 (Cp); 5.97 / 5.10, 5.03 (tBuCp).



(*syn*-11e) Second isomer

GCOSY (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 7.48 / 7.46 (α-pyrrole / α-pyrrole), 7.48 / 6.03, 5.92; 7.46 / 6.03, 5.92 (each α-pyrrole / β-pyrrole), 6.03 / 5.92 (β-pyrrole / β-pyrrole), 5.97 / 5.13, 4.98, 4.85; 5.13 / 4.98, 4.85; 4.95 / 4.85 (each Cp / Cp), 5.94 / 5.38, 5.07; 5.38 / 5.07 (each tBuCp / tBuCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 140.3 / 7.48, 136.3 / 7.46 (each α-pyrrole / α-pyrrole), 125.8 / 5.97, 121.1 / 4.98, 118.1 / 4.85, 112.5 / 5.13 (each Cp / Cp), 120.8 / 5.94, 112.7 / 5.07, 109.8 / 5.38 (each tBuCp / tBuCp), 101.8 / 6.03, 98.3 / 5.92 (β-pyrrole / β-pyrrole), 34.0 / 0.31 (Zr-*C*H_3 / Zr-C*H*$_3$), 29.9 / 0.95 (tBu-*C*H_3 / tBu-C*H*$_3$), -5.9 / 0.23, -6.1 / 0.16 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **^{1}D-TOCSY** (599.9 MHz, [D_6]-benzene, 298 K): δ_{irr} / δ_{res} = 7.48 / 7.46, 6.03, 5.92 (α-pyrrole / α-pyrrole, β-pyrrole, β-pyrrole); 5.97 / 5.13, 4.98, 4.85 (Cp); 5.94 / 5.38, 5.07 (tBuCp).

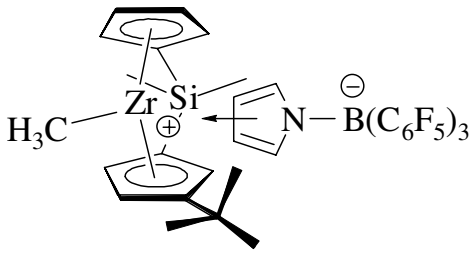


General

^{19}F-NMR (563.7 MHz, [D_6]-benzene, 298 K): δ = -130.1 (m, 6F, o-B(C_6F_5)$_3$), -157.4 (m, 3F, p-B(C_6F_5)$_3$), -162.7 (m, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D_6]-benzene, 298 K): δ = -8.3.

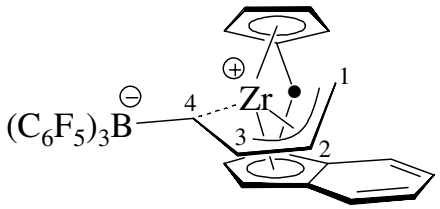
(*anti*-13e) Main isomer

GCOSY (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 7.21 / 7.18 (α-pyrrole / α-pyrrole), 7.21 / 5.83, 5.35; 7.18 / 5.83, 5.35 (each α-pyrrole / β-pyrrole), 6.55 / 5.46, 5.28, 4.28, 5.46 / 5.28, 4.86; 5.28 / 4.86 (each Cp / Cp), 6.12 / 5.31, 5.05; 5.31 / 5.05 (each tBuCp / tBuCp), 5.83 / 5.35 (β-pyrrole / β-pyrrole). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 139.1 / 7.21, 136.9 / 7.18 (each α-pyrrole / α-pyrrole), 125.9 / 6.55, 124.3 / 5.46, 115.8 / 4.82, 110.7 / 5.28 (each Cp / Cp), 120.5 / 6.12, 112.3 / 5.05, 111.4 / 5.31 (each tBuCp / tBuCp), 105.5 / 5.83, 98.9 / 5.35 (β-pyrrole / β-pyrrole), 41.3 / 0.23 (Zr-CH$_3$ / Zr-CH_3), 30.7 / 1.10 (tBu-CH$_3$ / tBu-CH_3), -5.6 / 0.21, -6.8 / -0.10 (each Si(CH$_3$)$_2$ / Si(CH_3)$_2$). **^{1}D-TOCSY** (599.9 MHz, [D_6]-benzene, 298 K): δ_{irr} / δ_{res} = 7.21 / 7.18, 5.83, 5.35 (α-pyrrole / α-pyrrole, β-pyrrole, β-pyrrole); 6.55 / 5.46, 5.28, 4.86 (Cp); 6.12 / 5.31, 5.05 (tBuCp).



(*syn*-13e) Second isomer

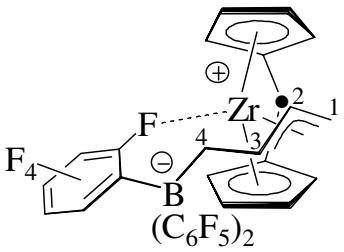
GCOSY (599.9 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^1H / δ^1H = 7.37 / 7.27 (α-pyrrole / α-pyrrole), 7.37 / 6.09, 5.81; 7.27 / 6.09, 5.81 (each α-pyrrole / β-pyrrole), 6.09 / 5.81 (β-pyrrole / β-pyrrole), 5.82 / 5.71 5.25, 5.22; 5.71 / 5.25, 5.22; 5.25 / 5.22 (each Cp / Cp), 6.07 / 5.47, 5.24; 5.47 / 5.24 (each tBuCp / tBuCp). **GHSQC** (150.8 MHz / 599.9 MHz, [D_6]-benzene, 298 K): δ^{13}C / δ^1H = 140.9 / 7.37, 139.4 / 7.27 (each α-pyrrole / α-pyrrole), 123.1 / 5.71, 121.4 / 5.22, 103.0 / 5.82, 101.6 / 5.25 (each Cp / Cp), 119.9 / 6.07, 113.1 / 5.24, 109.6 / 5.47 (each tBuCp / tBuCp), 102.7 / 5.81, 98.3 / 6.09 (β-pyrrole / (β-pyrrole), 34.0 / 0.37 (Zr-CH_3 / Zr-CH_3), 29.8 / 0.97 (tBu-CH_3 / tBu-CH_3), -5.7 / 0.23, -6.5 / 0.15 (each Si(CH_3)$_2$ / Si(CH_3)$_2$). **^{1}D-TOCSY** (599.9 MHz, [D_6]-benzene, 298 K): δ_{irr} / δ_{res} = 7.37 / 7.27, 6.09, 5.81 (α-pyrrole / α-pyrrole, β-pyrrole, β-pyrrole); 5.82 / 5.71, 5.25, 5.22 (Cp); 6.07 / 5.47, 5.24 (tBuCp).



(• = C(CH$_3$)$_2$)

(16) ^{1}H-NMR (599.9 MHz, [D_8]-toluene, 298 K): δ = 6.67 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.0 Hz, Ind-7-H), 6.40 (ddd, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.0 Hz, Ind-5-H), 6.32 (ddd, 1H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.0 Hz, Ind-6-H), 6.28 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.0 Hz, Ind-4-H), 5.77 (d, 1H, $^3J_{HH}$ = 3.7 Hz, Ind-2-H), 5.54 (m, 1H, Cp), 5.49 (d, 1H, $^3J_{HH}$ = 3.7 Hz, Ind-3-H), 5.09 (m, 1H, Cp), 4.93 (m, 1H, Cp), 4.86 (m, 1H, 3-H), 4.78 (m, 1H, Cp), 4.52 (m, 1H, 2-H), 1.32, 1.17 (each s, each 3H, C(CH_3)$_2$), 0.94 (br d, 2H, $^3J_{HH}$ = 10.6 Hz, 1_{syn}-H, 1_{anti}-H), -0.57, -0.74 (each br, each 1H, 4'-H, 4-H). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_8]-toluene, 298 K): δ = 148.6 (dm, $^1J_{CF}$ = 240 Hz, o-B(C_6F_5)$_3$), 139.4 (dm, $^1J_{CF}$ = 250 Hz, p-B(C_6F_5)$_3$), 137.5 (dm, $^1J_{CF}$ = 250 Hz, m-B(C_6F_5)$_3$), 135.2 (C2), 125.9 (Ind-C7), 125.7 (Ind-C4), 125.2 (Ind-C6), 124.3 (Ind-C5), 116.1, 110.8 (each Cp), 109.9 (C3), 109.8, 100.4 (Ind-C2, Ind-C3), 95.2, 93.7 (each Cp), 62.8 (C1), 25.5, 24.5 (each C(CH_3)$_2$), 22 (br C4). (The ipso-C[B] and CMe_2 of the isopropylidene bridge are not observed). **GCOSY** (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 298 K): δ^1H / δ^1H = 6.67 / 6.32 (Ind-7-H / Ind-6-H), 6.40 / 6.32, 6.28 (Ind-5-H / Ind-6-H, Ind-4-H), 6.32 / 6.28 (Ind-6-H / Ind-4-H), 5.77 / 5.49 (Ind-3-H / Ind-

2-H), 5.54 / 5.09, 4.93, 4.78 (Cp / Cp), 5.09 / 4.93, 4.78, (Cp / Cp), 4.86 / 4.52, -0.57, -0.74 (3-H / 2-H, 4'-H, 4-H), 4.52 / 0.94 (2-H / 1_{syn}-H, 1_{anti}-H), -0.57 / -0.74 (4'-H / 4-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 135.2 / 4.52 (C2 / 2-H), 125.9 / 6.67 (Ind-C7 / Ind-7-H), 125.7 / 6.28 (Ind-C4 / Ind-4-H), 125.2 / 6.32 (Ind-C6 / Ind-6-H), 124.3 / 6.40 (Ind-C5 / Ind-5-H), 116.1 / 5.09, 110.8 / 4.78 (each Cp / Cp), 109.9 / 4.86 (C3 / 3-H), 109.8 / 5.49 (Ind-C2 / Ind-2-H), 100.4 / 5.77 (Ind-C3 / Ind-3-H), 95.2 / 5.54, 93.7 / 4.93

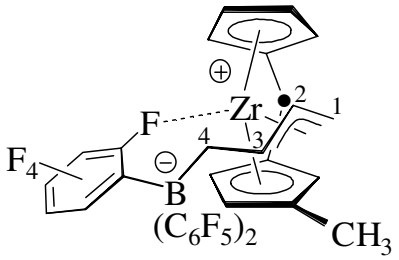


(• = $Si(CH_3)_2$)

(each Cp / Cp), 62.8 / 0.94 (C1 / 1'-H, 1-H), 25.5 / 1.17, 24.5 / 1.32 (each $C(CH_3)_2$ / $C(CH_3)_2$), 22 / -0.57, -0.74 (C4 / 4'-H, 4-H).

(**18a**)**: ^{1}H-NMR** (599.9 MHz, [D_8]-toluene, 298 K): δ = 6.11, 6.00 (each m, 1H, Cp), 5.92 (m, 2H, Cp und 2-H), 5.78, 5.55, 5.50 (each m, each 1H, Cp), 5.43 (m, 1H, 3-H), 4.40 (m, 2H, Cp), 2.63 (br d, 1H, $^{2}J_{HH}$ = 18.2 Hz, 4'-H), 2.31 (br dd,1H, $^{2}J_{HH}$ = 18.2 Hz, $^{3}J_{HH}$ = 6.0 Hz, 4-H), 1.86 (dd, 1H, $^{3}J_{HH}$ = 17.9 Hz, $^{2}J_{HH}$ = 5.0 Hz, 1_{anti}-H), 1.53 (dd,1H, $^{3}J_{HH}$ = 8.3 Hz, $^{2}J_{HH}$ = 5.0 Hz, 1_{syn}-H), 0.24, -0.17 (each s, each 3H, $Si(CH_3)_2$). **^{13}C{^{1}H}-NMR** (150.8 MHz, [D_8]-toluene, 298 K): δ = 149.5 (dm, $^{1}J_{CF}$ = 230 Hz, o-B(C_6F_5)$_3$), 138.9 (dm, $^{1}J_{CF}$ = 250 Hz, p-B(C_6F_5)$_3$), 137.3 (dm, $^{1}J_{CF}$ = 250 Hz, m-B(C_6F_5)$_3$), 130.4 (br, C2), 125.8 (br, ipso-B(C_6F_5)$_3$), 125.1, 123.7 (each Cp), 123.1 (C3), 121.9, 121.2, 109.9, 107.2 (2x), 106.6 (each Cp), 106.1, 102.7 (Cp-CSi), 52.0 (C1), 28.3 (br, C4), -5.7, -7.1 (each $Si(CH_3)_2$). **GCOSY** (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 298 K): $\delta^{1}H$ / $\delta^{1}H$ = 6.11 / 5.92, 5.55, 4.40; 6.00 / 5.78, 5.55, 4.40; 5.92 / 5.50, 4.40 (each Cp / Cp), 5.92 / 5.43, 1.86, 1.53 (2-H / 3-H, 1_{anti}-H, 1_{syn}-H), 5.78 / 5.50, 4.40; 5.55 / 4.40 (each Cp / Cp), 5.43 / 2.63, 2.31(3-H / 4'-H, 4-H), 2.63 / 2.31 (4'-H / 4-H), 1.86 / 1.53 (1_{anti}-H / 1_{syn}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 298 K): $\delta^{13}C$ / $\delta^{1}H$ = 130.4 / 5.92 (C2 / 2-H), 125.1 / 5.92, 123.7 / 6.00 (each Cp / Cp), 123.1 / 5.43 (C3 / 3-H), 121.9 / 6.11, 121.2 / 5.78, 109.9 / 4.40, 107.2 / 5.55, 106.6 / 4.40 (each Cp / Cp), 52.0 / 1.86, 1.53 (C1 / 1_{anti}-H, 1_{syn}-H), 28.3 / 2.63, 2.31 (C4 / 4'-H, 4-H), -5.7 / 0.24, -7.1 / -0.17 (each $Si(CH_3)_2$ / $Si(CH_3)_2$). **^{19}F-NMR** (564.3 MHz, [D_8]-toluene, 298 K): δ = -165.0

(broad, 6F, m-B(C_6F_5)$_3$), -161.1 (broad t, 3F, $^3J_{FF}$ = 21Hz , p-B(C_6F_5)$_3$). (The o-F resonanzes are not observed at 298 K due to the dynamic behaviour of the system)



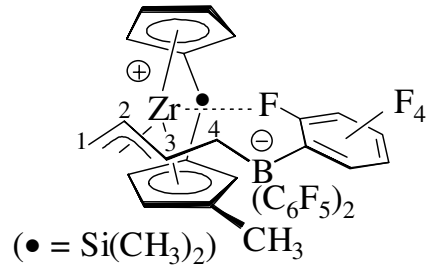
(• = $Si(CH_3)_2$)

General

^{19}F-NMR (563.7 MHz, [D_8]-toluene, 258 K): δ = -129.3 (broad, 6F, o-B(C_6F_5)$_3$), -160.6 (broad, 3F, p-B(C_6F_5)$_3$), -164.2 (broad, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D_6]-toluene, 258 K): δ = -14.4.

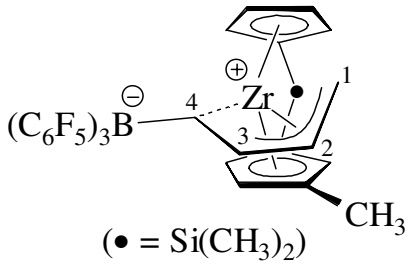
(*E*-18b) Main *E*-isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 258 K): δ^{1}H / δ^{1}H = 5.97 / 5.72, 5.51, 4.23; 5.72 / 5.51, 4.23; 5.51 / 4.23 (Cp / Cp), 5.58 / 5.17, 4.35; 5.17 / 4.35 (each MeCp / MeCp), 5.91 / 4.69, 1.61, 1.33 (2-H / 3-H, 1_{syn}-H, 1_{anti}-H), 4.69 / 2.50, 2.21 (3-H / 4'-H, 4-H), 2.50 / 2.21 (4'-H / 4-H), 1.61 / 1.33 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 258 K): δ^{13}C / δ^{1}H = 132.5 / 5.91 (C2 / 2-H), 123.5 / 5.97, 120.4 / 5.72, 106.5 / 4.23, 105.3 / 5.51 (each Cp / Cp), 121.3 / 5.58, 107.7 / 4.35, 106.0 / 5.17 (each MeCp / MeCp), 120.5 / 4.69 (C3 / 3-H), 53.5 / 1.61, 1.33 (C1 / 1_{syn}-H, 1_{anti}-H), 14.5 / 1.57 (MeCp-*C*H_3 / MeCp-C*H*$_3$), -6.4 / 0.17, -8.1 / -0.26 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 258 K): δ^{13}C / δ^{1}H = 136.3, 121.3, 107.7 / 1.57 (quart. MeCp, MeCp, MeCp / MeCp-C*H*$_3$), 104.0, 100.9, -6.4 / 0.17 (quart. MeCp-CSi, quart. Cp-CSi, Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$), 104.0, 100.9, -8.1 / -0.26 (quart. MeCp-CSi, quart. Cp-CSi, Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 258 K): δ_{irr} / δ_{res} = 2.21 / 5.91, 4.69, 2.50, 1.61, 1.33 (4-H / 2-H, 3-H, 4'-H, 1_{syn}-H, 1_{anti}-H); 5.58 / 5.17, 4.35 (MeCp); 5.97 / 5.72, 5.51, 4.23 (Cp).



(*E*-18b) Second *E*-isomer

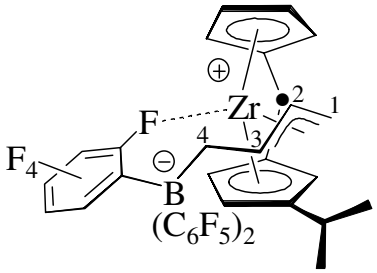
GCOSY (599.9 M,Hz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^1H / δ^1H = 6.01 / 5.78, 5.46, 4.41; 5.78 / 5.46, 4.41; 5.46 / 4.41 (each Cp / Cp), 5.64 / 5.51, 3.89; 5.51 / 3.89 (each MeCp / MeCp), 5.70 / 5.38, 1.67, 1.48 (2-H / 3-H, 1_{anti}-H, 1_{syn}-H), 5.38 / 2.51, 2.18 (3-H / 4'-H, 4-H), 2.51 / 2.18 (4'-H / 4-H), 1.67 / 1.48 (1_{anti}-H / 1_{syn}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^{13}C / δ^1H = 129.1 / 5.70 (C2 / 2-H), 124.0 / 5.78, 121.9 / 6.01, 110.2 / 4.41, 105.8 / 5.46 (each Cp / Cp), 121.8 / 5.64, 109.1 / 3.89, 108.1 / 5.51 (each MeCp / MeCp), 114.4 / 5.38 (C3 / 3-H), 51.4 / 1.67, 1.48 (C1 / 1_{anti}-H, 1_{syn}-H), 13.3 / 1.72 (MeCp-*C*H$_3$ / MeCp-C*H*$_3$), -6.4 / 0.17 , -7.5 / -0.23 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^{13}C / δ^1H = 136.5, 121.8, 105.8 / 1.72 (quart. MeCp, MeCp, MeCp / MeCp-C*H*$_3$), 105.6, 101.9, -6.4 / 0.22 (quart. MeCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$), 105.6, 101.9 -7.5 / -0.23 (quart. MeCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D$_8$]-toluene, 258 K): δ_{irr} / δ_{res} = 2.18 / 5.70, 5.38, 2.51, 1.67, 1.48 (4-H / 2-H, 3-H, 4'-H, 1_{anti}-H, 1_{syn}-H); 5.64 / 5.51, 3.89 (MeCp); 6.01 / 5.78, 5.46, 4.41 (Cp).



(*Z*-18b) *Z*-isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^1H / δ^1H = 5.82 / 4.74, 4.55; 4.74 / 4.55 (each MeCp / MeCp), 5.38 / 5.29, 4.91, 4.23; 5.29 / 4.91, 4.23; 4.91 / 4.23 (each Cp /

Cp), 5.16 / 4.49, 2.62, 0.27 (2-H / 3-H, 1_{anti}-H, 1_{syn}-H), 4.49 / -0.43, -1.83 (3-H / 4'-H, 4-H), 2.62 / 0.27 (1_{anti}-H / 1_{syn}-H), -0.43 / -1.83 (4'-H / 4-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 258 K): δ^{13}C / δ^{1}H = 131.4 / 5.16 (C2 / 2-H), 117.9 / 4.49 (C3 / 3-H), 117.6 / 4.55, 114.1 / 4.74, 103.2 / 5.82 (each MeCp / MeCp), 114.5 / 5.38, 113.2 / 4.91, 112.5 / 4.23, 109.2 / 5.29 (each Cp / Cp), 55.0 / 2.62, 0.27 (C1 / 1_{anti}-H, 1_{syn}-H), 14.5 / 1.53 (MeCp-*C*H_3 / MeCp-C*H*$_3$), -5.8 / 0.08 , -8.1 / 0.11 (each Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 258 K): δ^{13}C / δ^{1}H = 136.6, 114.1, 103.2 / 1.53 (quart. MeCp, MeCp, MeCp / MeCp-C*H*$_3$), 101.5, 99.6, -5.8 / 0.11 (quart. MeCp-CSi, quart. Cp-CSi, Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$), 101.5, 99.6 -8.1 / 0.08 (quart. MeCp-CSi, quart. Cp-CSi, Si(*C*H_3)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 258 K): δ_{irr} / δ_{res} = 2.62 / 5.16, 4.49, 0.27, -0.43, -1.83 (1_{anti}-H / 2-H, 3-H, 1_{syn}-H, 4'-H, 4-H); 5.82 / 4.74, 4.55 (MeCp); 5.38 / 5.29, 4.91, 4.23 (Cp). **^{19}F-NMR** (563.7 MHz, [D_8]-toluene, 268 K): δ = -136.7 (broad, 6F, o-B(C$_6$*F*$_5$)$_3$), -159.6 (broad, 3F, p-B(C$_6$*F*$_5$)$_3$), -164.1 (broad, 6F, m-B(C$_6$*F*$_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D_6]-toluene, 268 K): δ = -14.0. **IR** (KBr): $\tilde{\nu}$ = 2983 (m), 2882 (w), 1644 (s), 1524 (vs), 1484 (vs), 1370 (m), 1290 (s), 1089 (vs), 975 (vs), 801 (s) cm^{-1}.

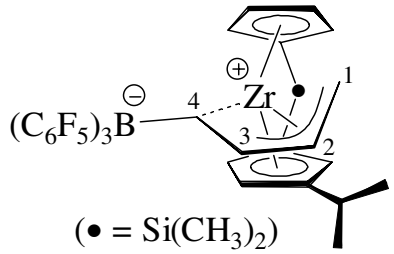


(• = Si(CH$_3$)$_2$)

(*E*-18d) *E*-isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 298 K): δ^{1}H / δ^{1}H = 6.04 / 5.82, 5.48, 4.54; 5.82 / 5.48, 5.48 / 4.54 (each Cp / Cp), 5.85 / 5.43, 4.57; 5.43 / 4.57 (each iPrCp / iPrCp), 5.77 / 5.48, 1.70, 1.60 (2-H / 3-H, 1_{syn}-H, 1_{anti}-H), 5.48 / 2.49, 2.22 (3-H / 4'-H, 4-H), 2.49 / 2.22 (4'-H / 4-H), 2.45 / 1.12, 0.97 (iPr-C*H* / iPr-C*H*$_3$), 1.70 / 1.60 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 298 K): δ^{13}C / δ^{1}H = 127.1 / 5.77 (C2 / 2-H), 123.9 / 5.82, 122.9 / 6.04, 110.5 / 4.54, 105.7 / 5.48 (Cp / Cp), 118.1 / 5.85, 107.8 / 4.57, 103.4 / 5.43 (iPrCp / iPrCp), 110.5 / 5.48 (C3 / 3-H), 51.3 / 1.70, 1.60 (C1 / 1_{syn}-H, 1_{anti}-H), 28.0 / 2.45 (iPr-C*H* / iPrCp-C*H*), 24.2 / 0.97, 22.1 / 1.12 (each iPr-*C*H$_3$ / iPr-C*H*$_3$), -5.4 / 0.22, -7.4 / -0.21

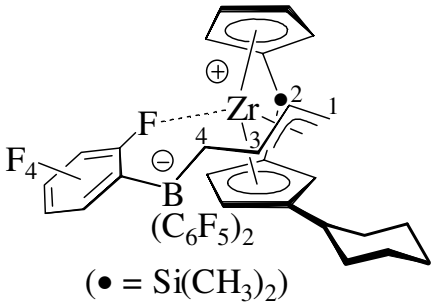
(each Si(CH_3)$_2$ / Si(CH_3)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 298 K): δ^{13}C / δ^{1}H = 149.0, 24.2 / 0.97 (quart. iPrCp , iPr-CH_3 / iPr-CH_3), 149.0, 22.1 / 1.12 (quart. iPrCp , iPr-CH_3 / iPr-CH_3), 105.1, 101.0, -5.4 / 0.22 (quart. iPrCp-CSi, quart. Cp-CSi, Si(CH_3)$_2$ / Si(CH_3)$_2$), 105.1, 101.0, -7.3 / -0.21 (quart. iPrCp-CSi, quart. Cp-CSi, Si(CH_3)$_2$ / Si(CH_3)$_2$). **1D-TOCSY** (599.9 MHz, [D$_8$]-toluene, 298 K): δ_{irr} / δ_{res} = 2.49 / 5.77, 5.48, 2.22, 1.70, 1.60 (4'-H / 2-H, 3-H, 4-H, 1$_{syn}$-H, 1$_{anti}$-H); 5.85 / 5.43, 4.57 (iPrCp); 6.04 / 5.82, 5.48, 4.54 (Cp). **^{19}F-NMR** (563.7 MHz, [D$_8$]-toluene, 298 K): δ = -129.0 (broad, 6F, o-B(C_6F_5)$_3$), -160.2 (broad, 3F, p-B(C_6F_5)$_3$), -164.3 (broad, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_6$]-toluene, 298 K): δ = -13.9.



(*Z*-18d) *Z*-isomer

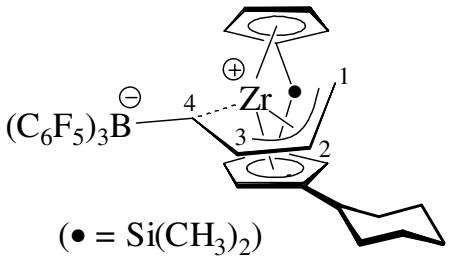
GCOSY (599.9 M,Hz / 599.9 MHz, [D$_8$]-toluene, 298 K): δ^{1}H / δ^{1}H = 6.10 / 5.80, 5.51, 4.16; 5.80 / 5.51, 4.16; 5.51 / 4.16 (each Cp / Cp), 5.99 / 5.51, 4.23; 5.51 / 4.23 (each iPrCp / iPrCp), 5.24 / 4.55, 2.71, 1.15 (2-H / 3-H, 1$_{syn}$-H, 1$_{anti}$-H), 4.55 / -0.30, -1.90 (3-H / 4'-H, 4-H), 2.71 / 1.15 (1$_{syn}$-H / 1$_{anti}$-H), 2.21 / 0.94, 2.21 / 0.73 (each iPr-C*H* / iPr-CH_3), -0.30 / -1.90 (4'-H / 4-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 298 K): δ^{13}C / δ^{1}H = 128.5 / 5.24 (C2 / 2-H), 117.6 / 5.80, 113.6 / 6.10, 110.5 / 5.51, 105.4 / 4.16 (each Cp / Cp), 116.3 / 5.99, 113.5 / 5.51, 104.2 / 4.23 (each iPrCp / iPrCp), 110.1 / 4.55 (C3 / 3-H), 55.2 / 2.71, 1.15 (C1 / 1$_{syn}$-H, 1$_{anti}$-H), 29.6 / 2.21 (iPr-*C*H / iPrCp-C*H*), 22.8 / 0.94, 22.1 / 0.73 (each iPr-CH_3 / iPr-CH_3) -6.3 / 0.31, -6.5 / -0.08 (each Si(CH_3)$_2$ / Si(CH_3)$_2$. **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 298 K): δ^{13}C / δ^{1}H = 149.4 / 0.94 (quart. iPrCp / iPr-CH_3), 149.4 / 0.73 (quart. iPrCp / iPr-CH_3), 105.7, 103.9, -6.3 / 0.31 (quart. iPrCp-CSi, quart. Cp-CSi, Si(CH_3)$_2$ / Si(CH_3)$_2$), 105.7, 103.9, -6.5 / -0.08 (quart. iPrCp-CSi, quart. Cp-CSi, Si(CH_3)$_2$ / Si(CH_3)$_2$). **1D-TOCSY** (599.9 MHz, [D$_8$]-toluene, 298 K): δ_{irr} / δ_{res} = 4.55 / 5.24, 2.71, 1.15, -0.30, -1.90 (3-H / 2-H, 1$_{syn}$-H, 1$_{anti}$-H, 4'-H, 4-H); 5.99 / 5.51, 4.23 (iPrCp); 6.10 / 5.80, 5.51, 4.16 (Cp). **^{19}F-NMR** (563.7 MHz, [D$_8$]-toluene, 298 K): δ = -134.7 (broad, 6F, o-B(C_6F_5)$_3$), -159.8

(broad, 3F, p-B(C_6F_5)$_3$), -164.4 (broad, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D_8]-toluene, 298 K): δ = -13.8. **IR** (KBr): $\tilde{\nu}$ = 2982 (m), 2926 (w), 1651 (vs), 1544 (vs), 1470 (vs), 1397 (s), 1270 (s), 1102 (vs), 982 (vs), 814 (s) cm^{-1}.



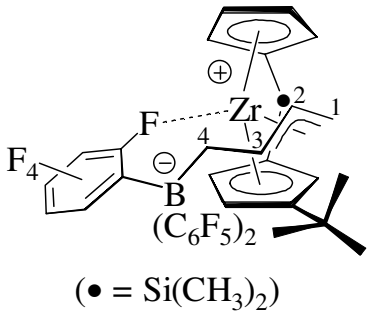
(*E*-18c) *E*-isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D_8]-toluene, 268 K): δ^1H / δ^1H = 6.04 / 5.79, 5.46, 4.46; 5.79 / 5.46, 4.46; 5.46 / 4.46 (each Cp / Cp), 5.82 / 5.43, 4.52; 5.43 / 4.52 (each cyCp / cyCp), 5.77 / 5.48, 1.67, 1.59 (2-H / 3-H, 1_{syn}-H, 1_{anti}-H), 5.48 / 2.54, 2.22 (3-H / 4'-H, 4-H), 2.54 / 2.22 (4'-H / 4-H), 1.67 / 1.59 (1_{syn}-H / 1_{anti}-H). Die Cross-Peaks für die cyclohexylgruppe können nicht eindeutig zugewiesen werden. **GHSQC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): δ^{13}C / δ^1H = 131.3 / 5.77 (C2 / 2-H), 123.8 / 5.79, 121.3 / 6.04, 109.9 / 4.46, 102.8 / 5.46 (each Cp / Cp), 120.4 / 5.48 (C3 / 3-H), 118.0 / 5.82, 107.3 / 4.52, 105.5 / 5.43, (each cyCp / cyCp), 58.4 / 3.12 (cy-*C*H / cy-C*H*), 51.0 / 1.67, 1.59 (C1 / 1_{syn}-H, 1_{anti}-H), 32.1, 25.8, 25.2, 23.6 / 1.90-0.80 (cy-*C*H$_2$ / cy-C*H*$_2$), -3.5 / -0.19, -4.3 / 0.21 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D_8]-toluene, 268 K): δ^{13}C / δ^1H = 102.4, 100.4, -4.3 / 0.21 (quart. cyCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$), 102.4, 100.4, -3.5 / -0.19 (quart. cyCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D_8]-toluene, 268 K): δ_{irr} / δ_{res} = 2.22 / 5.77, 5.48, 2.54, 1.67, 1.59 (4-H / 2-H, 3-H, 4'-H, 1_{syn}-H, 1_{anti}-H); 5.82 / 5.43, 4.52 (cyCp); 6.04 / 5.79, 5.46, 4.46 (Cp). **^{19}F-NMR** (563.7 MHz, [D_8]-toluene, 268 K): δ = -129.3 (broad, 6F, o-B(C_6F_5)$_3$), -160.7 (broad, 3F, p-B(C_6F_5)$_3$), -164.8 (broad, 6F, m-B(C_6F_5)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D_8]-toluene, 268 K): δ = -14.3.



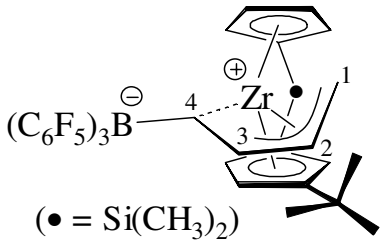
(*Z*-18c) *Z*-isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D$_8$]-toluene, 268 K): δ^{1}H / δ^{1}H = 5.90 / 5.02, 4.95; 5.02 / 4.95 (each cyCp / cyCp), 5.37 / 5.31, 4.95, 4.41; 5.31 / 4.95, 4.41; 4.95 / 4.41 (each Cp / Cp), 5.22 / 5.06, 2.66, 0.44 (2-H / 3-H, 1_{syn}-H, 1_{anti}-H), 5.06 / -0.36, -1.79 (3-H / 4'-H, 4-H), 2.66 / 0.44 (1_{syn}-H / 1_{anti}-H), -0.36 / -1.79 (4'-H / 4-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 268 K): δ^{13}C / δ^{1}H = 127.2 / 5.22 (C2 / 2-H), 121.2 / 4.95 (Cp-*C*H / Cp-C*H*), 119.3 / 5.90 (cycloh.Cp-*C*H / cycloh.Cp-C*H*), 115.3 / 5.37 (Cp-*C*H / Cp-C*H*), 112.3 / 5.06 (C3 / 3-H), 110.8 / 5.02 (cycloh.Cp-*C*H / cycloh.Cp-C*H*), 109.0 / 4.95 (cycloh.Cp-*C*H / cycloh.Cp-C*H*), 105.5 / 4.41 (Cp-*C*H / Cp-C*H*), 103.9 / 5.31 (Cp-*C*H / Cp-C*H*), 58.3 / 3.24 (cyclohexyl-*C*H / cyclohexyl-C*H*), 55.2 / 2.66 (C1 / 1_{syn}-H), 55.2 / 0.44 (C1 / 1_{anti}-H), 33.1, 27.8, 27.6, 24.9, 23.6 / 1.90-0.80 (cyclohexyl-*C*H$_2$ / cyclohexyl-C*H*$_2$), -5.1 / 0.33, -6.3 / -0.03 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 268 K): δ^{13}C / δ^{1}H = 102.7, 99.8, -5.1 / 0.33 (quart. cyCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$), 102.7, 99.8, -6.3 / -0.03 (quart. cyCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D$_8$]-toluene, 268 K): δ_{irr} / δ_{res} = 2.66 / 5.22, 5.06, 0.44, -0.36, -1.79 (1_{syn}-H / 2-H, 3-H, 1_{anti}-H, 4'-H, 4-H); 5.90 / 5.02, 4.95 (cyCp); 5.37 / 5.31, 4.95, 4.41 (Cp). **^{19}F-NMR** (563.7 MHz, [D$_8$]-toluene, 268 K): δ = -132.8 (broad, 6F, o-B(C$_6$*F*$_5$)$_3$), -159.7 (broad, 3F, p-B(C$_6$*F*$_5$)$_3$), -164.2 (broad, 6F, m-B(C$_6$*F*$_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_8$]-toluene, 268 K): δ = -14.3. **IR** (KBr): $\tilde{\nu}$ = 2960 (m), 2851 (w), 1648 (vs), 1521 (vs), 1454 (vs), 1371 (m), 1277 (s), 1227 (w), 1171 (w), 1082 (vs), 988 (s), 816 (vs) cm^{-1}.



(*E*-18e) *E*-isomer

GCOSY (599.9 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^1H / δ^1H = 6.06 / 5.73, 5.38, 4.36; 5.73 / 5.38, 4.36; 5.38 / 4.36 (each Cp / Cp), 5.73 / 5.45, 4.46; 5.45 / 4.46 (each tBuCp / tBuCp), 5.78 / 5.32, 1.59, 1.49 (2-H / 3-H, 1_{syn}-H, 1_{anti}-H), 5.32 / 2.66, 2.44 (3-H / 4'-H, 4-H), 2.66 / 2.44 (4'-H / 4-H), 1.59 / 1.49 (1_{syn}-H / 1_{anti}-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^{13}C / δ^1H = 132.2 / 5.78 (C2 / 2-H), 124.2 / 5.62 (C3 / 3-H), 124.2 / 5.73, 107.8 / 4.46, 100.9 / 5.45 (each tBuCp / tBuCp), 122.6 / 6.06, 119.2 / 5.73, 109.7 / 4.38, 104.9 / 5.38 (each Cp / Cp), 51.1 / 1.59, 1.49 (C1 / 1_{syn}-H, 1_{anti}-H), 30.5 / 1.02 (tBu-*C*H$_3$ / tBu-C*H*$_3$), -5.9 / 0.16, -7.4 / -0.25 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^{13}C / δ^1H = 153.2, 29.9 / 1.02 (quart. tBuCp, quart. *C*(CH$_3$)$_3$ / tBu-CH$_3$), 103.2, 99.6, -5.9 / 0.16 (quart. tBuCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$), 103.2, 99.6, -7.4 / -0.25 (quart. tBuCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D$_8$]-toluene, 258 K): δ_{irr} / δ_{res} = 5.78 / 5.62, 2.66, 2.44, 1.59, 1.49 (2-H / 3-H, 4'-H, 4-H, 1_{syn}-H, 1_{anti}-H); 5.73 / 5.45, 4.46 (tBuCp); 6.06 / 5.73, 5.38, 4.36 (Cp). **^{19}F-NMR** (563.7 MHz, [D$_8$]-toluene, 268 K): δ = -130.3 (broad, 6F, o-B(C$_6$*F*$_5$)$_3$), -161.2 (broad, 3F, p-B(C$_6$*F*$_5$)$_3$), -164.8 (broad, 6F, m-B(C$_6$*F*$_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_8$]-toluene, 268 K): δ = -14.3.



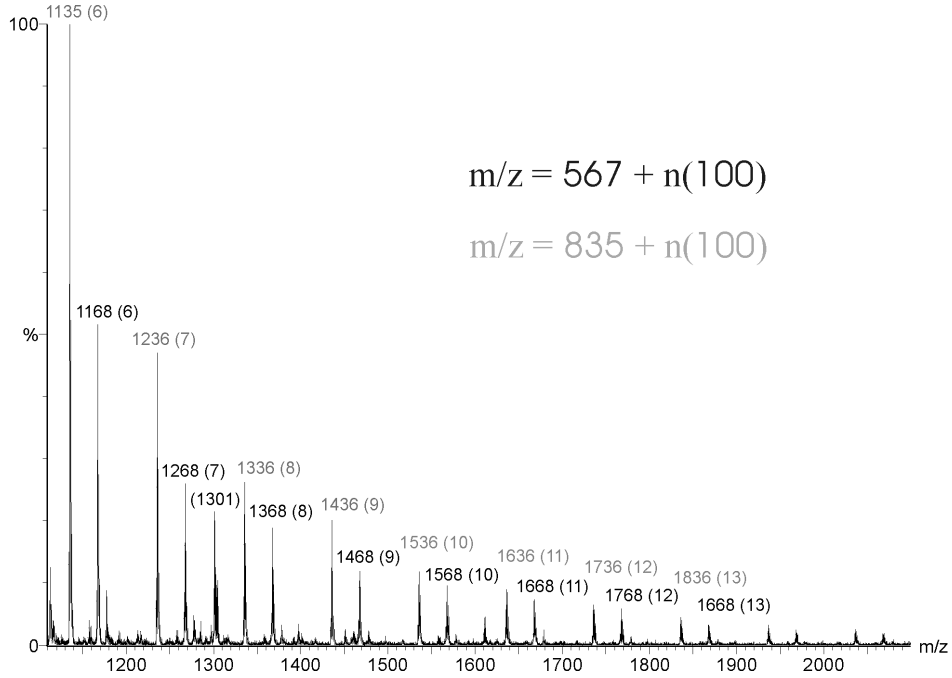
(*Z*-18e) *Z*-isomer

GCOSY (599.9 M,Hz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^1H / δ^1H = 5.36 / 5.31, 4.86, 4.39; 5.31 / 4.86, 4.39; 4.86 / 4.39 (each Cp / Cp), 5.95 / 5.08, 4.95; 5.08 / 4.95 (each tBuCp / tBuCp), 5.08 / 4.54, 2.54, 0.95 (2-H / 3-H, 1_{syn}-H, 1_{anti}-H), 4.54 / -0.39, -1.74 (3-H / 4'-H, 4-H), 2.54 / 0.95 (1_{syn}-H / 1_{anti}-H), -0.39 / -1.74 (4'-H / 4-H). **GHSQC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^{13}C / δ^1H = 133.9 / 5.08 (C2 / 2-H), 115.2 / 5.36, 114.5 / 4.39, 112.0 / 4.86, 108.1 / 5.31 (each Cp / Cp), 110.6 / 4.54 (C3 / 3-H), 109.2 / 5.95, 108.1 / 5.08, 98.3 / 4.95 (tBuCp-*C*H / tBuCp-C*H*), 55.8 / 2.54, 0.95 (C1 / 1_{syn}-H, 1_{anti}-H), 34.1 / 0.83 (tBu-

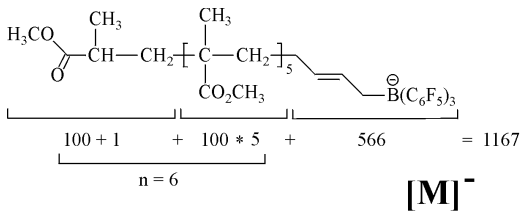
*C*H$_3$/ tBu-C*H*$_3$), -4.7 / 0.14, -7.8 / 0.13 (each Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **GHMBC** (150.8 MHz / 599.9 MHz, [D$_8$]-toluene, 258 K): δ^{13}C / δ^{1}H = 156.3, 33.4 / 0.83 (quart. tBuCp, quart. *C*(CH$_3$)$_3$ / tBu-CH$_3$), 110.0, 99.3, -4.7 / 0.14 (quart. tBuCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$), 110.0, 99.3, -7.8 / 0.13 (quart. tBuCp-CSi, quart. Cp-CSi, Si(*C*H$_3$)$_2$ / Si(C*H*$_3$)$_2$). **1D-TOCSY** (599.9 MHz, [D$_8$]-toluene, 258 K): δ_{irr} / δ_{res} = 2.54 / 5.08, 4.54, 0.95, -0.39, -1.74 (1_{syn}-H / 2-H, 3-H, 1_{anti}-H, 4'-H, 4-H); 5.95 / 5.08, 4.95 (tBuCp); 5.36 / 5.31, 4.86, 4.39 (Cp). **^{19}F-NMR** (563.7 MHz, [D$_8$]-toluene, 268 K): δ = -132.8 (broad, 6F, o-B(C$_6$*F*$_5$)$_3$), -160.3 (broad, 3F, p-B(C$_6$*F*$_5$)$_3$), -164.3 (broad, 6F, m-B(C$_6$*F*$_5$)$_3$). **^{11}B{^{1}H}-NMR** (64.2 MHz, [D$_8$]-toluene, 268 K): δ = -14.0. **IR** (KBr): $\tilde{\nu}$ = 2968 (m), 2879 (w), 1654 (vs), 1526 (vs), 1471 (vs), 1371 (s), 1294 (s), 1265 (vs), 1177 (s), 977 (vs), 827 (vs) cm^{-1}.

ESI MS spectra

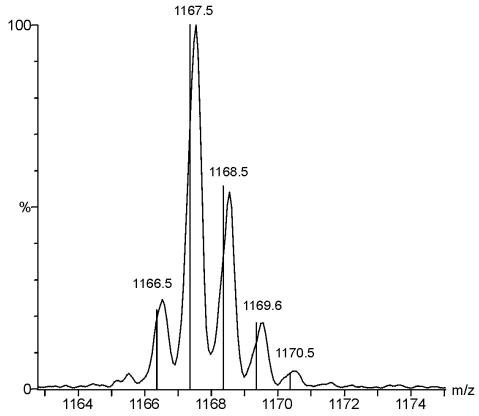
Reaction of **16** with MMA; reaction time 15 minutes at 25°C (1301: *Coulomb* dimer).

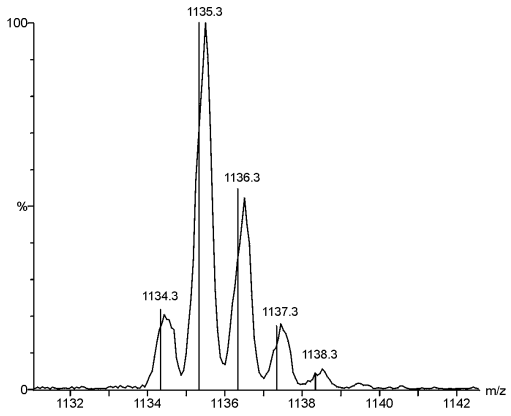


Expanded peaks:

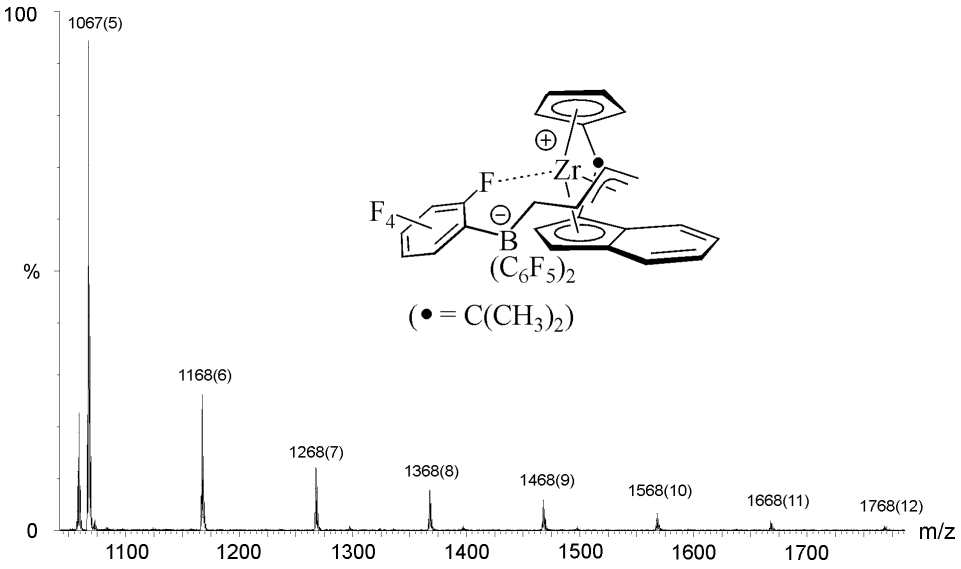


[M]⁻ **[M-(HOCH₃)]⁻**

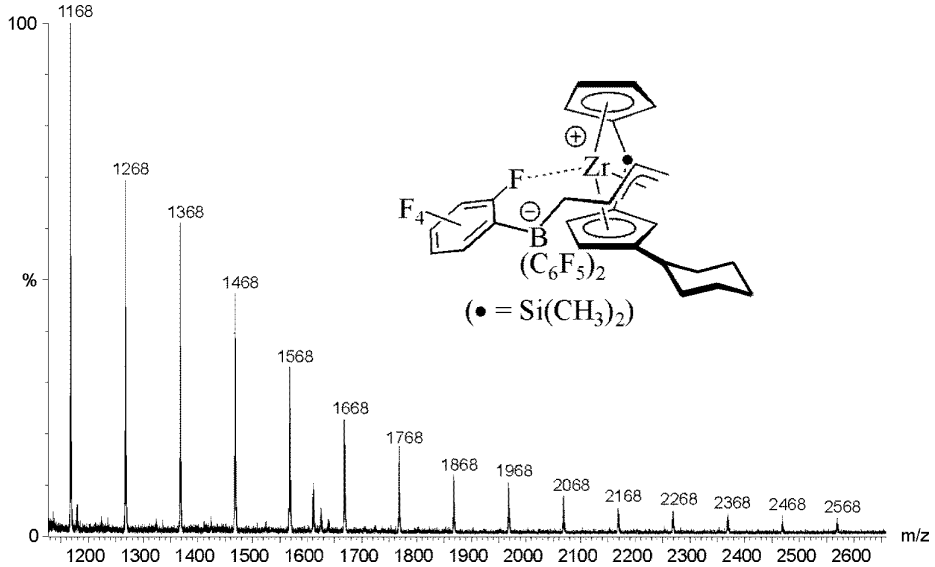




Reaction of **16** with MMA; reaction time 5 minutes at -20°C.



Reaction of **18c** with MMA; reaction time 20 minutes at 25°C.



Comp.	m_{cat} [mg]	n_{cat} [µmol]	activator	m_{act} [mg]	n_{act} [µmol]	yield %	M_n	M_w / M_n	% mm	% mr	% rr
3	18	57	$B(C_6F_5)_3$	29	57	97	44300	1.36	76	12	13
3	18	57	$B(C_6F_5)_3$	29	57	92	49600	1.39	76	14	12
9a	17	56	$B(C_6F_5)_3$	28	56	42	68600	1.81	16	24	60
9b	20	62	$B(C_6F_5)_3$	32	62	39	51600	2.17	41	27	32
9b	18	56	$B(C_6F_5)_3$	28	56	55	n. b.	n. b.	43	23	34
9d	20	57	$B(C_6F_5)_3$	29	57	48	36100	1.88	75	12	13
9d	20	57	$B(C_6F_5)_3$	29	57	41	34400	1.63	74	13	13
9c	22	56	$B(C_6F_5)_3$	28	56	36	27400	2.32	64	12	24
9e	21	58	$B(C_6F_5)_3$	30	58	53	22700	1.19	83	10	7
11e	20	55	$(C_4H_5N)B(C_6F_5)_3$	32	55	0	-	-	-	-	-
13e	20	55	$(C_4H_5N)B(C_6F_5)_3$	32	55	0	-	-	-	-	-

Results of the polymerization reactions of MMA with the methyl zirconocene cation catalysts **3**, **9**, and **13**. Yield (%) per hour. M_n in g mol^{-1}. M_w / M_n = D (polydispersity). The mm, mr, and rr triads were analysed by ^{1}H-NMR experiments.

comp.	m_{cat} [mg]	n_{cat} [µmol]	activator	m_{act} [mg]	n_{act} [µmol]	yield %	M_n	M_w / M_n	% mm	% mr	% rr
16 *	24	66	$B(C_6F_5)_3$	34	66	94	62500	1.47	81	11	8
16	24	66	$B(C_6F_5)_3$	34	66	91	65300	1.14	85	9	6
16	24	66	$B(C_6F_5)_3$	34	66	89	54000	1.21	n. o.	n. o.	n. o.
18a *	22	66	$B(C_6F_5)_3$	34	66	27	34000	1.70	16	21	65
18b *	23	66	$B(C_6F_5)_3$	34	66	19	13100§	2.43§	34§	27§	39§
18b	23	66	$B(C_6F_5)_3$	34	66	13	36300	1.18	21	31	48
18b	23	66	$B(C_6F_5)_3$	34	66	12	36100	1.26	n. o.	n. o.	n. o.
18d *	25	66	$B(C_6F_5)_3$	34	66	33	19000	1.67	48§	23§	29§
18d	25	66	$B(C_6F_5)_3$	34	66	26	33200	1.22	n. o. §	n. o. §	n. o. §
18d	25	66	$B(C_6F_5)_3$	34	66	21	34000	1.23	n. o. §	n. o. §	n. o. §
18c *	27	66	$B(C_6F_5)_3$	34	66	24	18600§	1.46	32	30	38
18c	27	66	$B(C_6F_5)_3$	34	66	19	37700	1.14	35	24	41
18e *	26	66	$B(C_6F_5)_3$	34	66	31§	14800§	1.32	65	18	17
18e	26	66	$B(C_6F_5)_3$	34	66	22	21900	1.18	67	16	17
18e	26	66	$B(C_6F_5)_3$	34	66	17	18400	1.20	n. o.	n. o.	n. o.

Results of the polymerization reactions of MMA with the butadiene zirconocene betaine catalysts **16** and **18**. Yield (%) per hour. M_n in g mol^{-1}. M_w / M_n = D (polydispersity). The mm, mr, and rr triads were analysed by ^{1}H-NMR experiments. * Data from an early series of experiments. § Data not used for the calculation of the averaged values.

comp.	time (min)	m_{cat} [mg]	n_{cat} [µmol]	activator	m_{act} [mg]	n_{act} [µmol]	yield %	Mn	Mw / Mn	% mm	% mr	% rr
18d #	60	25	67	$B(C_6F_5)_3$	34	67	29	22400	1.1	53	19	28
18d #	60	25	67	$B(C_6F_5)_3$	34	67	29.5	23100	1.1	58	17	25
18d	10	25	67	$B(C_6F_5)_3$	34	67	3	41 #	1.2	32	27	41
18d	20	25	67	$B(C_6F_5)_3$	34	67	6	9350	1.1	28	27	45
18d	30	25	67	$B(C_6F_5)_3$	34	67	12	11800	1.1	38	24	38
18d	40	25	67	$B(C_6F_5)_3$	34	67	24	17850	1.1	37	24	39
18d	50	25	67	$B(C_6F_5)_3$	34	67	28	18750	1.1	41	22	37
18d	60	25	67	$B(C_6F_5)_3$	34	67	35	24100	1.1	30	26	44
18d #	10	25	67	$B(C_6F_5)_3$	34	67	3.2	5800	1.1	51	20	29
18d	20	25	67	$B(C_6F_5)_3$	34	67	5.9	8600	1.1	42	22	36
18d #	30	25	67	$B(C_6F_5)_3$	34	67	8.1	10950	1.2	59	16	25
18d	40	25	67	$B(C_6F_5)_3$	34	67	11.3	13350	1.1	39	23	38
18d	50	25	67	$B(C_6F_5)_3$	34	67	16.1	15950	1.1	35	24	41
18d	60	25	67	$B(C_6F_5)_3$	34	67	24.2	20400	1.1	30	25	45
18d	120	25	67	$B(C_6F_5)_3$	34	67	46.8	32700	1.1	38	22	40

Results of the polymerization reactions of MMA with the butadiene zirconocene betaine catalysts **18d**. Yield (%) per hour. M_n in g mol^{-1}. M_w / M_n = D (polydispersity). The mm, mr, and rr triads were analysed by ^{1}H-NMR experiments. # Data not used for the calculation of the average values.

comp.	time (min)	m_{cat} [mg]	n_{cat} [µmol]	activator	m_{act} [mg]	n_{act} [µmol]	yield %	Mn	Mw / Mn	% mm	% mr	% rr
18d	10	20	53.5	$B(C_6F_5)_3$	27	53.5	3.2	6700	1.1	45	22	33
18d	20	20	53.5	$B(C_6F_5)_3$	27	53.5	4.8	8900	1.1	40	23	37
18d	30	20	53.5	$B(C_6F_5)_3$	27	53.5	7.5	10950	1.2	65 #	17 #	18 #
18d	40	20	53.5	$B(C_6F_5)_3$	27	53.5	11.8	13800	1.1	43	22	35
18d	50	20	53.5	$B(C_6F_5)_3$	27	53.5	15.6	17600	1.1	56 #	22 #	22 #
18d	60	20	53.5	$B(C_6F_5)_3$	27	53.5	18.3	19600	1.1	42	22	36
18d	120	20	53.5	$B(C_6F_5)_3$	27	53.5	33.3	30400	1.1	39	23	38

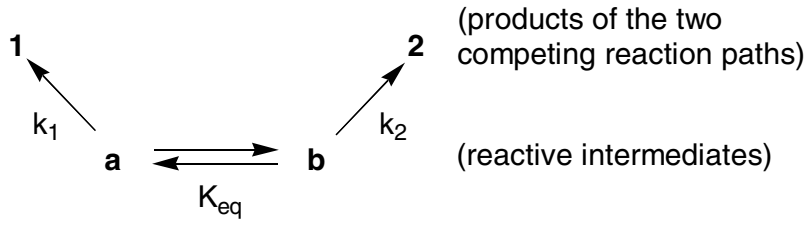
Results of the polymerization reactions of MMA with the butadiene zirconocene betaine catalysts **18d**. Yield (%) per hour. M_n in g mol^{-1}. M_w / M_n = D (polydispersity). The mm, mr, and rr triads were analysed by ^{1}H-NMR experiments. # Data not used for the calculation of the average values.

comp.	time (min)	m_{cat} [mg]	n_{cat} [µmol]	activator	m_{act} [mg]	n_{act} [µmol]	yield %	Mn	Mw / Mn	% mm	% mr	% rr
9d	60	20	57	$B(C_6F_5)_3$	29	57	33	22700	1.2	88	7	5
9d	60	20	57	$B(C_6F_5)_3$	29	57	35	28000	1.1	90	6	4
9d	10	20	57	$B(C_6F_5)_3$	29	57	1	4500	1.1	57 [#]	19 [#]	24 [#]
9d	20	20	57	$B(C_6F_5)_3$	29	57	3	8900	1.1	85	9	6
9d	30	20	57	$B(C_6F_5)_3$	29	57	11	14150	1.1	90	6	4
9d	40	20	57	$B(C_6F_5)_3$	29	57	17	19500	1.1	92	6	2
9d	50	20	57	$B(C_6F_5)_3$	29	57	32	25600	1.1	90	6	4
9d	60	20	57	$B(C_6F_5)_3$	29	57	35	31000	1.1	90	6	4
9d	10	20	57	$B(C_6F_5)_3$	29	57	3.2	5700	1.2	84	9	7
9d	20	20	57	$B(C_6F_5)_3$	29	57	10.7	10800	1.1	84	9	7
9d	30	20	57	$B(C_6F_5)_3$	29	57	21.5	15200	1.1	88	7	5
9d	40	20	57	$B(C_6F_5)_3$	29	57	30.1	18600	1.1	88	7	5
9d	50	20	57	$B(C_6F_5)_3$	29	57	35.5	23700	1.1	90	6	4
9d	60	20	57	$B(C_6F_5)_3$	29	57	47.3	27100	1.1	88	8	4
9d	120	20	57	$B(C_6F_5)_3$	34	67	69.9	36850	1.1	91	6	3

Results of the polymerization reactions of MMA with the butadiene zirconocene betaine catalysts **18d**. Yield (%) per hour. M_n in g mol^{-1}. M_w / M_n = D (polydispersity). The mm, mr, and rr triads were analysed by ^{1}H-NMR experiments. [#] Data not used for the calculation of the average values.

Curtin-Hammett Situation

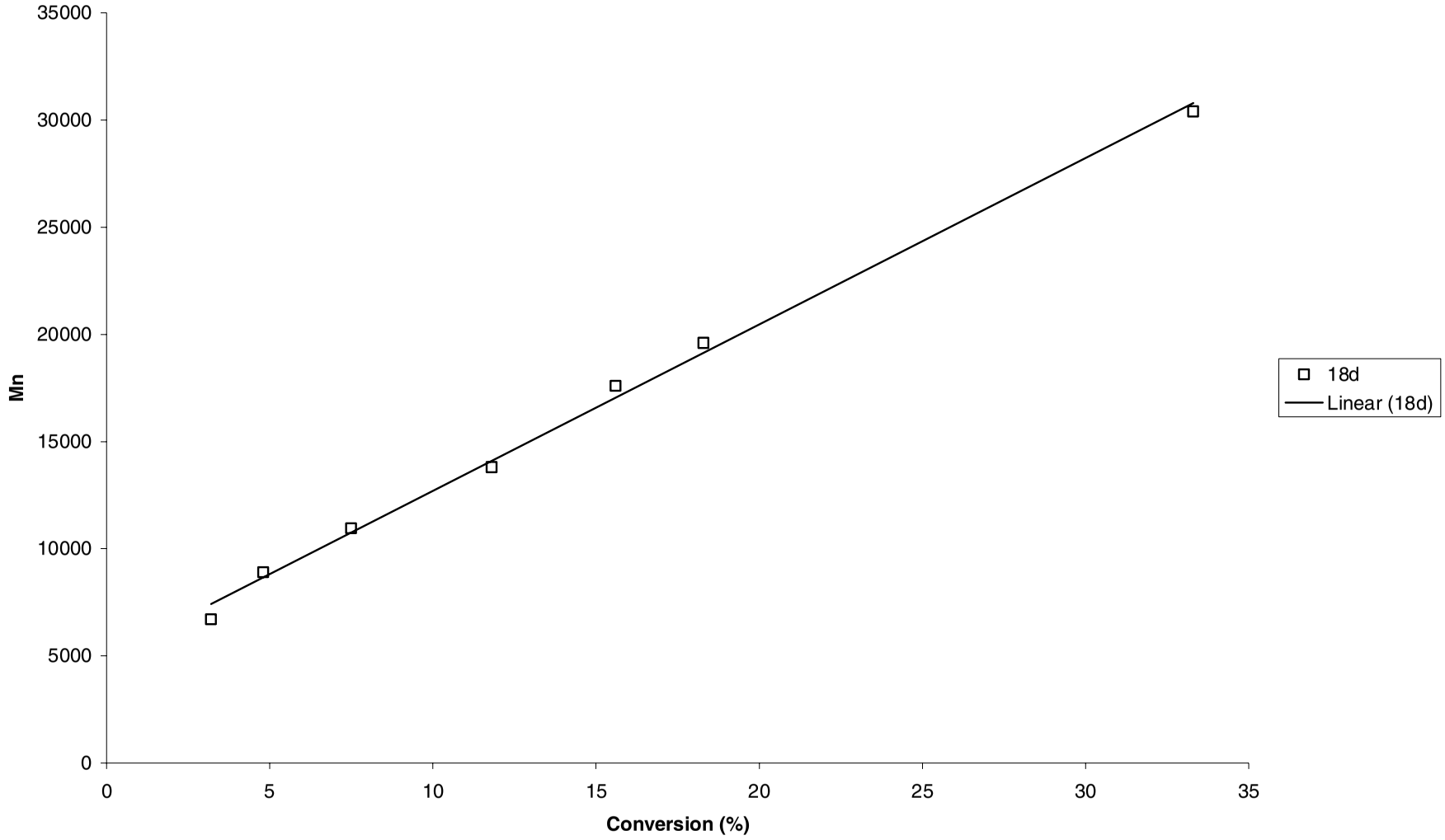
Kinetic Scheme:



$$v_1 = k_1[a]; \quad v_2 = k_2[b];$$

$$\frac{v_1}{v_2} = \frac{k_1}{k_2}\frac{[a]}{[b]}; \quad \frac{[a]}{[b]} = K_{eq}; \quad [a] = [b]\,K_{eq};$$

$$\frac{v_1}{v_2} = \frac{k_1}{k_2}K_{eq}; \quad (1)$$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Mn
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5
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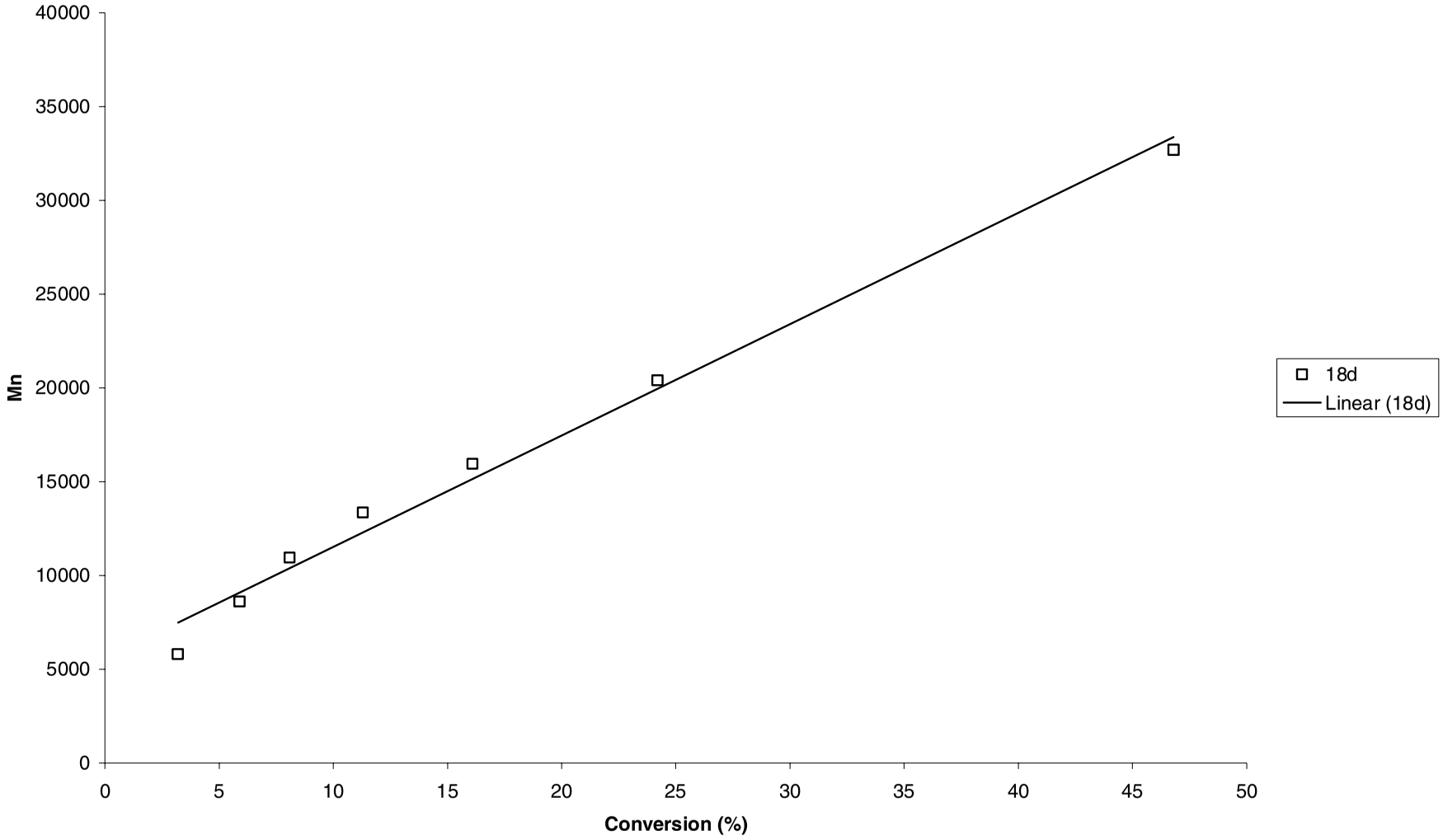
15
20
25
30
35
Conversion (%)
18d
Linear (18d)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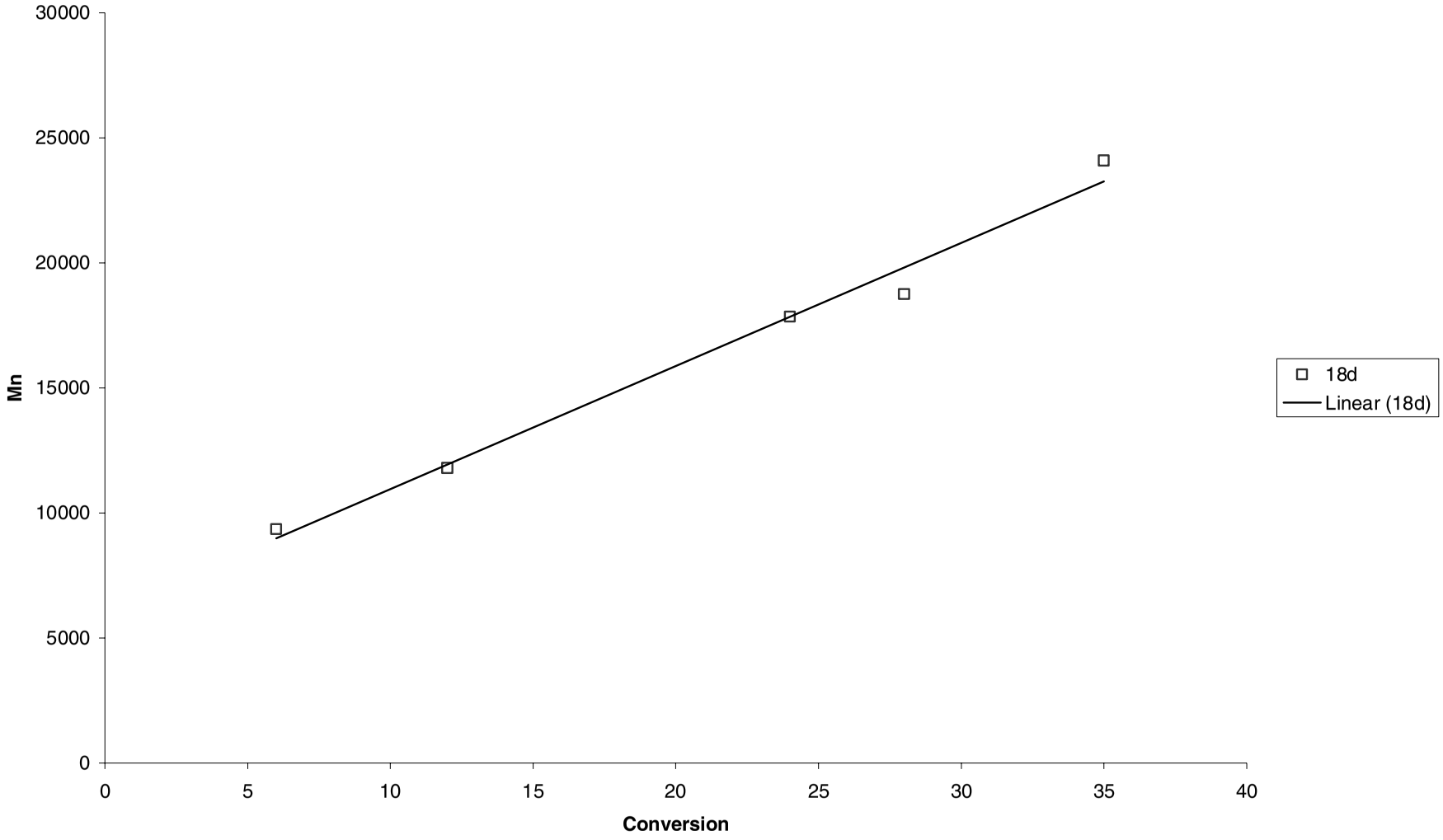
45
50
Conversion (%)
18d
Linear (18d)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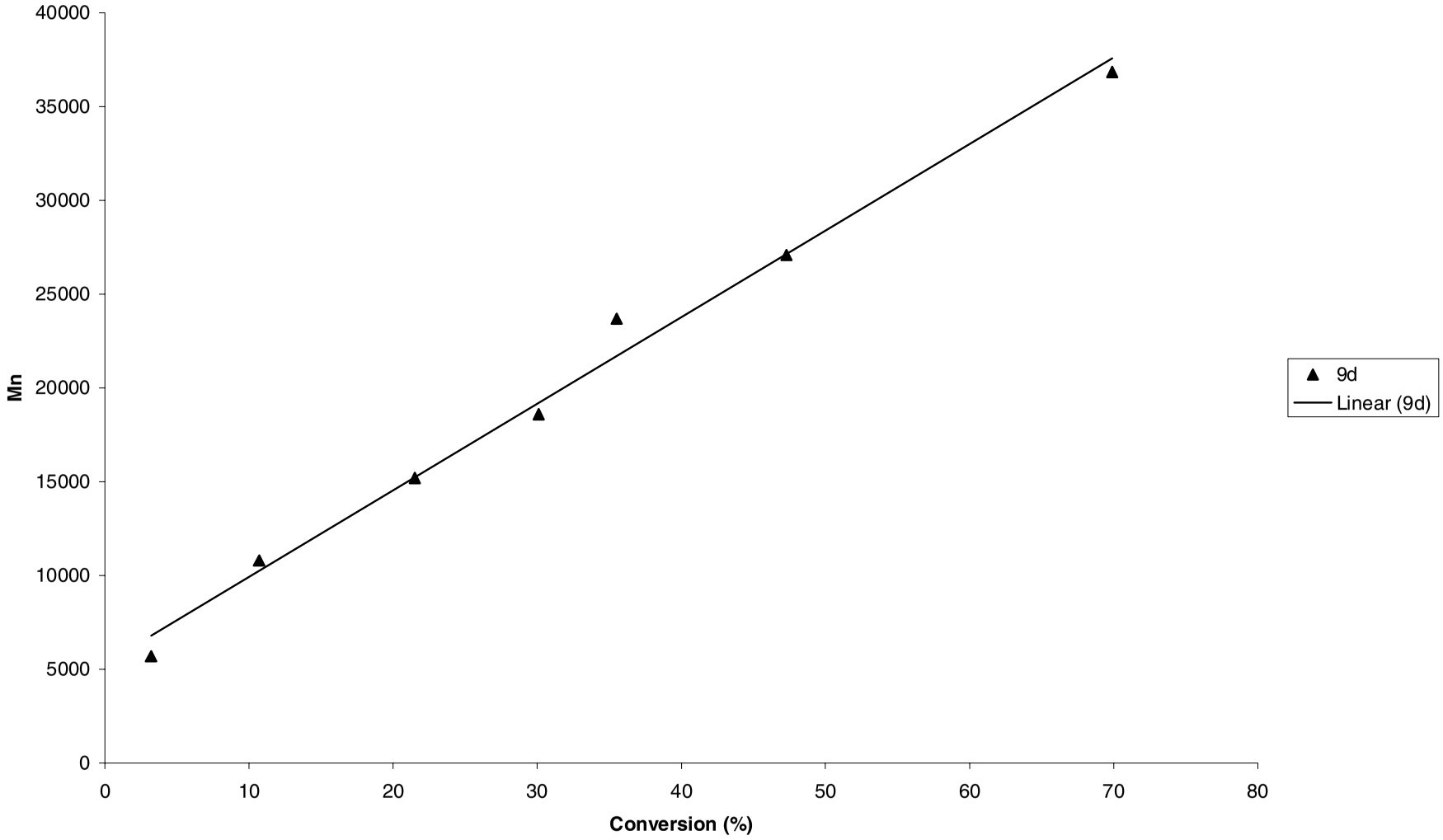
Conversion
18d
Linear (18d)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60
70
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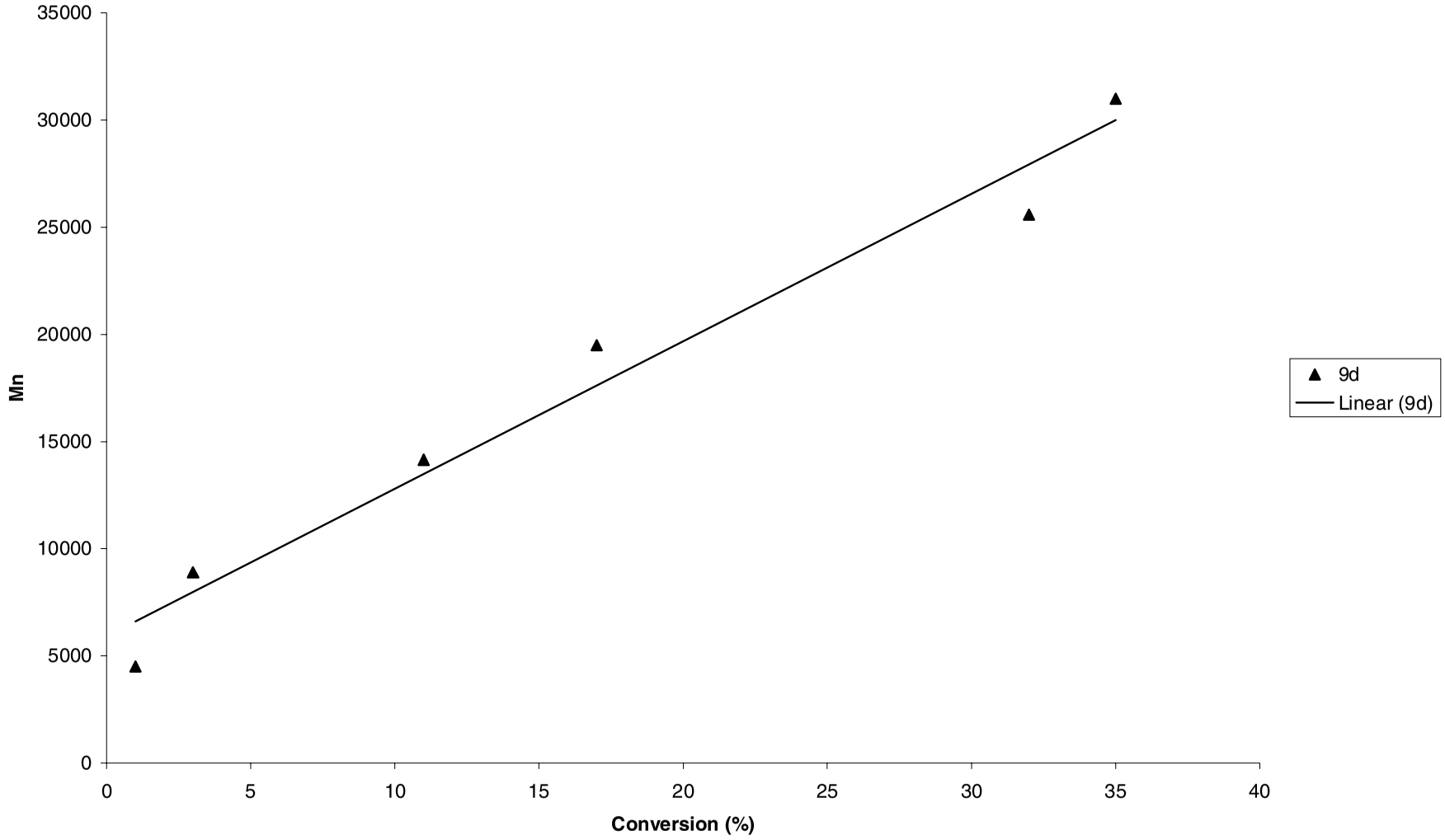
Conversion (%)
9d
Linear (9d)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35
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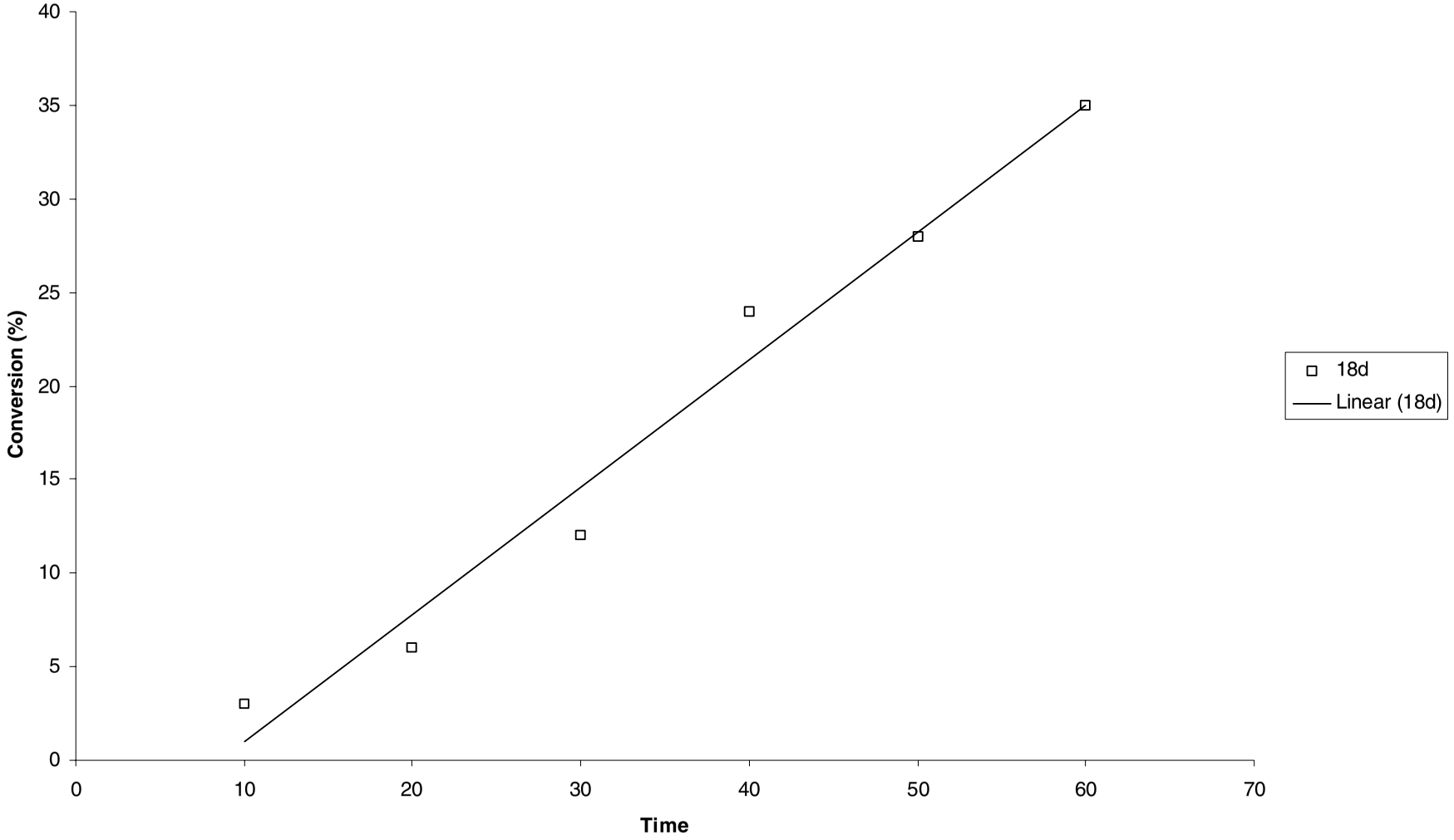
Conversion (%)
9d
Linear (9d)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Conversion (%)
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20
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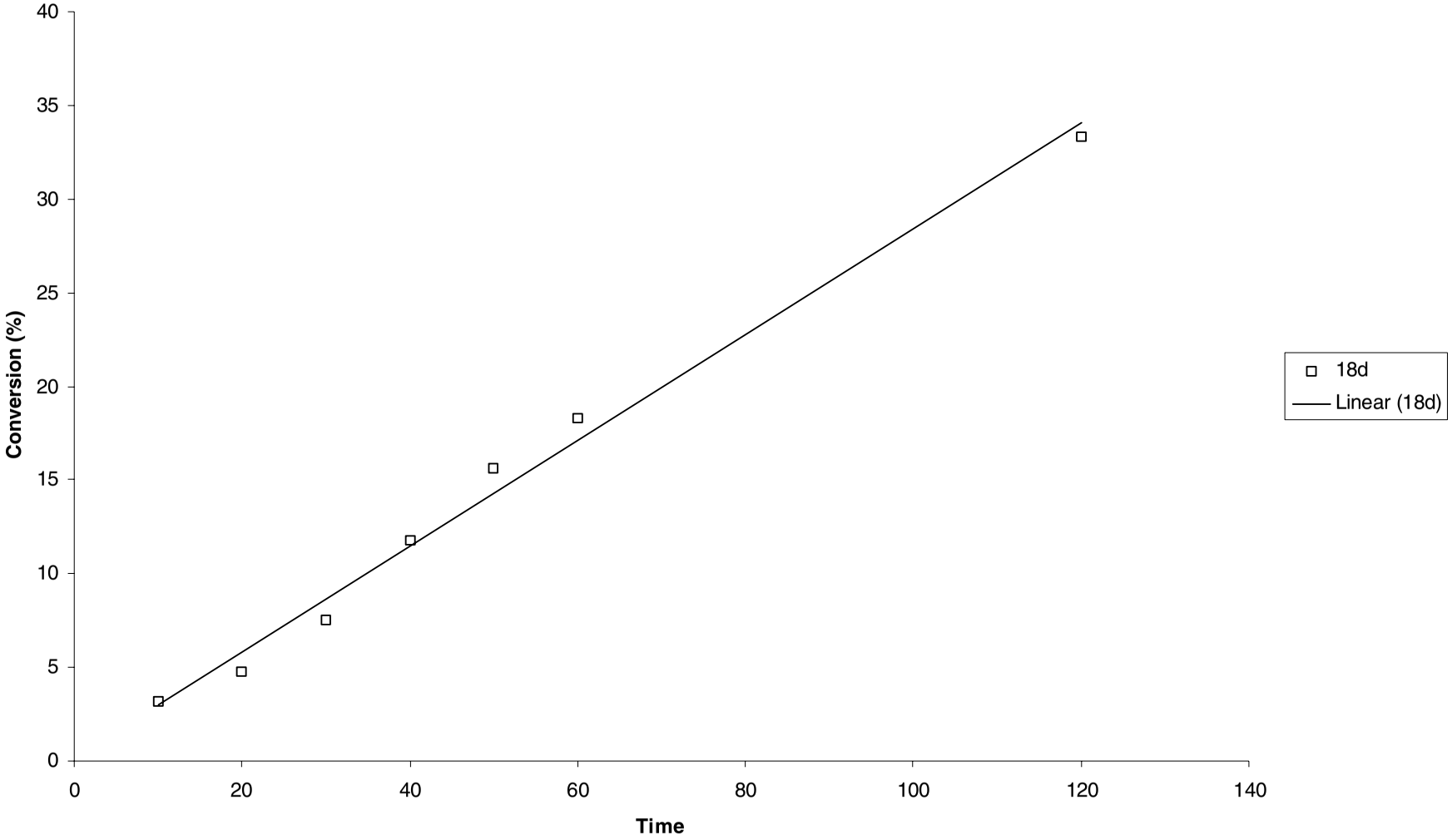
40
50
60
70
Time
18d
Linear (18d)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Conversion (%)
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100
120
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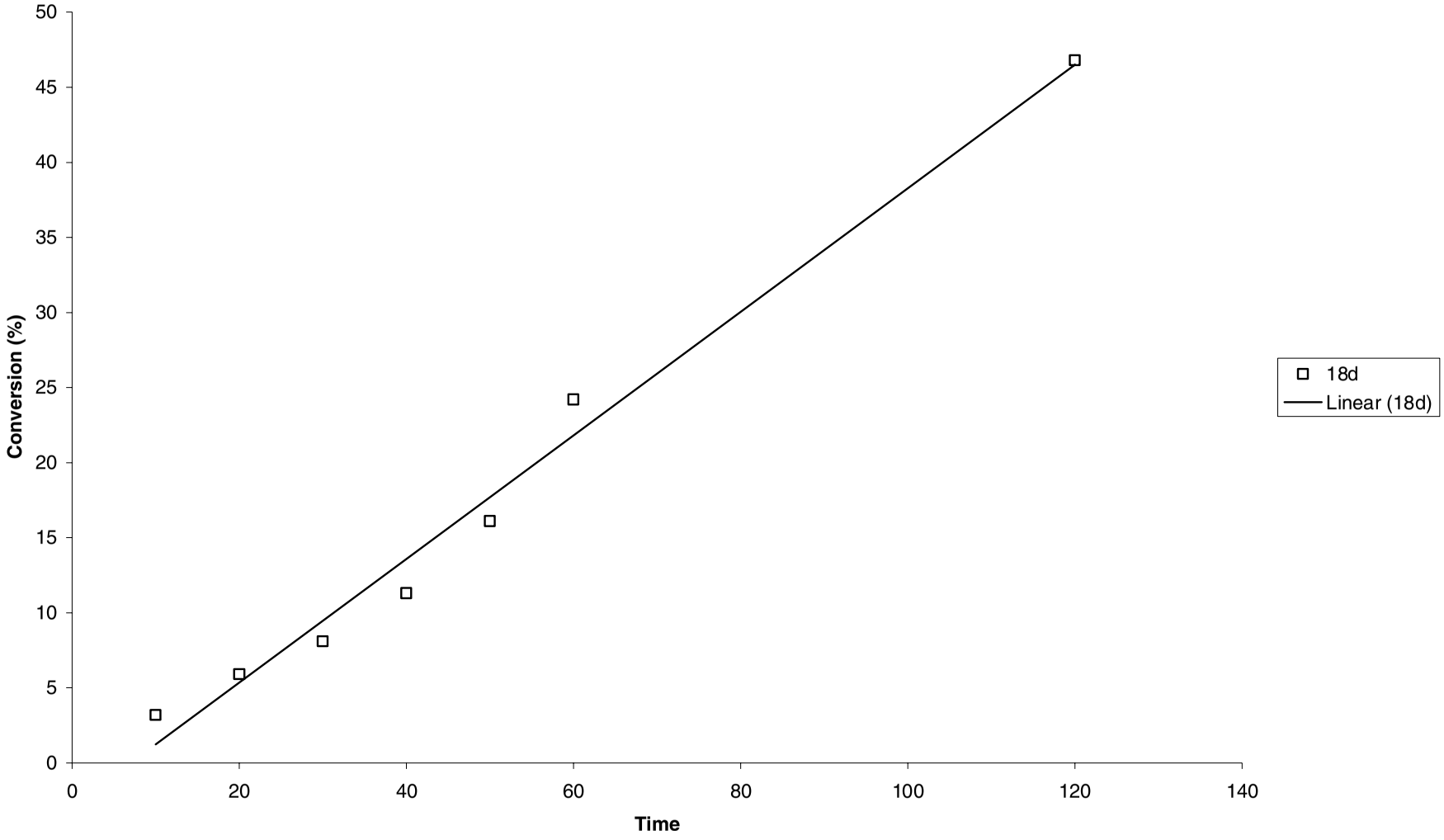
Time
18d
Linear (18d)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Conversion (%)
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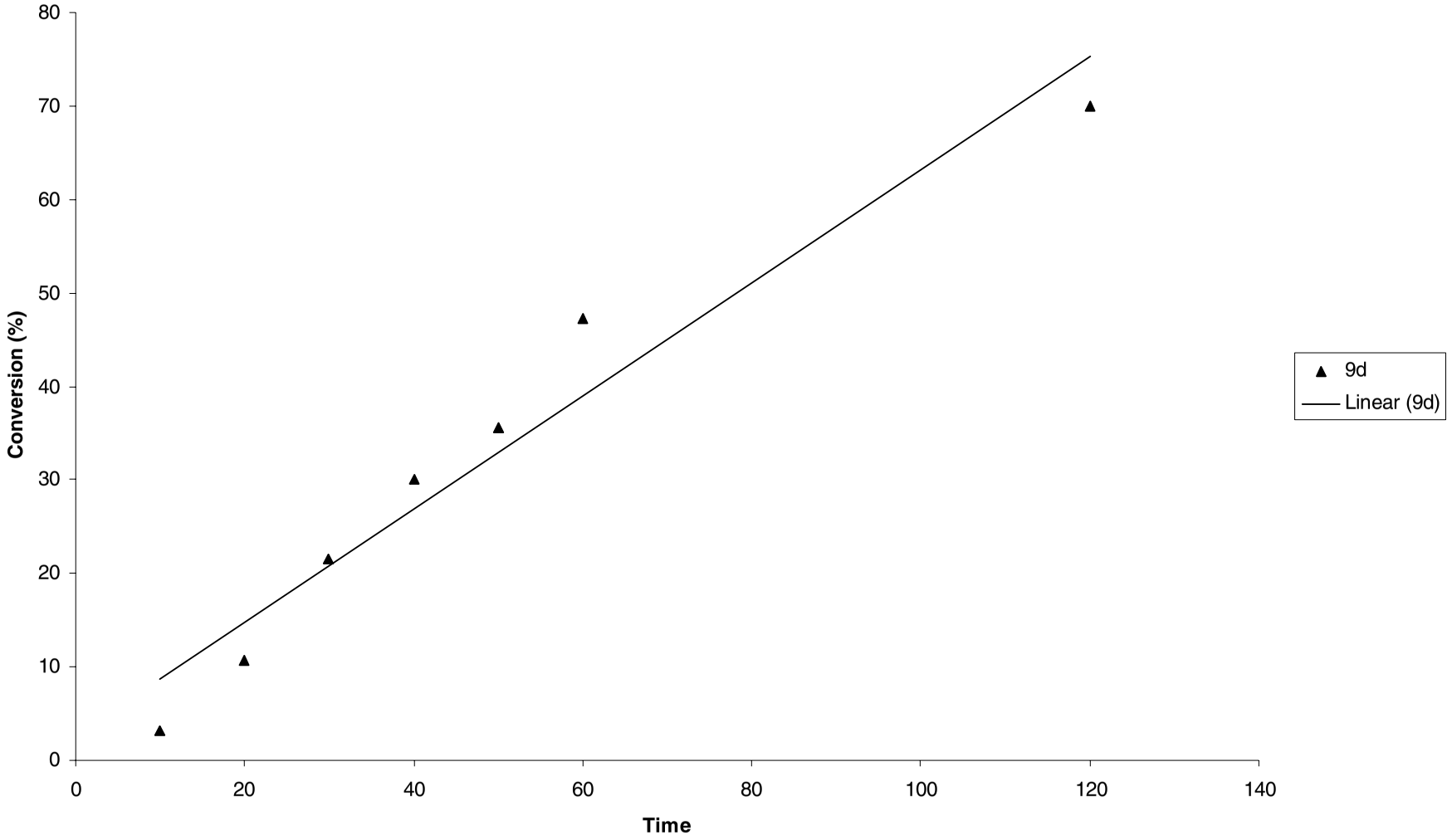
80
100
120
140
Time
18d
Linear (18d)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Conversion (%)
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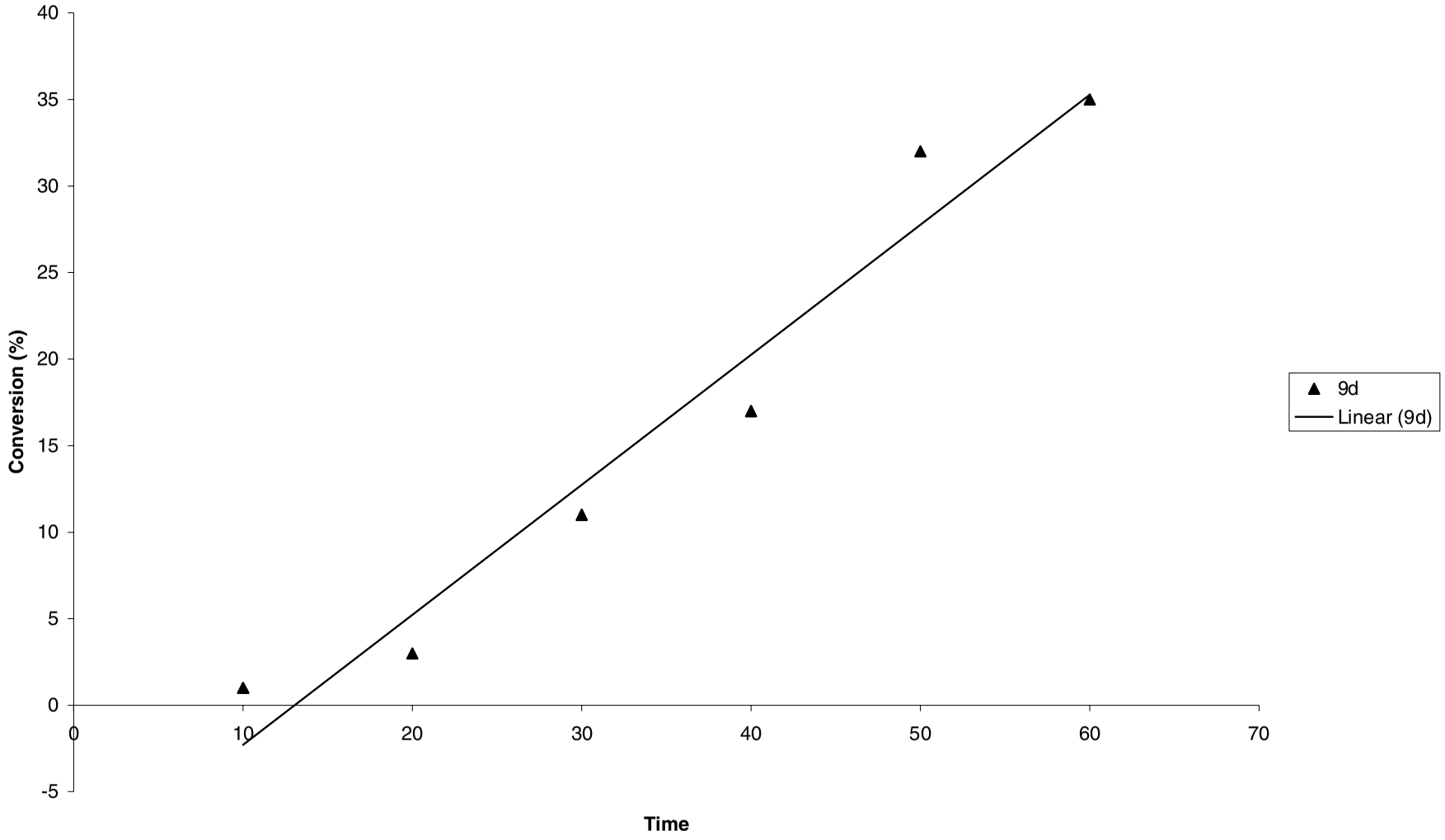
60
80
100
120
140
Time
9d
Linear (9d)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20
15
10
5
0
-5
Conversion (%)
0
10
20
30
40
50
60
70
Time
9d
Linear (9d)