Zirconocene Complexes Bearing Novel 3-Dimethylamino-1,2-dihydropentalene Derived Ligand Systems

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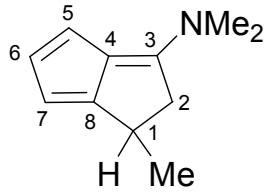
Supporting Information

Compound 2a.

Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.96; H, 9.50; N, 8.71.



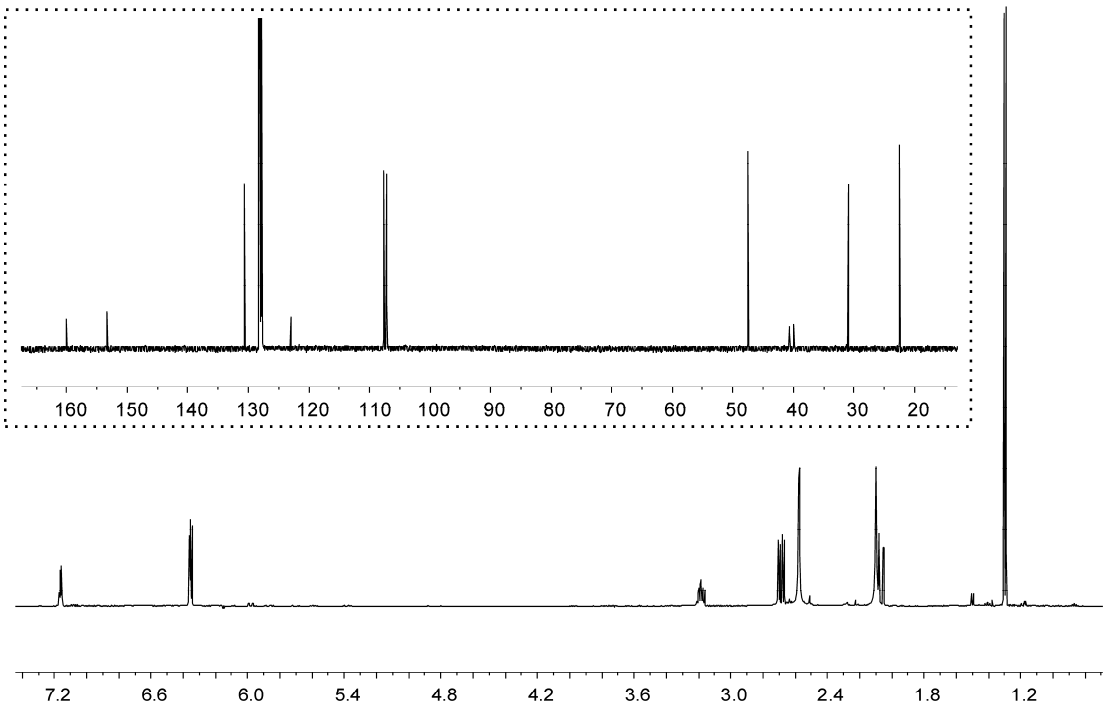
^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 7.16 (dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, 6-H), 6.36 (dt, $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ ~ J_{HH} = 1.2 Hz, 1H, 7-H), 6.35 (ddd, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.2 Hz, J_{HH} = 0.5 Hz, 1H, 5-H), 3.19 (quint m, $^3J_{HH}$ = 6.9 Hz, 1H, 1-H), 2.69 (dd, $^2J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, 2-H_b), 2.58 (br s, 3H, NMe_2), 2.10 (br s, 3H, NMe_2), 2.06 (dd, $^2J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, 2-H_a), 1.29 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Me).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 160.1 (C3), 153.3 (C8), 130.6 (C6), 122.9 (C4), 107.7 (C7), 107.2 (C5), 47.5 (C2), 40.7, 39.9 (br, NMe_2), 31.0 (C1), 22.5 (Me).

^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 7.16 / 130.6 (C6), 6.36 / 107.7 (C7), 6.35 / 107.2 (C5), 3.19 / 31.0 (C1), 2.69, 2.06 / 47.5 (C2), 2.57 / 40.7, 2.10 / 39.9 (NMe_2), 1.29 / 22.5 (Me).

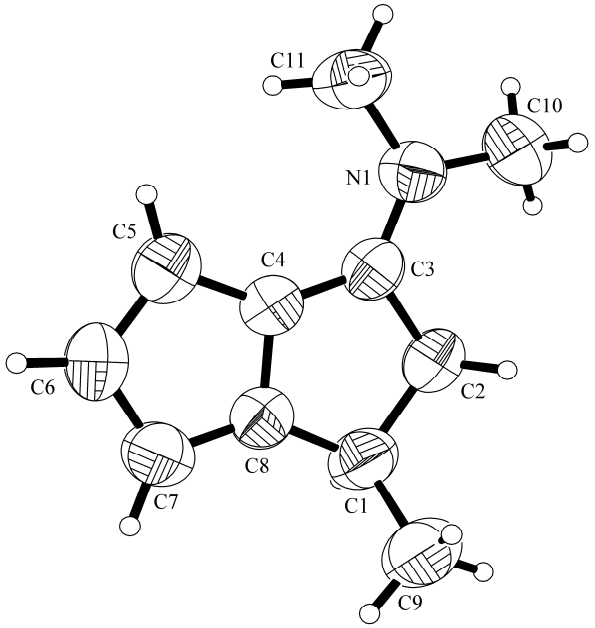
^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 2.69 / 160.1, 153.3, 122.9, 31.0, 22.5 (2-H_b / C3, C8, C4, C1, Me), 2.57 / 160.1, 39.9 (NMe_2 / C3, NMe_2), 1.29 / 153.3, 47.5, 31.0, 22.5 (Me / C8, C2, C1, Me).

^{1}H{^{1}H, NOE} NMR (600 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 3.19 / 6.36, 2.69, 2.06, 1.29 (1-H / 7-H, 2-H_b, 2-H_a, Me), 2.57, 2.10 / 6.35 (NMe_2 / 5-H), 1.29 / 6.36, 3.19, 2.06 (Me / 7-H, 1-H, 2-H_a).



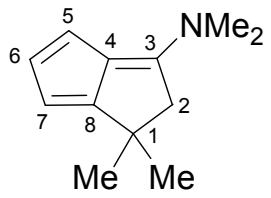
^{1}H NMR (600 MHz, C_6D_6, 298 K) and $^{13}C\{^{1}H\}$ NMR (151 MHz) of **2a**.

Crystal data for $C_{11}H_{15}N$ (**2a**), M = 161.24, monoclinic, space group $P2_1/c$ (No. 14), a = 8.2200(12), b = 13.0061(12), c = 18.295(2) Å, β = 101.899(5)°, V = 1913.8(4) Å^3, D_c = 1.119 g cm^{-3}, μ = 0.490 mm^{-1}, Z = 8, λ = 1.54178 Å, T = 223(2) K, 10363 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.59 Å^{-1}, 2744 independent (R_{int} = 0.062), and 1671 observed reflections [$I \geq 2\sigma(I)$], 223 refined parameters, R = 0.073, wR^2 = 0.212.



Compound 2b.

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.11; H, 9.83; N, 7.97.



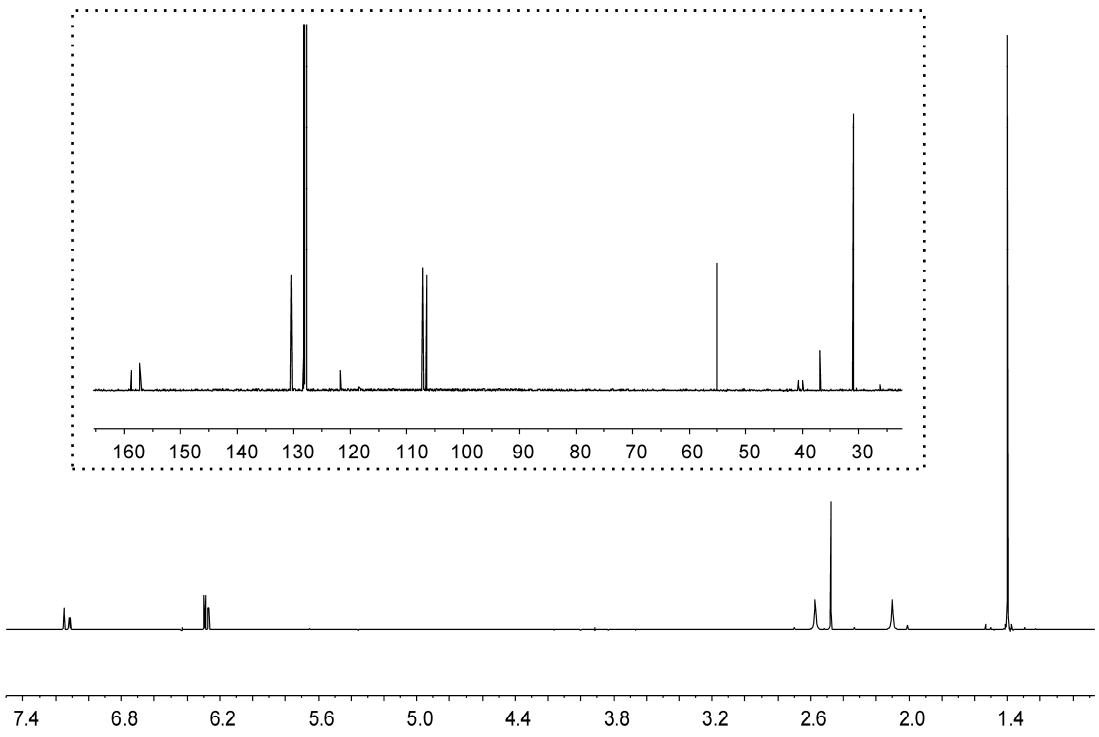
^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 7.12 (dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, 6-H), 6.29 (dd, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, 5-H), 6.27 (dd, $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, 7-H), 2.57 (br s, 3H, NMe_2), 2.48 (s, 2H, 2-H), 2.10 (br s, 3H, NMe_2), 1.40 (s, 6H, Me).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 158.8 (C3), 157.2 (C8), 130.5 (C6), 121.8 (C4), 107.1 (C5), 106.4 (C7), 55.0 (C2), 40.7 (br, NMe_2), 39.9 (br, NMe_2), 36.8 (C1), 31.0 (Me).

^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^1H/ δ^{13}C = 7.12 / 130.5 (C6), 6.29 / 107.1 (C5), 6.27 / 106.4 (C7), 2.57 / 40.7 (NMe_2), 2.48 / 55.0 (C2), 2.10 / 39.9 (NMe_2), 1.40 / 31.0 (Me).

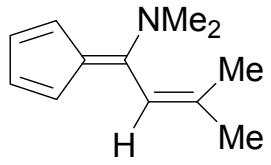
^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^1H/ δ^{13}C = 2.48 / 158.8, 157.2, 130.5, 121.8, 107.1, 36.8, 31.0 (2-H / C3, C8, C6 (weak), C4, C5 (weak), C1, Me), 2.57 / 158.8, 55.0, 39.9 (NMe_2 / C3, C2, NMe_2), 1.40 / 157.2, 55.0, 36.8, 31.0 (Me / C8, C2, C1, Me).

^{1}H{^{1}H, NOE} NMR (600 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 2.57, 2.10 / 6.29 (NMe_2 / 5-H), 1.40 / 6.27, 2.48 (Me / 7-H, 2-H).



^{1}H NMR (600 MHz, C_6D_6, 298 K) and ^{13}C{^{1}H} NMR (151 MHz) of **2b**.

Preparation of the mixture 7b : 2b: Into a Schlenk flask, dimethyl sulfate (38.5 g, 305.6 mmol) was added dropwise at 50–60 °C under argon to N,N-dimethylsenecioamide (38.8 g, 305.6 mmol). The reaction mixture was stirred at 70–80 °C for 2.5 hours. The amide complex formed as a viscous, yellow liquid, which was added lowly to a solution of cyclopentadienyl lithium (22.0 g, 305.6 mmol) in 50 mL of THF at −15 °C. The reaction mixture was kept below −15 °C during the addition and stirred at room temperature overnight. The solvent was removed under vacuum and the residue was treated with 50 mL of pentane three times. The organic phase was separated and the solvent was removed under vacuum to give a deep red viscous liquid, which was crystallized from diethyl ether at −30 °C to give yellow solid of the mixture **2b** and **7b** (ratio **7b** : **2b** ~ 1 : 3).



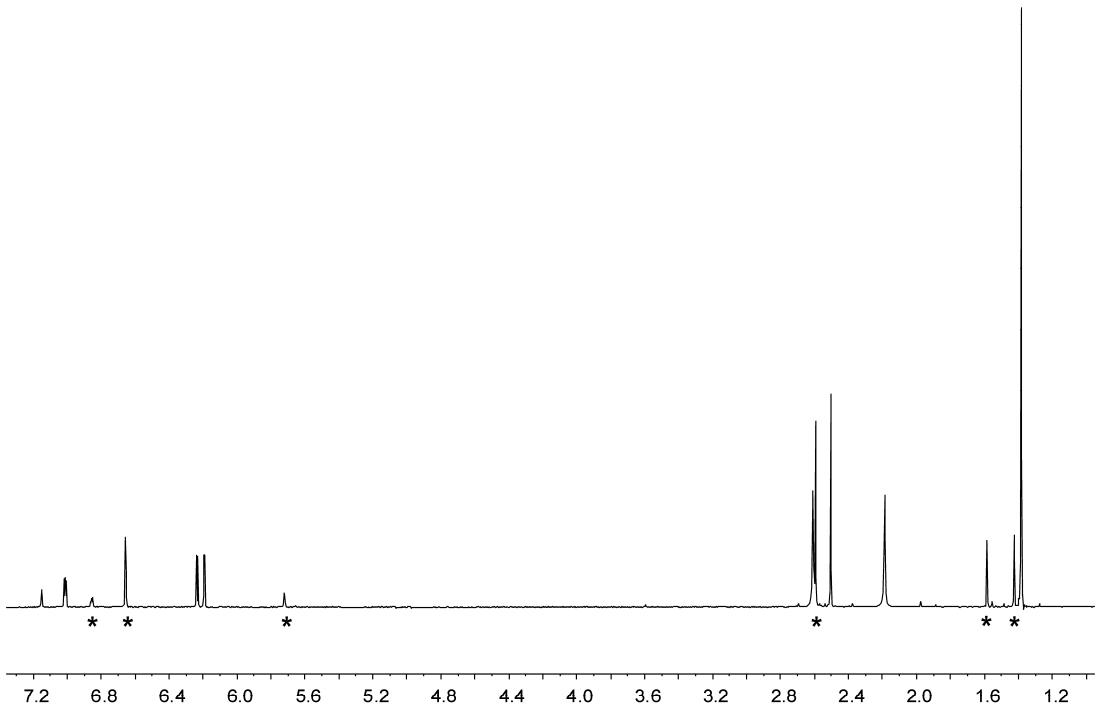
^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 6.86 (m, 1H), 6.66 (m, 3H)(C_5H_4), 5.72 (s, 1H, =CH), 2.59 (s, 6H, NMe_2), 1.58 (m, 3H, Me^E), 1.41 (m, 3H, Me^Z).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 155.6 (=CN), 141.7 (=CMe_2), 123.9, 123.8, 120.1, 116.9 (C_5H_4), 123.0 (=CH), 119.2 (C=), 42.4 (NMe_2), 25.1 (Me^E), 20.3 (Me^Z).

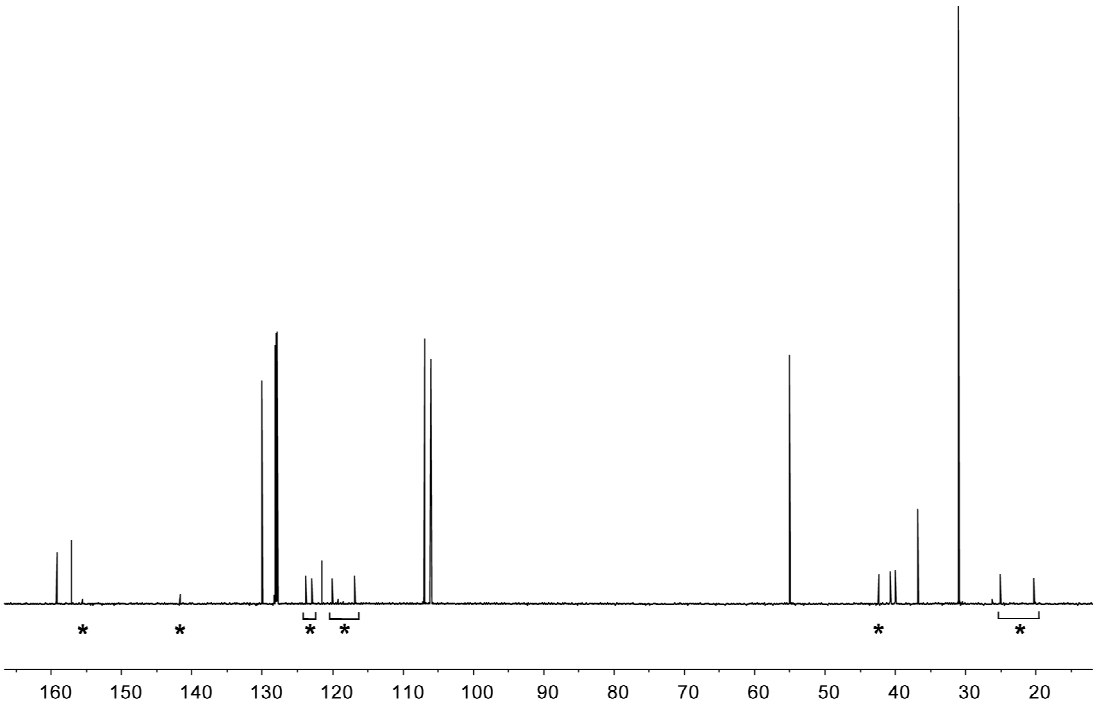
^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.86 / 123.8, 6.66 / 123.9, 120.1, 116.9 (C_5H_4), 5.72 / 123.0 (=CH), 2.59 / 42.4 (NMe_2), 1.58 / 25.1, 1.41 / 20.3 (Me).

^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 6.66 / 123.8, 120.1, 116.9, 119.2 (C_5H_4 / 3 × C_5H_4, C=), 2.59 / 155.6, 42.4 (NMe_2 / =CN, NMe_2), 1.58 / 141.7, 123.0, 20.3 (Me^E / =CMe_2, =CH, Me^Z).

^{1}H{^{1}H, NOE} NMR (600 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 5.72 / 6.66, 2.59, 1.58 (=CH / C_5H_4, NMe_2, Me^E).



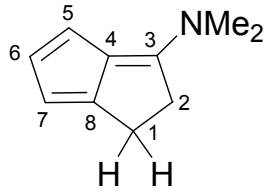
^{1}H NMR (600 MHz, C_6D_6, 298 K) of a mixture of **7b**(*) and **2b**



$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298 K) of a mixture of **7b** (*) and **2b**

Compound 2c.

Anal. Calcd for $C_{10}H_{13}N \times 0.25\ (C_2H_5)_2O$: C, 79.71; H, 9.43; N, 8.45. Found: C, 79.46; H, 9.55; N, 8.74.

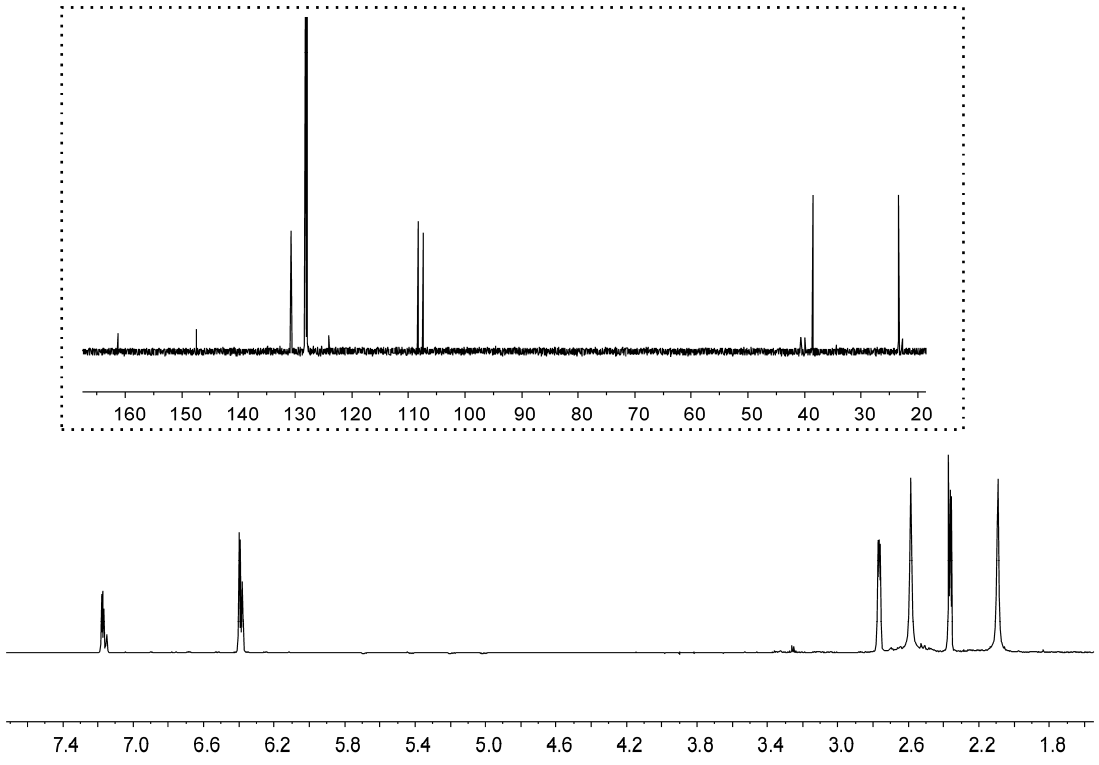


^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 7.17 (dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 2.5, 1H, 6-H), 6.39 (ddt, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.0 Hz, J_{HH} = 0.5 Hz, 1H, 5-H), 6.38 (m, 1H, 7-H), 2.77 (m, 2H, 1-H), 2.59 (br s, 3H, NMe_2), 2.36 (m, 2H, 2-H), 2.09 (br s, 3H, NMe_2).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 161.3 (C3), 147.4 (C8), 130.7 (C6), 124.0 (C4), 108.3 (C7), 107.4 (C5), 40.7, 39.9 (br, NMe_2), 38.6 (C2), 23.3 (C1).

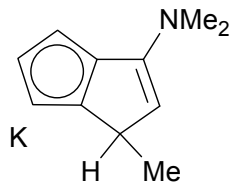
^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 7.17 / 130.7 (C6), 6.39 / 107.4 (C5), 6.38 / 108.3 (C7), 2.77 / 23.3 (C1), 2.59 / 40.7, 2.09 / 39.9 (NMe_2), 2.36 / 38.6 (C2).

^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 2.77 / 161.3, 147.4, 130.7, 124.0, 108.3, 38.6 (1-H / C3, C8, C6 (weak), C4 (weak), C7, C2), 2.59 / 161.3, 39.9 (NMe_2 / C3, NMe_2), 2.36 / 161.3, 147.4, 130.7, 124.0, 23.3 (2-H / C3, C8, C6 (weak), C4, C1).

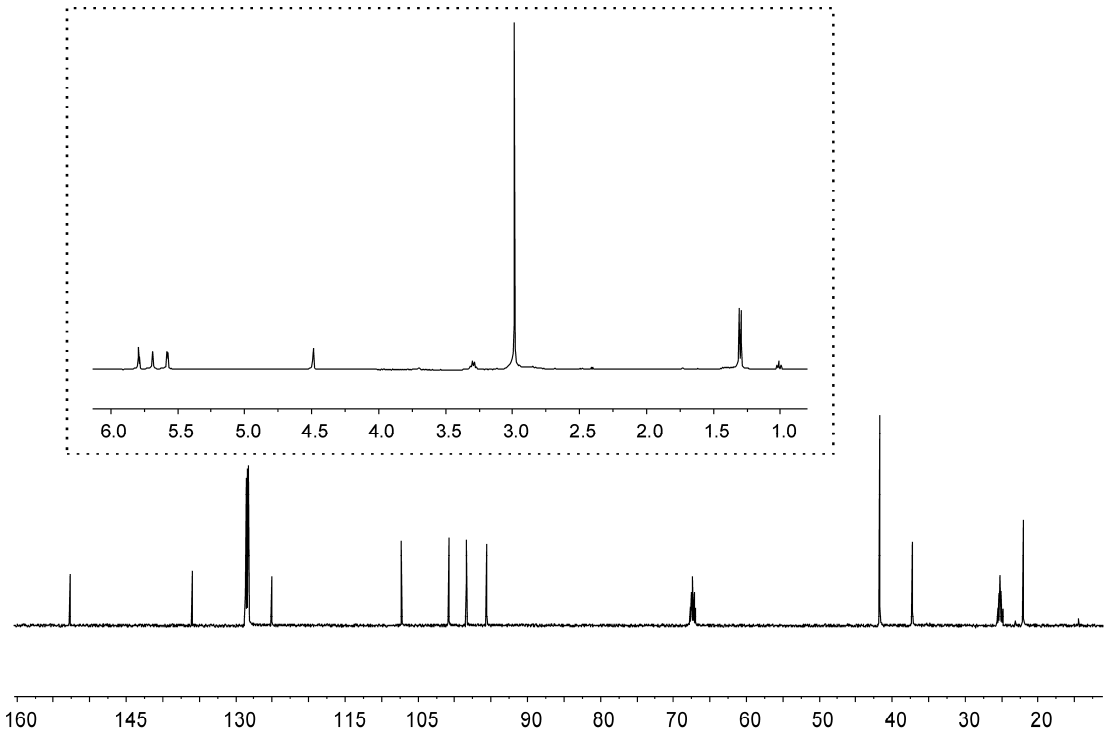


^{1}H NMR (600 MHz, C_6D_6, 298 K) and ^{13}C{^{1}H} NMR (151 MHz) of **2c**.

Potasium salt 8a.

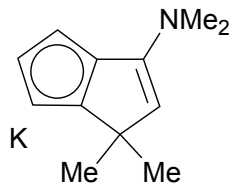


^{1}H NMR (500 MHz, C_6D_6/TDF = 2/3, 298 K): δ = 5.79 (td, $^{3}J_{HH}$ = 3.1 Hz, J_{HH} = 0.9 Hz, 1H, 6-H), 5.69 (m, 1H, 7-H), 5.58 (dd, $^{3}J_{HH}$ = 3.1 Hz, J_{HH} = 1.4 Hz, 1H, 5-H), 4.49 (m, 1H, 2-H), 3.29 (qd, $^{3}J_{HH}$ = 7.1 Hz, J_{HH} = 1.9 Hz, 1H, 1-H), 2.98 (s, 6H, NMe_2), 1.30 (d, $^{3}J_{HH}$ = 7.1 Hz, 3H, Me).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6/ TDF = 2/3, 298 K): δ = 152.7 (C3), 136.0 (C8), 125.0 (C4), 107.3 (C6), 100.8 (C2), 98.3 (C7), 95.6 (C5), 41.7 (NMe_2), 37.2 (C1), 22.0 (Me).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6/ TDF = 2/3, 298 K): δ^{1}H/ δ^{13}C = 5.79 / 107.3 (C6), 5.69 / 98.3 (C7), 5.58 / 95.6 (C5), 4.49 / 100.8 (C2), 3.29 / 37.2 (C1), 2.98 / 41.7 (NMe_2), 1.30 / 22.0 (Me).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6/ TDF = 2/3, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 2.98 / 152.7, 100.8, 41.7 (NMe_2 / C3, C2 (weak), NMe_2), 4.49 / 152.7, 136.0, 125.0, 37.2 (2-H / C3 (weak), C8, C4, C1), 1.30 / 136.0, 100.8, 37.2 (Me / C8, C2, C1).
^{1}H{^{1}H, NOE} NMR (500 MHz, C_6D_6/TDF = 2/3, 298 K): [selected experiments] δ_{ir} / δ_{res} = 4.49 / 3.29, 2.98, 1.30 (2-H / 1-H, NMe_2, Me), 3.29 / 5.69, 4.49 (1-H / 7-H, 2-H), 1.30 / 5.69, 4.49, 3.29, 2.98 (Me / 7-H, 1-H, NMe_2).

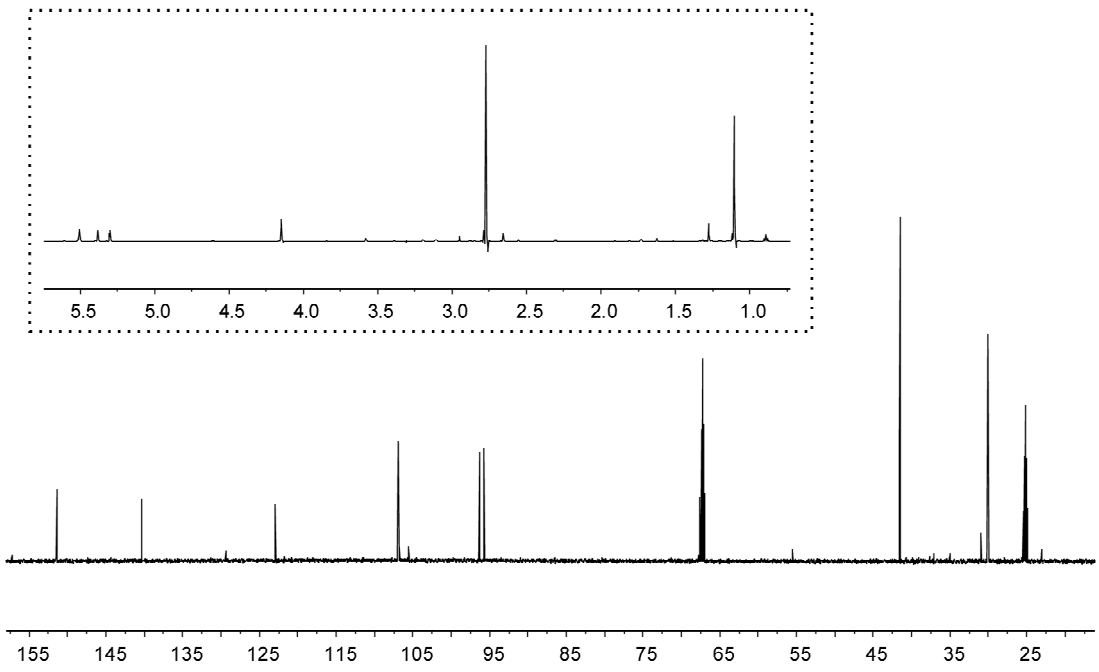


^{13}C{^{1}H} NMR (126 MHz, C_6D_6/ TDF = 2/3, 298 K) and ^{1}H NMR (500 MHz) of **8a**.

Potasium salt 8b.

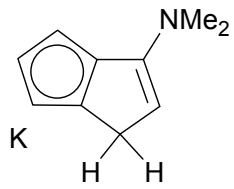


^{1}H NMR (600 MHz, TDF, 298 K): δ = 5.50 (tm, $^{3}J_{HH}$ = 3.0 Hz, 1H, 6-H), 5.38 (dd, $^{3}J_{HH}$ = 3.0 Hz, J_{HH} = 1.4 Hz, 1H, 7-H), 5.30 (dd, $^{3}J_{HH}$ = 3.0 Hz, J_{HH} = 1.4 Hz, 1H, 5-H), 4.15 (s, 1H, 2-H), 2.77 (s, 6H, NMe_2), 1.11 (s, 6H, Me).
^{13}C{^{1}H} NMR (151 MHz, TDF, 298 K): δ = 151.4 (C3), 140.3 (C8), 123.0 (C4), 106.90, 106.88 (C6, C2), 96.4 (C7), 95.7 (C5), 41.6 (C1), 41.5 (NMe_2), 30.1 (Me).
^{1}H,^{13}C ghsqc (600 / 151 MHz, TDF, 298 K): δ^{1}H/ δ^{13}C = 5.50 / 106.9 (C6), 5.38 / 96.4 (C7), 5.30 / 95.7 (C5), 4.15 / 106.9 (C2), 2.77 / 41.5 (NMe_2), 1.11 / 30.1 (Me).
^{1}H,^{13}C ghmbc (600 / 151 MHz, TDF, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 4.15 / 151.4, 140.3, 123.0, 96.4, 95.7, 41.6, 30.1 (2-H / C3, C8, C4, C7 (weak), C5 (weak), C1, Me (weak)), 2.77 / 151.4, 41.5 (NMe_2 / C3, NMe_2), 1.11 / 140.3, 106.9, 41.6, 30.1 (Me / C8, C2, C1, Me).
^{1}H{^{1}H, NOE} NMR (600 MHz, TDF, 298 K): [selected experiments] δ_{ir} / δ_{res} = 4.15 / 2.77, 1.11 (2-H / NMe_2, Me), 2.77 / 5.30, 4.15 (NMe_2 / 5-H, 2-H), 1.11 / 5.38, 4.15 (Me / 7-H, 2-H).

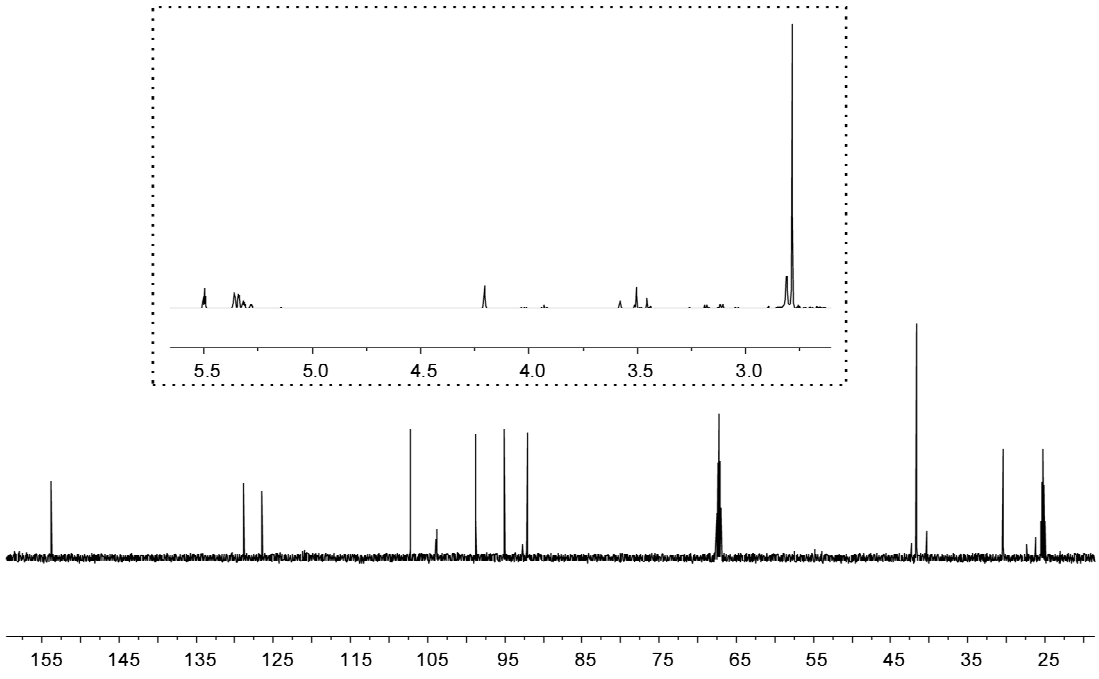


^{13}C{^{1}H} NMR (151 MHz, TDF, 298 K) and ^{1}H NMR (600 MHz) of **8b**.

Potasium salt 8c.



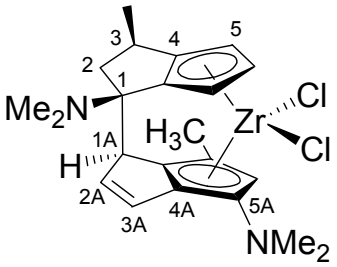
^{1}H NMR (600 MHz, TDF, 298 K): δ = 5.50 (tm, $^{3}J_{HH}$ = 3.1 Hz, 1H, 6-H), 5.36 (m, 1H, 7-H), 5.34 (m, 1H, 5-H), 4.20 (m, 1H, 2-H), 2.81 (br, 2H, 1-H), 2.79 (s, 6H, NMe_2).
^{13}C{^{1}H} NMR (151 MHz, TDF, 298 K): δ = 153.8 (C3), 128.9 (C8), 126.5 (C4), 107.2 (C6), 98.8 (C7), 95.1 (C5), 92.1 (C2), 41.7 (NMe_2), 30.4 (C1).
^{1}H,^{13}C ghsqc (600 / 151 MHz, TDF, 298 K): δ^{1}H/ δ^{13}C = 5.50 / 107.2 (C6), 5.36 / 98.8 (C7), 5.34 / 95.1 (C5), 4.20 / 92.1 (C2), 2.81 / 30.4 (C1), 2.79 / 41.7 (NMe_2).
^{1}H,^{13}C ghmbc (600 / 151 MHz, TDF, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 4.20 / 128.9, 126.5 (2-H / C8, C4), 2.81 / 128.9, 92.1 (1-H / C8, C2), 2.79 / 153.8, 41.7 (NMe_2 / C3(weak), NMe_2).
^{1}H{^{1}H, NOE} NMR (600 MHz, TDF, 298 K): [selected experiments] δ_{ir} / δ_{res} = 4.20 / 2.81, 2.79 (2-H / 1-H, NMe_2), 2.79 / 5.34, 4.20 (NMe_2 / 5-H, 2-H).



^{13}C{^{1}H} NMR (151 MHz, TDF, 298 K) and ^{1}H NMR (600 MHz) of **8c**.

Zirconium Complex 9a.

HRMS (ESI) exact mass for $[M+H]^+$ ($C_{22}H_{29}N_2Cl_2Zr$): calcd *m/z* 481.0749, found 481.0743.



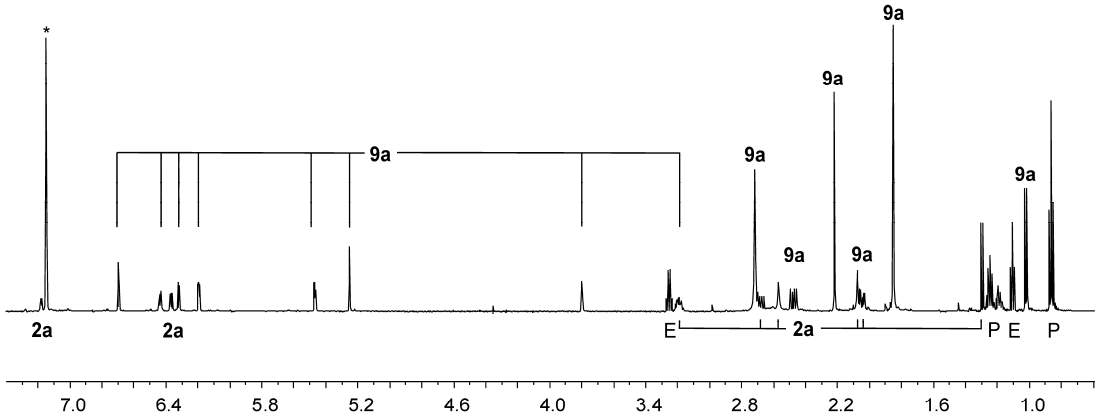
^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 6.70 (t, $^3J_{HH}$ = 3.2 Hz, 1H, 6-H), 6.44 (dd, $^3J_{HH}$ = 5.7 Hz, $^3J_{HH}$ = 2.2 Hz, 1H, 2A-H), 6.32 (dd, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, 3A-H), 6.19 (dd, $^3J_{HH}$ = 3.2 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 5-H), 5.47 (dd, $^3J_{HH}$ = 3.2 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 7-H), 5.25 (s, 1H, 6A-H), 3.80 (br, 1H, 1A-H), 3.19 (m, 1H, 3-H), 2.72 (s, 6H, 5A-NMe_2), 2.48 (dd, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 9.7 Hz, 1H, 2-H^b), 2.22 (s, 3H, 7A-Me), 2.05 (dd, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 4.1, 1H, 2-H^a), 1.85 (s, 6H, 1-NMe_2), 1.02 (d, $^3J_{HH}$ = 7.1 Hz, 3H, 3-Me).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 148.3 (C5A), 141.5 (C8), 137.7 (C4), 137.1 (C2A), 128.2 (C8A), 127.4 (C3A), 127.0 (C6), 122.4 (C7A), 118.0 (C4A), 113.8 (C5), 104.4 (C7), 102.8 (C6A), 75.6 (C1), 58.7 (C1A), 41.4 (C2), 40.6 (br, 5A-NMe_2), 39.3 (1-NMe_2), 33.6 (C3), 22.1 (3-Me), 16.7 (7A-Me).

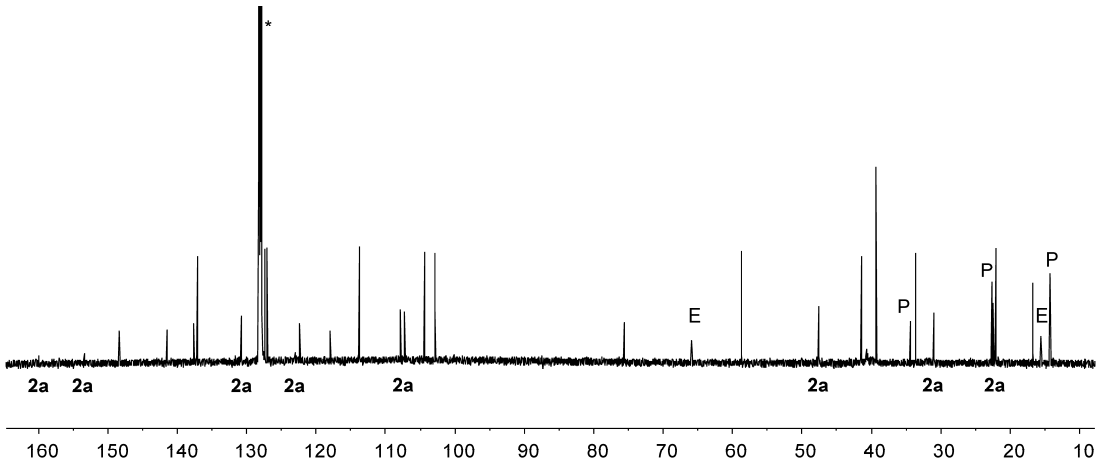
^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.70 / 127.0 (C6), 6.44 / 137.1 (C2A), 6.32 / 127.4 (C3A), 6.19 / 113.8 (C5), 5.47 / 104.4 (C7), 5.25 / 102.8 (C6A), 3.80 / 58.7 (C1A), 3.19 / 33.6 (C3), 2.72 / 40.6 (5A- NMe_2), 2.48, 2.05 / 41.4 (C2),, 2.22 / 16.7 (7A-Me), 1.85 / 39.3 (1-NMe_2), 1.02 / 22.1 (3-Me).

^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 6.44 / 128.2, 127.4, 118.0, 58.7 (2A-H / C8A, C3A, C4A, C1A), 5.25 / 148.3, 128.2, 122.4, 118.0 (6A-H / C5A, C8A, C7A, C4A), 2.72 / 148.3 (5A-NMe_2 / C5A), 2.48 / 141.5, 137.7, 75.6, 58.7, 33.6, 22.1 (2-H^b / C8, C4, C1, C1A, C3, 3-Me), 2.22 / 102.8, 122.4, 128.2 (7A-Me / C6A, C7A, C8A), 1.85 / 75.6, 39.3 (1-NMe_2 / C1, 1-NMe_2), 1.02 / 137.7, 41.4, 33.6 (3-Me / C4, C2, C3).

^{1}H{^{1}H, NOE} NMR (600 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 6.19 / 6.70, 1.02 (5-H / 6-H, 3-Me), 5.47 / 6.70, 1.85 (7-H / 6-H, 1-NMe_2), 5.25 / 2.72, 2.22 (6A-H / 5A-NMe_2, 7A-Me), 3.80 / 6.44, 2.48, 1.85 (1A-H / 2A-H, 2-H^b, 1-NMe_2), 2.72 / 6.32, 5.25 (5A-NMe_2 / 3A-H, 6A-H), 2.22 / 5.25, 3.19, 2.48 (7A-Me / 6A-H, 3-H, 2-H^b), 1.85 / 6.44, 5.47, 3.80, 2.05, 1.02 (1-NMe_2 / 2A-H, 7-H, 1A-H, 2-H^a, 3-Me), 1.02 / 6.19, 3.19, 2.05, 1.85 (3-Me / 5-H, 3-H, 2-H^a, 1-NMe_2).

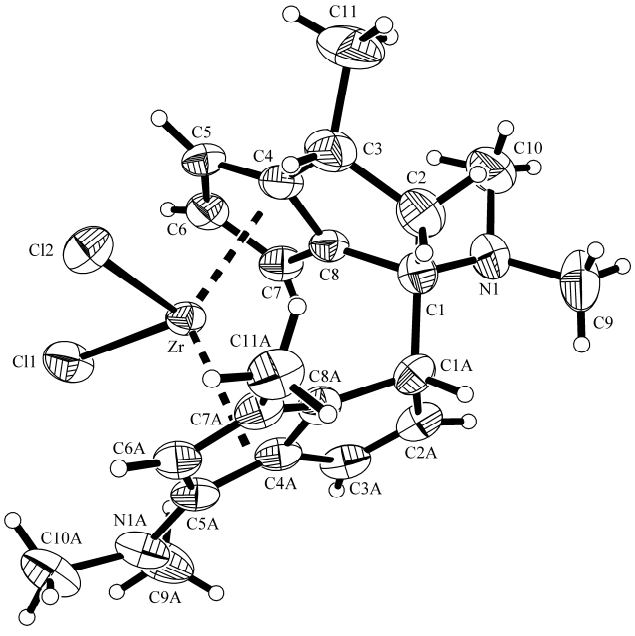


^{1}H NMR (600 MHz, C_6D_6(*), 298 K) of a mixture of **9a** and **2a** (2 : 1)
(P: pentane; E: ether).

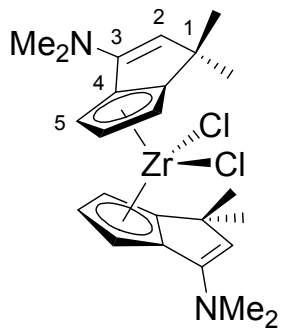


$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6 (*), 298 K) of a mixture of **9a** and **2a** (2 : 1) (P: pentane; E: ether).

Crystal data for $C_{22}H_{28}Cl_2N_2Zr$ (**9a**), M = 482.58, triclinic, space group $P\bar{1}$ (No. 2), a = 9.1539(2), b = 10.5147(2), c = 12.1510(3) Å, α = 66.631(1), β = 81.662(1), γ = 84.245(2)°, V = 1061.08(4) Å^3, D_c = 1.510 g cm^{-3}, μ = 0.780 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 223(2) K, 9087 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 4883 independent (R_{int} = 0.043), and 4565 observed reflections [$I \geq 2\sigma(I)$], 250 refined parameters, R = 0.045, wR^2 = 0.110.



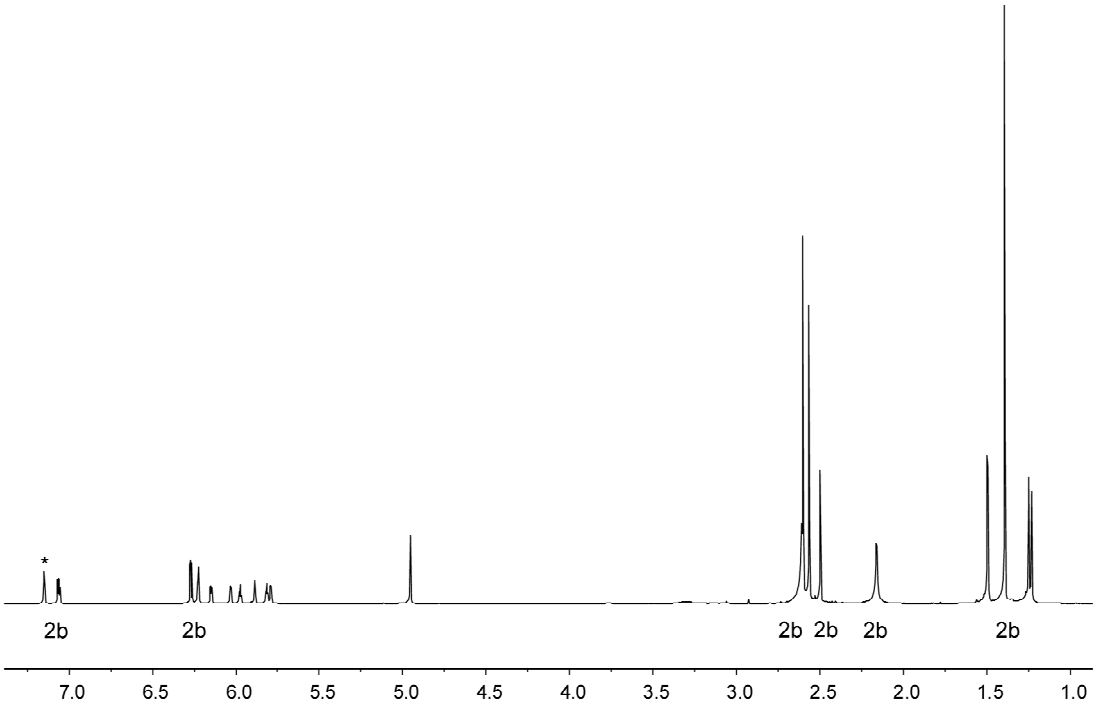
Zirconium Complexes 10b.



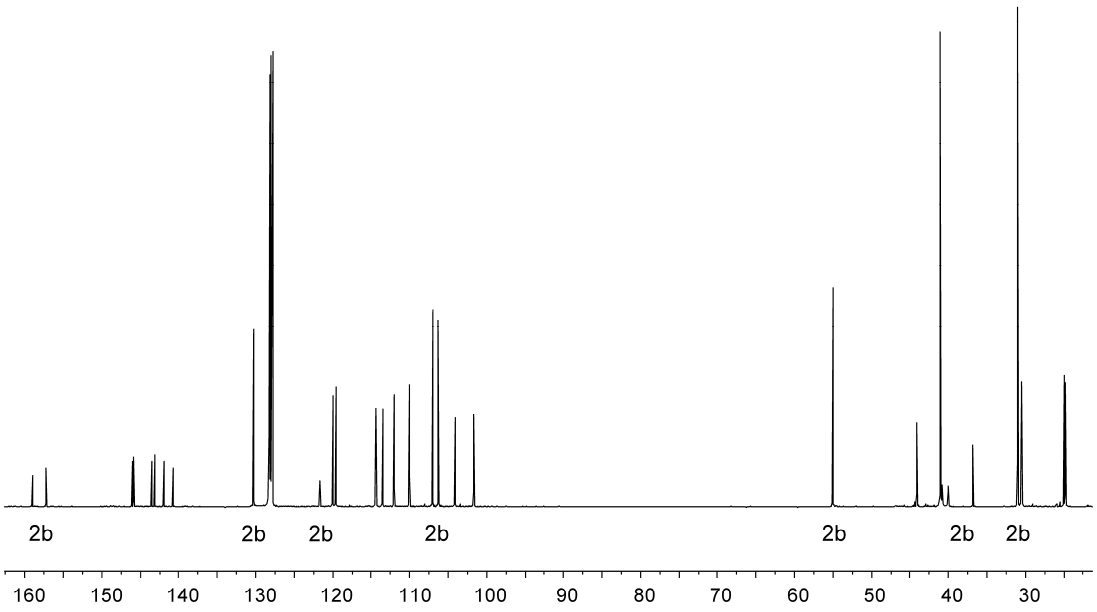
Tentatively assigned as *rac*-**10b**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.15 (dd, $^{3}J_{HH}$ = 3.1 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, 7-H), 5.97 (ddd, $^{3}J_{HH}$ = 3.1 Hz, $^{3}J_{HH}$ = 2.8 Hz, J_{HH} = 1.0 Hz, 1H, 6-H), 5.79 (dd, $^{3}J_{HH}$ = 2.8, $^{4}J_{HH}$ =1.5, 1H, 5-H), 4.96 (s, 1H, 2-H), 2.56 (s, 6H, NMe_2), 1.49 (s, 3H, Me^a), 1.23 (s, 3H, Me^b).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 146.1 (C3), 143.6 (C8), 140.8 (C4), 120.0 (C2), 114.4 (C6), 113.5 (C7), 101.7 (C5), 44.1 (C1), 41.0 (NMe_2), 30.5 (Me^b), 24.8 (Me^a).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.15 / 113.5 (C7), 5.97 / 114.4 (C6), 5.79 / 101.7 (C5), 4.96 / 120.0 (C2), 2.56 / 41.0 (NMe_2), 1.49 / 24.8 (Me^a), 1.23 / 30.5 (Me^b).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 6.15 / 143.6, 140.8, 114.4, 101.7 (7-H / C8, C4, C6, C5), 2.56 / 146.1, 41.0 (NMe_2 / C3, NMe_2), 1.23 / 143.6, 120.0, 44.1, 24.8 (Me^b / C8, C2, C1, Me^a).

Tentatively assigned as *meso*-**10b**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.03 (dd, $^{3}J_{HH}$ = 3.1 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, 7-H), 5.89 (dd, $^{3}J_{HH}$ = 2.8 Hz, $^{4}J_{HH}$ = 1.5, 1H, 5-H), 5.81 (ddd, $^{3}J_{HH}$ = 3.1 Hz, $^{3}J_{HH}$ = 2.8 Hz, J_{HH} = 1.0 Hz, 1H, 6-H), 4.96 (s, 1H, 2-H), 2.60 (s, 6H, NMe_2), 1.50 (s, 3H, Me^a), 1.25 (s, 3H, Me^b).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 145.9 (C3), 143.2 (C8), 142.0 (C4), 119.6 (C2), 112.0 (C7), 110.0 (C6), 104.1 (C5), 44.1 (C1), 41.0 (NMe_2), 30.4 (Me^b), 25.0 (Me^a).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.03 / 112.0 (C7), 5.89 / 104.1 (C5), 5.81 / 110.0 (C6), 4.96 / 119.6 (C2), 2.60 / 41.0 (NMe_2), 1.50 / 25.0 (Me^a), 1.25 / 30.4 (Me^b).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 6.03 / 143.2, 142.0, 110.0, 104.1 (7-H / C8, C4, C6, C5), 2.60 / 145.9, 41.0 (NMe_2 / C3, NMe_2), 1.25 / 143.2, 119.6, 44.1, 25.0 (Me^b / C8, C2, C1, Me^a).

^{1}H{^{1}H, NOE} NMR (500 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 6.15 / 5.97, 5.79, 2.56, 1.49, 1.23 (^{rac}7-H / ^{rac}6-H, ^{rac}5-H, $^{rac}NMe_2$(weak), $^{rac}Me^a$, $^{rac}Me^b$); 6.03 / 5.89, 5.81, 2.60, 1.50, 1.25 (^{meso}7-H / ^{meso}5-H, ^{meso}6-H, $^{meso}NMe_2$, $^{meso}Me^a$, $^{meso}Me^b$); 2.60 / 5.89, 4.96 ($^{meso}NMe_2$ / ^{meso}5-H, ^{rac,meso}2-H); 2.60 (weak), 2.56 / 5.89 (weak), 5.79, 4.96 ($^{meso}NMe_2$, $^{rac}NMe_2$ / ^{meso}5-H, ^{rac}5-H, ^{rac,meso}2-H); 1.25, 1.23 / 6.15, 6.03, 4.96 ($^{meso}Me^b$, $^{rac}Me^b$ / ^{rac}7-H, ^{meso}7-H, ^{rac,meso}2-H).

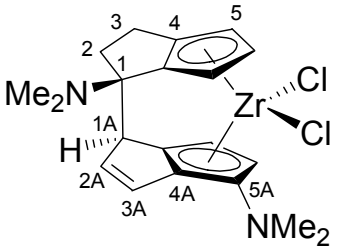


^{1}H NMR (500 MHz, C_6D_6 (*), 298 K) of *rac*-**10b** / *meso*-**10b** and free ligand **2b**).

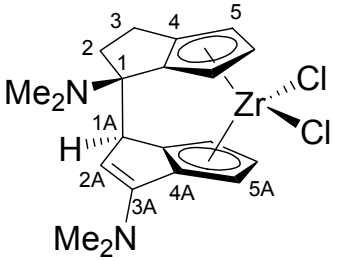


^{13}C{^{1}H} NMR (126 MHz, C_6D_6 (*), 298 K) of *rac*-**10b** / *meso*-**10b** and the free ligand **2b**.

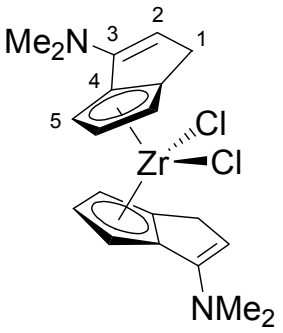
Zirconium Complexes 9c, 11c and 10c.



For **9c:** ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.69 (t, $^{3}J_{HH}$ = 3.2 Hz, 1H, 6-H), 6.41 (m, 1H, 2A-H), 6.32 (ddd, $^{3}J_{HH}$ = 5.7 Hz, J_{HH} = 1.8 Hz, J_{HH} = 0.8 Hz, 1H, 3A-H), 6.19 (dd, $^{3}J_{HH}$ = 3.2, $^{4}J_{HH}$ = 1.6 Hz, 1H, 5-H), 5.55 (dt, $^{3}J_{HH}$ = 3.0 Hz, J_{HH} = 0.8 Hz, 1H, 7A-H), 5.43 (dd, $^{3}J_{HH}$ = 3.0 Hz, J_{HH} = 0.8 Hz, 1H, 6A-H), 5.40 (dd, $^{3}J_{HH}$ = 3.2 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, 7-H), 3.62 (m, 1H, 1A-H), 2.73 (s, 6H, 5A-NMe_2), 2.75, 2.35 (each m, each 1H, 3-H[t]), 2.40, 1.95 (each m, each 1H, 2-H[t]), 1.82 (s, 6H, 1-NMe_2).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 146.8 (C5A), 137.1 (C2A), 128.1 (C3A), 126.7 (C6), 114.8 (C5), 104.9 (C7), 104.4 (C7A), 99.2 (C6A), 74.4 (C1), 57.2 (C1A), 40.6 (5A-NMe_2), 39.0 (1-NMe_2), 31.3 (C2[t]), 28.4 (C3[t]), n.o. (C4, C8, C4A, C8A).([t] tentatively assigned).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.69 / 126.7 (C6), 6.41 / 137.1 (C2A), 6.32 / 128.1 (C3A), 6.19 / 114.8 (C5), 5.55 / 104.4 (C7A), 5.43 / 99.2 (C6A), 5.40 / 104.9 (C7), 3.62 / 57.2 (C1A), 2.73 / 40.6 (5A-NMe_2), 2.75, 2.35 / 28.4 (C3), 2.40, 1.95 / 31.3 (C2), 1.82 / 39.0 (1-NMe_2).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 2.73 / 146.8, 40.6 (5A-NMe_2 / C5A, 5A-NMe_2), 1.82 / 74.4, 39.0 (1-NMe_2 / C1, 1-NMe_2).
^{1}H,^{1}H 1dtocsy (500 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 5.55 / 6.41, 6.32, 5.43, 3.62 (7A-H / 2A-H, 3A-H, 6A-H, 1A-H), 6.41 / 6.32, 5.55, 5.43, 3.62, (2A-H / 3A-H, 7A-H, 6A-H, 1A-H).



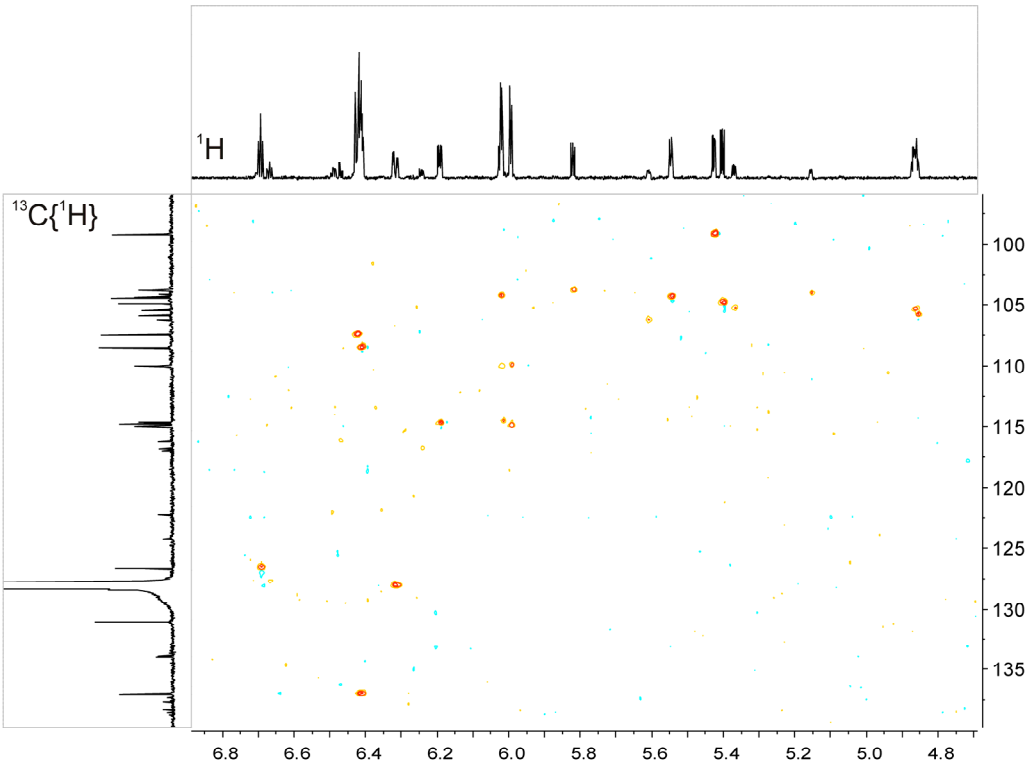
For **11c**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.67 (dd, $^{3}J_{HH}$ = 3.3 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H, 6-H), 6.49 (m, 1H, 6A-H), 6.47 (dd, $^{3}J_{HH}$ = 3.3 Hz, J_{HH} = 1.4 Hz, 1H, 5A-H), 6.24 (dd, $^{3}J_{HH}$ = 3.3, J_{HH} = 1.7 Hz, 1H, 5-H[t]), 5.61 (m, 1H, 7A-H), 5.37 (dd, $^{3}J_{HH}$ = 2.9 Hz, J_{HH} = 1.7 Hz, 1H, 7-H[t]), 5.16 (m, 1H, 2A-H), 3.67 (m, 1H, 1A-H), 2.57 (s, 6H, 3A-NMe_2), 2.61, 2.34 (each m, each 1H, 3-H[t]), 2.36, 1.88 (each m, each 1H, 2-H[t]), 1.84 (s, 6H, 1-NMe_2).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 148.0 (C3A), 127.8 (C6), 122.2 (C6A), 116.8 (C5[t]), 116.2 (C5A), 106.3 (C7A), 105.4 (C7[t]), 104.1 (C2A), 75.3 (C1), 54.3 (C1A), 40.8 (3A-NMe_2), 39.1 (1-NMe_2), 30.7 (C2[t]), 28.1 (C3[t]), n.o. (C4, C8, C4A, C8A). ([t] tentatively assigned).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.67 / 127.8 (C6), 6.49 / 122.2 (C6A), 6.47 / 116.2 (C5A), 6.24 / 116.8 (C5), 5.61 / 106.3 (C7A), 5.37 / 105.4 (C7), 5.16 / 104.1 (C2A), 3.67 / 54.3 (C1A), 2.57 / 40.8 (3A-NMe_2), 2.61, 2.34 / 28.1 (C3), 2.36, 1.88 / 30.7 (C2), 1.84 / 39.1 (1-NMe_2).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 2.57 / 148.0, 40.8 (3A-NMe_2 / C3A, 3A-NMe_2), 1.84 / 75.3, 39.1 (1-NMe_2 / C1, 1-NMe_2).
^{1}H,^{1}H 1dtocsy (500 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 5.61 / 6.49, 6.47 (7A-H / 6A-H, 5A-H), 5.16 / 3.67, 2.57 (2A-H / 1A-H, 3A-NMe_2).
^{1}H{^{1}H, NOE} NMR (500 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 5.16 / 2.57, 1.84 (2A-H / 3A-NMe_2, 1-NMe_2)



Tentatively assigned as *rac*-**10c**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 4.87 (t, $^{3}J_{HH}$ ~ 2.5 Hz, 1H, 2-H), 3.14 (ddm, $^{2}J_{HH}$ ~ 22 Hz, $^{3}J_{HH}$ ~ 2.5 Hz, 1H, 1-H), 2.92 (each ddm, $^{2}J_{HH}$ ~ 22 Hz, $^{3}J_{HH}$ ~ 2.5 Hz, 1H, 1-H'), 2.55 (s, 6H, NMe_2).
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 148.6 (C3), 105.5 (C2), 41.1 (NMe_2), 32.1 (C1).
$^{1}H,^{13}C$ ghsqc (500 / 126 MHz, C_6D_6, 298 K): $\delta^{1}H/\ \delta^{13}C$ = 4.87 / 105.5 (C2), 3.14, 2.92 / 32.1 (C1), 2.55 / 41.1 (NMe_2).
$^{1}H,^{13}C$ ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] $\delta^{1}H/\ \delta^{13}C$ = 2.55 / 148.6, 41.1 (NMe_2 / C3, NMe_2).

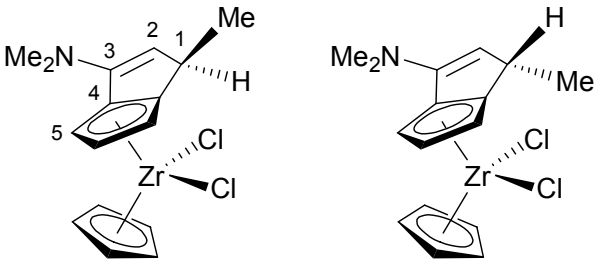
Tentatively assigned as *meso*-**10c**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 4.86 (t, $^{3}J_{HH}$ ~ 2.5 Hz, 1H, 2-H), 3.10 (ddm, $^{2}J_{HH}$ ~ 22 Hz, $^{3}J_{HH}$ ~ 2.5 Hz, 1H, 1-H), 2.87 (ddm, $^{2}J_{HH}$ ~ 22 Hz, $^{3}J_{HH}$ ~ 2.5 Hz, 1H, 1-H), 2.56 (s, 6H, NMe_2).
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 148.6 (C3), 105.9 (C2), 41.2 (NMe_2), 32.0 (C1).
$^{1}H,^{13}C$ ghsqc (500 / 126 MHz, C_6D_6, 298 K): $\delta^{1}H/\ \delta^{13}C$ = 4.86 / 105.9 (C2), 3.10, 2.87 / 32.0 (C1), 2.56 / 41.2 (NMe_2).
$^{1}H,^{13}C$ ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] $\delta^{1}H/\ \delta^{13}C$ = 2.56 / 148.6, 41.2 (NMe_2 / C3, NMe_2).

For both isomers of **10c** without assignment: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.02 (m, 3H), 5.99 (m, 2H), 5.82 (dd, J_{HH} = 2.6 Hz, J_{HH} = 2.0 Hz, 1H) (5,6,7-H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 115.0, 114.7, 110.12, 110.05, 104.1, 103.8 (C5,6,7), n.o. (C4, C8).
$^{1}H,^{13}C$ ghsqc (500 / 126 MHz, C_6D_6, 298 K): $\delta^{1}H/\ \delta^{13}C$ = 6.02 / 114.7, 110.12, 104.1; 5.99 / 115.0, 110.05; 5.82 / 103.8 (C5,6,7).



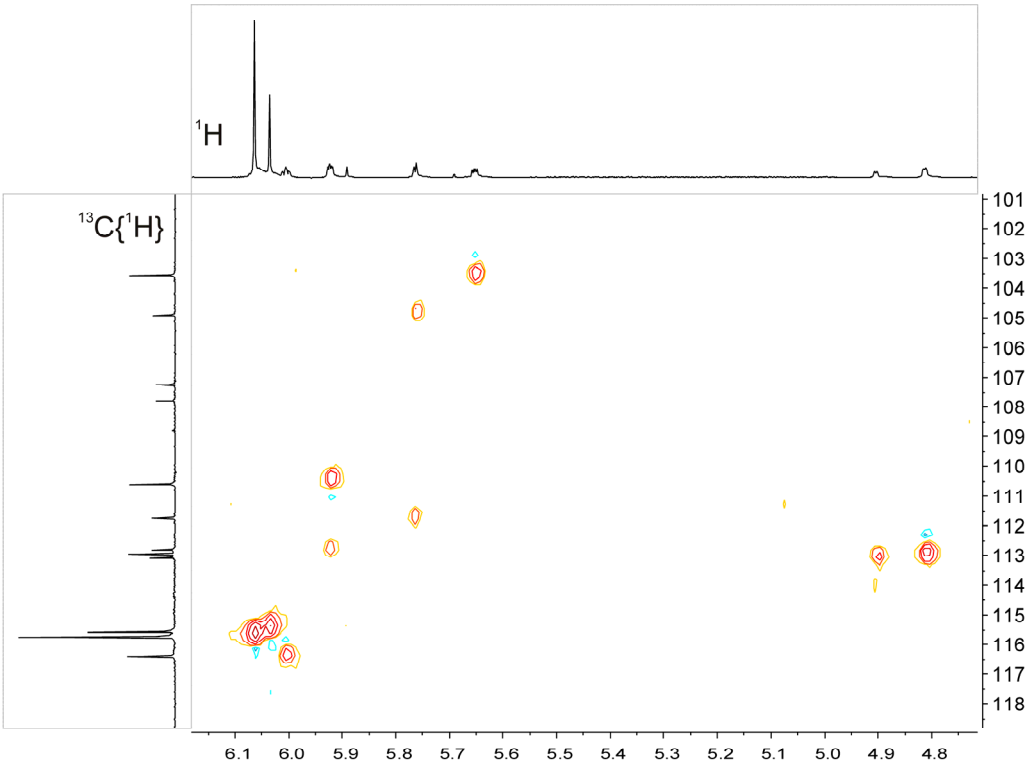
Olefinic area of the ^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K) experiment of the *rac*-**10c** : *meso*-**10c** : **9c** : **11c** mixture (1 : 1 : 3 : 1). Projections: ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum and ^{13}C{^{1}H} NMR (126 MHz) spectrum.

Zirconium Complexes 12a.



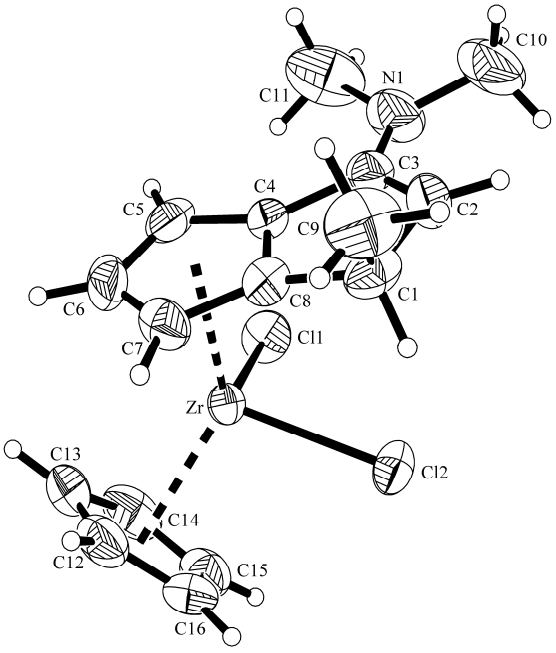
For (p-*R**, 1-*R**)-**12a**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.06 (m, 5H, Cp), 6.00 (m, 1H, 6-H), 5.92 (m, 1H, 7-H), 5.65 (m, 1H, 5-H), 4.81 (m, 1H, 2-H), 3.30 (m, 1H, 1-H), 2.49 (s, 6H, NMe_2), 1.09 (d, $^{3}J_{HH}$ = 7.3 Hz, 3H, Me).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 147.4 (C3), 143.6 (C8), 136.8 (C4), 116.4 (C6), 115.8 (Cp), 113.0 (C2), 110.6 (C7), 103.6 (C5), 41.01 (NMe_2), 39.1 (C1), 19.2 (Me).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.06 / 115.8 (Cp), 6.00 / 116.4 (C6), 5.92 / 110.6 (C7), 5.65 / 103.6 (C5), 4.81 / 113.0 (C2), 3.30 / 39.1 (C1), 2.49 / 41.01 (NMe_2), 1.09 / 19.2 (Me).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 4.81 / 143.6, 136.8, 39.1 (2-H / C8, C4, C1), 2.49 / 147.4, 41.01 (NMe_2 / C3, NMe_2), 1.09 / 143.6, 113.0, 39.1 (Me / C8, C2, C1).
^{1}H{^{1}H, NOE} NMR (500 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 2.49 / 5.65, 4.81 (NMe_2 / 5-H, 2-H), 1.09 / 5.92, 4.81, 3.30 (Me / 7-H (weak), 2-H, 1-H).

For (p-*R**, 1-*S**)-**12a**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 6.03 (m, 5H, Cp), 5.92, 5.77, 5.76 (each m, each 1H, 5,6,7-H), 4.90 (m, 1H, 2-H), 3.17 (m, 1H, 1-H), 2.56 (s, 6H, NMe_2), 1.20 (d, $^{3}J_{HH}$ = 7.4 Hz, 3H, Me).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 147.6 (C3), 142.3 (C4), 138.5 (C8), 115.6 (Cp), 113.1 (C2), 112.8, 111.8, 104.9 (C5,6,7), 40.97 (NMe_2), 38.4 (C1), 17.0 (Me).
^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.03 / 115.6 (Cp), 5.92 / 112.8, 5.77 / 111.8, 5.76 / 104.9 (C5,6,7), 4.90 / 113.1 (C2), 3.17 / 38.4 (C1), 2.56 / 40.97 (NMe_2), 1.20 / 17.0 (Me).
^{1}H,^{13}C ghmbc (500 / 126 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 4.90 / 142.3, 138.5, 38.4 (2-H / C4, C8, C1), 2.56 / 147.6, 40.97 (NMe_2 / C3, NMe_2), 1.20 / 138.5, 113.1, 38.4 (Me / C8, C2, C1).
^{1}H{^{1}H, NOE} NMR (500 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 1.20 / 6.03, 4.90, 3.17 (Me / Cp, 2-H, 1-H).



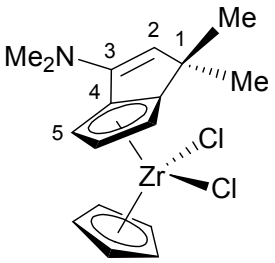
Olefinic area of the ^{1}H,^{13}C ghsqc (500 / 126 MHz, C_6D_6, 298 K) experiment of the 2:1 mixture of (p-*R**, 1-*R**)-**12a** / (p-*R**, 1-*S**)-**12a**. Projections: ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum and ^{13}C{^{1}H} NMR (126 MHz) spectrum.

Crystal data for $C_{16}H_{19}Cl_2NZr$ (**12a**), M = 387.44, monoclinic, space group $P2_1/n$ (No. 14), a = 13.5034(3), b = 6.6071(2), c = 19.0188(7) Å, β = 107.548(1)°, V = 1617.86(9) Å^3, D_c = 1.591 g cm^{-3}, μ = 0.999 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 10618 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 3772 independent (R_{int} = 0.048), and 2985 observed reflections [I ≥ 2σ(I)], 184 refined parameters, R = 0.053, wR^2 = 0.114.



Zirconium Complex 12b.

Anal. Calcd for $C_{17}H_{21}NCl_2Zr$: C, 50.86; H, 5.27; N, 3.49. Found: C, 50.50; H, 5.69; N, 3.65.



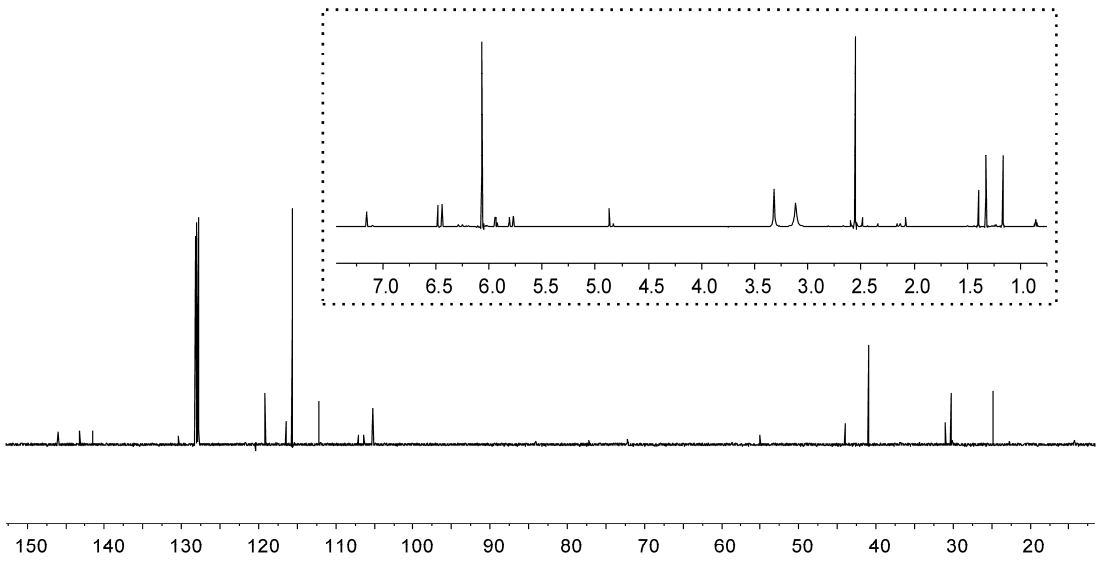
^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 6.07 (s, 5H, Cp), 5.94 (dd, $^3J_{HH}$ = 2.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, 7-H), 5.81 (tm, $^3J_{HH}$ = 2.9 Hz, 1H, 6-H), 5.77 (dd, $^3J_{HH}$ = 2.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, 5-H), 4.87 (s, 1H, 2-H), 2.55 (s, 6H, NMe_2), 1.32 (s, 3H, Me^a), 1.16 (s, 3H, Me^b) [^{a} toward Cp].

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 146.0 (C3), 143.2 (C8), 141.5 (C4), 119.2 (C2), 115.7 (Cp), 112.2 (C6), 112.1 (C7), 105.2 (C5), 43.9 (C1), 40.9 (NMe_2), 30.3 (Me^b), 24.8 (Me^a).

^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^1H/ δ^{13}C = 6.07 / 115.7 (Cp), 5.94 / 112.1 (C7), 5.81 / 112.2 (C6), 5.77 / 105.2 (C5), 4.87 / 119.2 (C2), 2.55 / 40.9 (NMe_2), 1.32 / 24.8 (Me^a), 1.16 / 30.3 (Me^b).

^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^1H/ δ^{13}C = 4.87 / 146.0, 143.2, 141.5, 43.9 (2-H / C3, C8, C4, C1), 2.55 / 146.0, 119.2, 40.9 (NMe_2 / C3, C2 (weak), NMe_2), 1.32 / 143.2, 119.2, 43.9, 30.3 (Me^a / C8, C2, C1, Me^b).

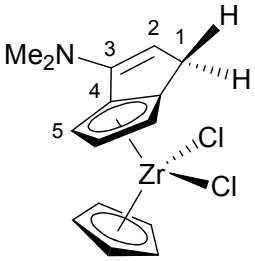
^{1}H{^{1}H, NOE} NMR (600 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 4.87 / 6.07, 2.55, 1.32, 1.16 (2-H / Cp, NMe_2, Me^a, Me^b), 2.55 / 6.07, 5.77, 4.87 (NMe_2 / Cp, 5-H, 2-H), 1.32 / 6.07, 5.94, 4.87, 1.16 (Me^a / Cp, 7-H, 2-H, Me^b).



^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K) and ^{1}H NMR (600 MHz) of **12b**.
(dme and traces of **2b**)

Zirconium Complex 12c.

Anal. Calcd for $C_{15}H_{17}NCl_2Zr$: C, 48.25; H, 4.59; N, 3.75. Found: 49.15; H, 5.31; N, 3.23.



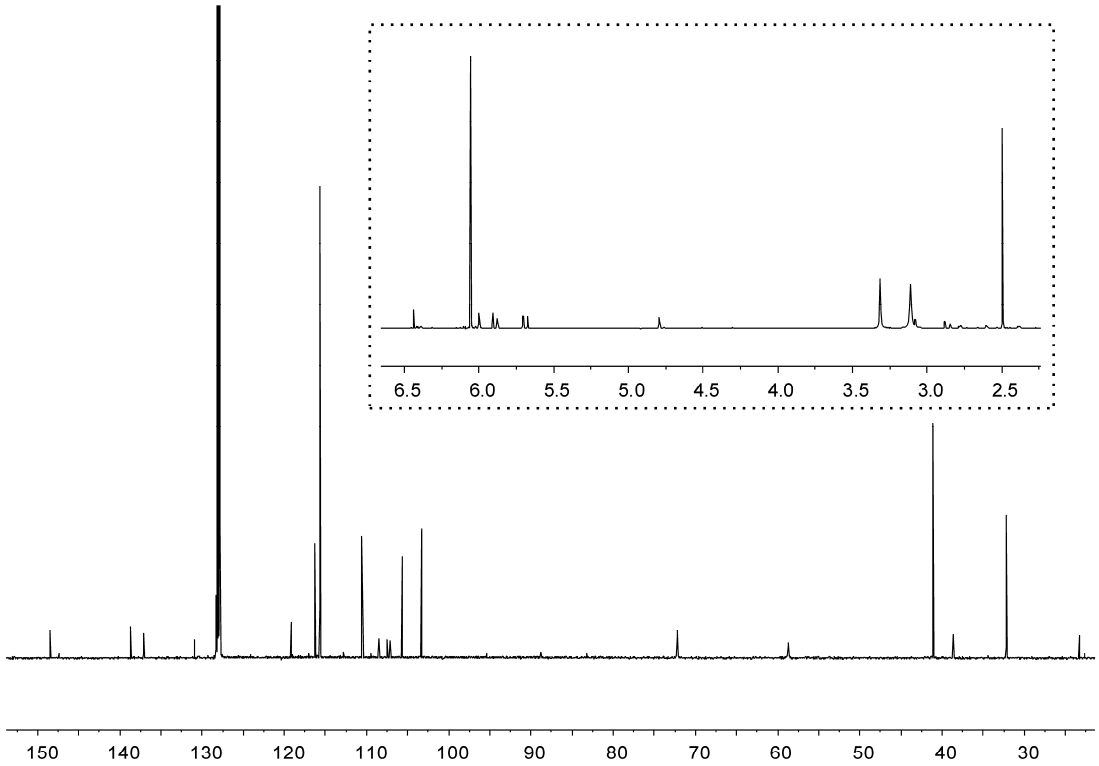
^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 6.05 (s, 5H, Cp), 5.99 (td, $^3J_{HH}$ = 3.0 Hz, J_{HH} = 1.1 Hz, 1H, 6-H), 5.87 (ddt, $^3J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = 1.6 Hz, J_{HH} = 0.7, 1H, 7-H), 5.69 (dd, $^3J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, 5-H), 4.80 (td, $^3J_{HH}$ = 2.5, J_{HH} = 1.1, 1H, 2-H), 3.10 (dd, $^2J_{HH}$ = 22.5 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, 1-H^a), 2.86 (dd, $^2J_{HH}$ = 22.5 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, 1-H^b), 2.49 (s, 6H, NMe_2).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 148.5 (C3), 138.7 (C8), 137.1 (C4), 116.3 (C6), 115.7 (Cp), 110.5 (C7), 105.7 (C2), 103.3 (C5), 41.1 (NMe_2), 32.2 (C1).

^{1}H,^{13}C ghsqc (600 / 151 MHz, C_6D_6, 298 K): δ^{1}H/ δ^{13}C = 6.05 / 115.7 (Cp), 5.99 / 116.3 (C6), 5.87 / 110.5 (C7), 5.69 / 103.3 (C5), 4.80 / 105.7 (C2), 3.10, 2.86 / 32.2 (C1), 2.49 / 41.1 (NMe_2).

^{1}H,^{13}C ghmbc (600 / 151 MHz, C_6D_6, 298 K): [selected traces] δ^{1}H/ δ^{13}C = 4.80 / 138.7, 137.1, 32.2 (2-H / C8, C4, C1), 3.10 / 148.5, 138.7, 105.7 (1-H^a / C3, C8, C2), 2.49 / 148.5, 105.7, 41.1 (NMe_2 / C3, C2, NMe_2)

^{1}H{^{1}H, NOE} NMR (600 MHz, C_6D_6, 298 K): [selected experiments] δ_{ir} / δ_{res} = 4.80 / 6.05, 3.10, 2.86, 2.49 (2-H / Cp, 1-H^a, 1-H^b, NMe_2), 3.10 / 6.05, 5.87, 4.80, 2.86 (1-H^a / Cp, 7-H, 2-H, 1-H^b), 2.49 / 6.05, 5.69, 4.80 (NMe_2 / Cp, 5-H, 2-H).



^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K) an ^{1}H NMR (600 MHz) of **12c** (dme and traces of **2c**).

Crystal data for $C_{15}H_{17}Cl_2NZr$ (**12c**), M = 373.42, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 6.6449(2), b = 11.6187(3), c = 19.6379(5) Å, V = 1516.15(7) Å^3, D_c = 1.636 g cm^{-3}, μ = 1.063 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 7197 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 3548 independent (R_{int} = 0.032), and 3433 observed reflections [I ≥ 2σ(I)], 174 refined parameters, R = 0.038, wR^2 = 0.084, Flack parameter 0.15(7).