SUPPORTING INFORMATION

Axially Chiral Racemic Half-Sandwich Nickel(II) Complex by Ring-Closing Metathesis

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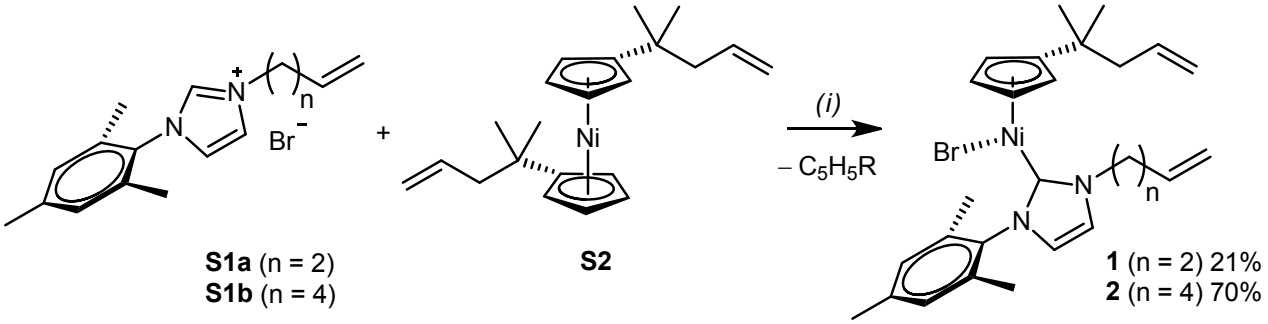
Experimental Details

General. All manipulations (except work-up of the catalytic tests) were performed under an inert atmosphere of argon using Schlenk tube techniques. Toluene, hexanes, ether, THF were purified by distillation from Na-K alloy with benzophenone as indicator; CH_2Cl_2 was distilled from CaH_2. 4-Bromo-1-butene and 6-bromo-1-hexene were distilled under reduced pressure. [Ru(=CHPh)Cl_2(PCy_3)(SIMes)] was purchased from Aldrich. A solution of MAO in toluene (10% wt. from Aldrich) was used as received. Salts **S1a** and **S1b** were obtained from *N*-mesitylimidazole[1] and 4-bromo-1-butene or 6-bromo-1-hexene, respectively, according to the published procedure.[2]

NMR spectra were recorded at ambient temperature on a Mercury-400BB spectrometer operating at 400 MHz for ^{1}H NMR and at 101 MHz for ^{13}C NMR or on a Varian NMR System 500 MHz (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). EI MS (70 eV) were measured on an AutoSpec Premier (Waters) spectrometer. Elemental analyses were performed on a CHNS Elementar Vario EL III analyser. Catalytic tests were performed as described previously: Suzuki cross-coupling,[3] styrene polymerization,[4] methyl methacrylate polymerization.[5,6]

1,1'-Bis(1,1-dimethylbut-3-enyl)nickelocene (S2). (1,1-Dimethylbut-3-enyl)cyclopentadiene[7] (4.36 mmol, 1.50 mL, solution in THF) was added to finely cut potassium (0.50 g, 13 mmol) in THF (3.0 mL) at 0°C. The resulting mixture was stirred and warmed to ambient temperature until the gas evolution stopped. This solution was cannulated to a suspension of [$NiCl_2(NH_3)_6$] (0.50 g, 2.18 mmol) in THF (15 mL). The reaction mixture was stirred and heated to reflux for 6 hours, and then evaporated to dryness. The residue was extracted with hexanes (2 × 20 mL), the extracts were passed through a short layer of Al_2O_3. Nickelocene

derivative **S2** was obtained as a green oil (0.71 g, 2.0 mmol) after the solvent removal. **EI-MS** (70 eV, ^{58}Ni) *m/z* (rel. intensity): 352 (M^+, 35), 311 (8), 270 (13), 205 (100), 163 (51), 124 (31), 91 (15), 41 (38). This crude product was used in the next step without further purification.



Scheme S1. Synthesis of complexes **1** and **2**: *(i)* THF, heating.

Complex 1. Nickelocene derivative **S2** (0.60 mmol, a THF solution) was added to a suspension of **S1a** (0.175 g, 0.545 mmol) in THF (15 mL). The resulting mixture was stirred and heated to reflux for 5 h. The volatiles were removed under vacuum, and the residue was extracted with hexanes (2 × 10 mL). The extracts were filtered through Celite and reduced in volume. Complex **1** (0.059 g, 0.11 mmol, 21%, red solid) was obtained after repeated crystallizations from hexanes at -78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.14 (d, J = 1.6 Hz, 1H, ^{Im}C*H*), 7.06 (bs, 2H, *m*-Ar*H*), 6.82 (d, J = 1.5 Hz, 1H, ^{Im}C*H*), 5.93 (ddt, J = 13.8, 8.2, 5.5 Hz, 1H, -C*H*=CH_2), 5.68 (ddt, J = 13.7, 8.1, 5.9 Hz, 1H, -C*H*=CH_2), 5.13 (m, 4H, =CH_2), 4.93 (m, 4H, C_5H_4R), 2.81 (bs, 2H, CH_2), 2.41 (s, 3H, *p*-CH_3), 2.10 (dd, J = 6.2, 3.1 Hz, 2H, CH_2), 1.06 (s, 6H, C(CH_3)$_2$). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ (ppm): 165.1, 139.0, 136.9, 135.8, 134.4, 129.1 (b), 127.3, 123.5, 122.5, 117.6, 116.6, 91.5 (b), 51.8, 48.6, 35.4, 34.3, 27.3, 21.1, 18.0 (b). **EI-MS** (70 eV, ^{58}Ni, ^{79}Br) *m/z* (rel. intensity): 524 (M^+, 10), 444 ([M-HBr]$^+$, 3), 352 (31), 239 (100), 205 (81), 163 (37), 124 (14), 91(11). Calc. for $C_{27}H_{35}BrN_2Ni$: C 61.63, H 6.70, N 5.32, found C 61.42, H 6.67, N 5.24.

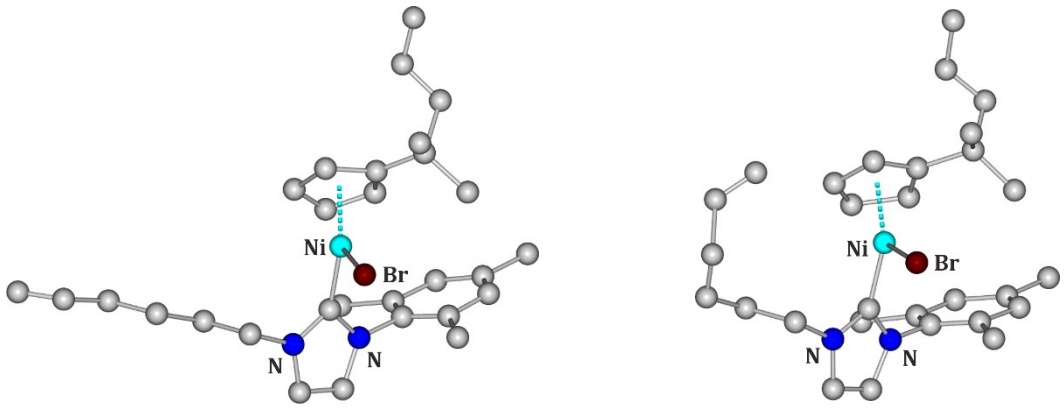
Complex 2 was obtained similarly as described for **1** from **S2** (0.220 g, 0.60 mmol) and **S1b** (0.210 g, 0.60 mmol) in THF (5.0 mL) for 24 h. Yield: 0.250 g, 0.47 mmol, 70% (red solid). **^{1}H NMR** (400 MHz, C_6D_6) δ (ppm): 6.80 (bs, 2H, *m*-Ar*H*), 6.32 (d, J = 1.2 Hz, 1H, ^{Im}C*H*), 5.98 (d, J = 1.6 Hz, 1H, ^{Im}C*H*), 5.90-5.80 (m, 1H, -C*H*=CH_2),5.79-5.70 (m, 1H, -C*H*=CH_2), 5.05-4.98 (m, 8H, -CH=CH_2 and C_5H_4R), 2.29 (d, J = 5.9 Hz, CH_2), 2.13 (s, 3H, *p*-ArCH_3), 1.98 (m, 2H, CH_2), 1.78 (bs, 2H, CH_2), 1.34 (m, partially overlapping with singlet at 1.31, CH_2), 1.31 (s, C(CH_3)$_2$, 8H for m and s). **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6) δ (ppm): 166.2, 138.9, 138.5, 137.5, 136.3, 128.3, 127.9, 126.7, 123.1, 122.1, 116.8, 115.1, 92.0 (b), 52.6, 49.2, 34.8, 33.7, 30.5, 27.7, 26.2, 21.0, 18.0 (b). **EI-MS** (70 eV, ^{58}Ni, ^{79}Br) *m/z* (rel. intensity): 552

(M^+, 31), 472 ([M-HBr]$^+$, 11), 431 (22), 415 (31), 352 (47), 325 (46), 267 (71), 205 (100), 163 (59), 124 (33), 91 (32). Calc. for $C_{29}H_{39}BrN_2Ni$: C 62.85, H 7.09, N 5.05, found C 62.65, H 6.94, N 4.79.

Complex 4. A solution of complex **2** (0.173 g, 0.312 mmol) in toluene (22 mL) was added to a toluene (12 mL) solution of [Ru(=CHPh)Cl_2(PCy_3)(SIMes)] (16.6 mg, 0.0195 mmol, 6%$_{mol}$). The reaction mixture was vigorously stirred at 100°C for 12 h and overnight at room temperature. The reaction was quenched with a few drops of ethyl vinyl ether and evaporated to dryness. The solid residue was extracted with ether (50 mL), the extracts were filtered through Celite and concentrated. Complex **4** was obtained as red crystals from the extracts (0.063 g, 36%).**^{1}H NMR** (500 MHz, C_6D_6) δ (ppm) (*E* isomer): 6.90 (s,1H, *m*-Ar*H*), 6.62 (s,1H, *m*-Ar*H*), 6.32 (d, *J* = 1.9 Hz, 1H, ^{Im}C*H*), 6.21 (td, *J* = 13.5, 5.0 Hz, 1H, =C*H*), 5.97 (d, *J* = 1.9 Hz 1H, ^{Im}C*H*), 5.43-5.38 (m, 1H, =C*H*), 4.96 (dt, *J* = 3.0, 2.0 Hz, 1H, C_5H_4R), 4.86 (dt, *J* = 5.0, 1.9 Hz, 1H, C_5H_4R), 4.61 (q, *J* = 2.0 Hz, 1H, C_5H_4R), 4.02 (m, 1H, C_5H_4R), 3.43 (td, *J* = 13.3, 4.0 Hz, 1H, CH_2), 2.74 (s, 3H, *o*-CH_3), 2.51 (overlapping m, 3H, -CH_2), 2.38 (d, *J* = 10.3 Hz, 1H, CH_2), 2.36 (d, *J* = 10.4 Hz, 1H, CH_2), 2.26 (overlapping m, 2H, CH_2), 2.16-2.13 (m, 2H, CH_2), 2.12 (s, 3H, *p*-CH_3), 1.50 (s, 3H, *o*-CH_3), 1.26 (s, 3H, C(CH_3)$_2$), 1.01 (s, 3H, C(CH_3)$_2$). **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6) δ (ppm) (*E* isomer): 165.3, 138.4, 132.2, 129.6, 128.9, 128.2, 127.5, 127.4, 122.7, 122.1, 95.1, 93.0, 89.7, 85.2 (b), 82.5 (b), 78.0, 50.6, 45.0, 34.9, 31.5, 30.1, 29.3, 28.7, 24.5, 20.6, 20.0, 17.2. **EI-MS** (70 eV, ^{58}Ni, ^{79}Br) *m/z* (rel. intensity): 524 (M^+, 30), 444 ([M-HBr]$^+$, 24), 388 (41), 387 (100), 338 (9), 282 (26), 281 (78), 91 (16). HRMS calc. for $C_{27}H_{35}{}^{79}BrN_2{}^{58}Ni$: 524.1337; found: 524.1332. Calc. for $C_{27}H_{35}BrN_2Ni$: C 61.63, H 6.70, N 5.32, found C 61.26, H 6.66, N 5.26.

X-ray diffraction studies. Single crystals of **1** and **2** were grown from hexanes at −78°C. Crystals of **4** suitable for X-ray measurements were obtained from Et_2O at −20°C. The X-ray diffraction measurements of all three complexes were carried out on an either Bruker AXS Kappa APEX II Ultra diffractometer equipped with a TXS rotating anode (Mo-K_α radiation, λ = 0.71073 Å), or Rigaku Oxford Diffraction SuperNova instrument with microfocus Mo X-ray source. In all cases the crystal was maintained at low temperature with the use of Oxford Cryosystems nitrogen gas-flow device (100 K and 112 K for **1** and **4**, respectively). Data collection strategies were optimized and monitored applying the appropriate algorithms implemented within the *APEX2*[8] or *CRYSALISPRO*[9] suites of programs, respectively. Unit cell parameter determination and raw diffraction image processing were performed with the native diffractometer software. All structures were solved using a charge-flipping method

implemented in the *SUPERFLIP* program[10] and refined with the *JANA* package[11] within the independent atom model (IAM) approximation. Scattering factors, in their analytical form, were taken from the International Tables for Crystallography.[12] It is important to note that due to the severe disorder and very poor data quality the refinement of structure **2** was not possible (despite fairly good quality of X-ray diffraction patterns). Therefore only qualitative confirmation of the chemical composition and crystal structure was established for compound **2** (Figure S1). In the remaining cases, orientations of methyl groups were determined on the basis of Fourier residual maps. In the case of compound **4** a small portion (*ca.* 3%) of the *Z* isomer is present in the crystal lattice (Figure S2), however, the full refinement is not possible. Final crystal, data collection and refinement parameters for compounds **1** and **4** are summarized in associated CIF files, which are present in the Supporting Information, or can be retrieved from the Cambridge Structural Database[13] (deposition numbers: 1504275-6).



(a) (b)

Figure S1. Molecular structure of two symmetry-independent species present in the crystal structure of **2** (space group: $P2_1/n$, a = 20.554(2) Å, b = 11.3298(11) Å, c = 27.610(3) Å, β = 105.8624(19)°). Note that the structure is severely disordered and no full refinement is possible. Both symmetry-independent molecules (panels (a) and (b)) are shown separately with different orientations to indicate similarity with complex **1** (Figure 1a).

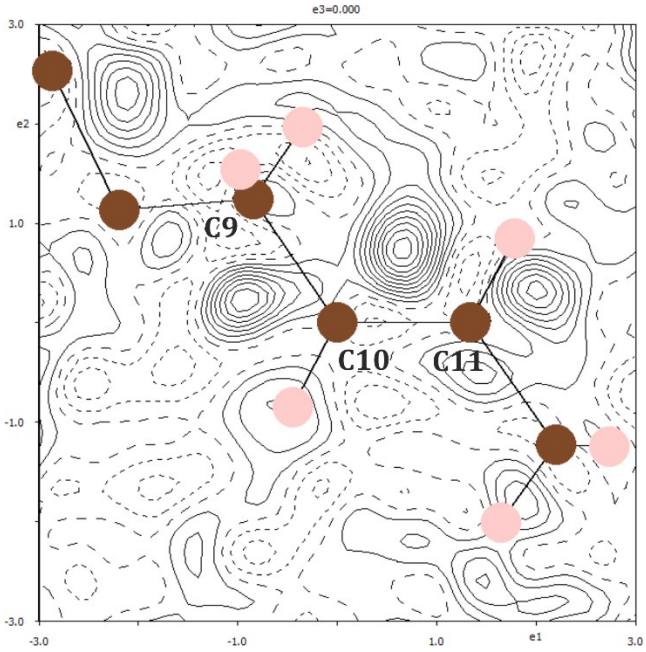


Figure S2. Fourier residual density map in the vicinity of the C10=C11 double bond in the crystal structure of complex **4**; the *Z* configuration is clearly visible (though the refinement was not possible). Largest residual density peak amounts to about 0.5 e·Å^{-3}.

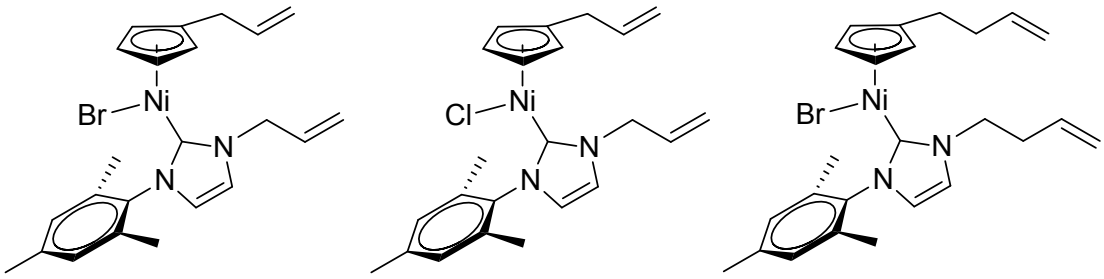


Figure S3. Examples of complexes that do not undergo efficient RCM under the studied conditions.

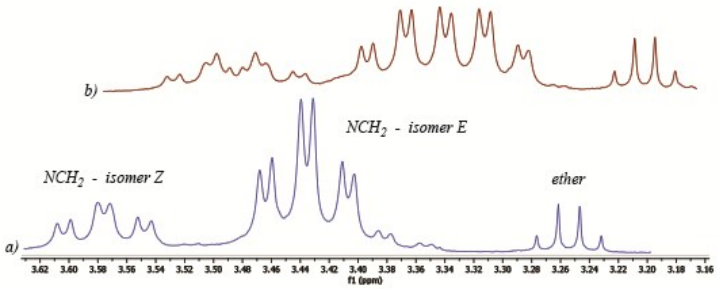
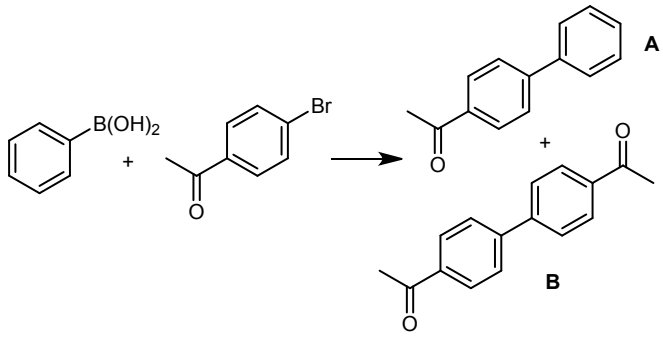
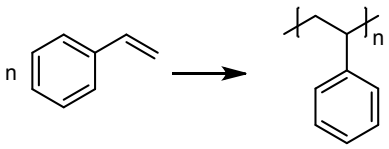
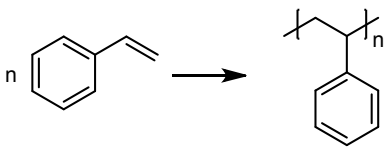
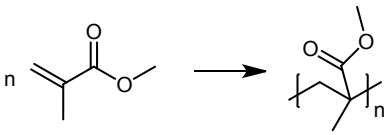
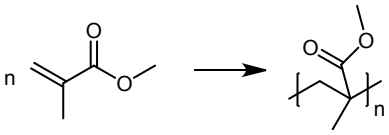


Figure S4. (*a*) Selected sections of ^{1}H NMR (500 MHz, C_6D_6) spectrum of complex **4**, signals assigned to the -NC*H*$_2$ proton of *Z* and *E* isomers; (*b*) the same sample after addition of *ca.* equimolar amount of chiral reagent **5** (brown top line).

Table S1. Catalytic activity of racemic complex **4** in the C-C bond formation reactions.

Entry	Reaction	Yield [%]	Comments
1[a]		58	B product was not detected
2[b]		100	M_n 8 900 M_w/M_n2.7 atactic
3[c]		20	M_n 9 300 M_w/M_n3.0 atactic
4[d]		20	65:27:8[e]
5[f]		3	67:23:10[e]

[a] 3%$_{mol}$ of **6** in toluene, K_3PO_4 (2.6 equiv), 90°C, 1 h.
[b] styrene:Ni = 15 000:1, Al:Ni = 300:1, toluene, 30 min at 20°C, then 3 h at 50°C.
[c] styrene:Ni = 15 000:1, Al:Ni = 100:1, toluene, 30 min at 20°C, then 3 h at 50°C.
[d] MMA:Ni = 1000:1, Al:Ni = 100:1, toluene, 30 min at 20°C, then 3 h at 50°C.
[e] triad fraction (*rr:mr:mm*) determined by ^{1}H NMR.
[f] MMA:Ni = 1000:1, Al:Ni = 100:1, toluene, 30 min at 20°C, then 24 h at 20°C.

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[8] *APEX2*, Bruker AXS, Madison, Wisconsin, USA, **2016**.

[9] *CRYSALISPRO*, Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England, UK, **2016**.

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