SUPPORTING INFORMATION

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

Włodzimierz Buchowicz, Łukasz Banach, Radosław Kamiński, Piotr Buchalski

a Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
b Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland
* Corresponding author: e-mail: wbuch@ch.pw.edu.pl; Fax: +48 22 234 5462; Tel: +48 22 234 5150

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; CH₂Cl₂ was distilled from CaH₂. 4-Bromo-1-butene and 6-bromo-1-hexene were distilled under reduced pressure. [Ru(=CHPh)Cl₂(PCy₃)(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-mesitylimidazole¹ 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 ¹H NMR and at 101 MHz for ¹³C NMR or on a Varian NMR System 500 MHz (500 MHz for ¹H NMR and 125 MHz for ¹³C 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)cyclopentadiene⁷ (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 [NiCl₂(NH₃)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 Al₂O₃. 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.](image)

**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 $\times$ 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$_3$) $\delta$ (ppm): 7.14 (d, $J = 1.6$ Hz, 1H, Im$_2$CH), 7.06 (bs, 2H, m-ArH), 6.82 (d, $J = 1.5$ Hz, 1H, Im$_2$CH), 5.93 (ddt, $J = 13.8$, 8.2, 5.5 Hz, 1H, -CH=CH$_2$), 5.68 (ddt, $J = 13.7$, 8.1, 5.9 Hz, 1H, -CH=CH$_2$), 5.13 (m, 4H, =C$_2$H$_2$), 4.93 (m, 4H, C$_5$H$_4$R), 2.81 (bs, 2H, C$_2$H$_2$), 2.41 (s, 3H, p-ArCH$_3$), 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$_3$) $\delta$ (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$_{35}$BrNi$_2$: 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$_6$D$_6$) $\delta$ (ppm): 6.80 (bs, 2H, m-ArH), 6.32 (d, $J = 1.2$ Hz, 1H, Im$_2$CH), 5.98 (d, $J = 1.6$ Hz, 1H, Im$_2$CH), 5.90-5.80 (m, 1H, -CH=CH$_2$), 5.79-5.70 (m, 1H, -CH=CH$_2$), 2.29 (d, $J = 5.8$ Hz, C$_2$H$_2$), 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$_6$D$_6$) $\delta$ (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 C₂₉H₃₉BrN₂Ni: 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)Cl₂(PCy₃)(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%).

¹H NMR (500 MHz, C₆D₆) 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, =CH₂), 6.21 (td, J = 13.5, 5.0 Hz, 1H, =CH), 5.97 (d, J = 1.9 Hz 1H, =CH), 5.43-5.38 (m, 1H, =CH), 4.96 (dt, J = 3.0, 2.0 Hz, 1H, C₅H₄R), 4.86 (dt, J = 5.0, 1.9 Hz, 1H, C₅H₄R), 4.61 (q, J = 2.0 Hz, 1H, C₅H₄R), 4.02 (m, 1H, C₅H₄R), 3.43 (td, J = 13.3, 4.0 Hz, 1H, CH₂), 2.74 (s, 3H, o-CH₃), 2.51 (overlapping m, 3H, -CH₂), 2.38 (d, J = 10.3 Hz, 1H, CH₂), 2.36 (d, J = 10.4 Hz, 1H, CH₂), 2.26 (overlapping m, 2H, CH₂), 2.16-2.13 (m, 2H, CH₂), 2.12 (s, 3H, p-CH₃), 1.50 (s, 3H, o-CH₃), 1.26 (s, 3H, C(CH₃)₂), 1.01 (s, 3H, C(CH₃)₂).

¹³C{¹H} NMR (125 MHz, C₆D₆) 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, ⁵⁸Ni, ⁷⁹Br) 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 C₂₇H₃₅BrN₂⁵⁸Ni: 524.1337; found: 524.1332. Calc. for C₂₇H₃₅BrN₂⁵⁸Ni: 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 Et₂O 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-Kα 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 APEX2⁸ or CRYSTALS9 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\textsuperscript{10} and refined with the JANA package\textsuperscript{11} within the independent atom model (IAM) approximation. Scattering factors, in their analytical form, were taken from the International Tables for Crystallography.\textsuperscript{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 (\textit{ca.} 3\%) of the \textit{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\textsuperscript{13} (deposition numbers: 1504275-6).

\textbf{Figure S1.} Molecular structure of two symmetry-independent species present in the crystal structure of 2 (space group: \textit{P2}_1/n, \textit{a} = 20.554(2) Å, \textit{b} = 11.3298(11) Å, \textit{c} = 27.610(3) Å, \textit{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$_6$D$_6$) spectrum of complex 4, signals assigned to the -NCH$_2$ 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>Yield [%]</th>
<th>Comments</th>
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<td>1[a]</td>
<td><img src="image1" alt="Reaction 1" /></td>
<td>58</td>
<td>B product was not detected</td>
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<tr>
<td>2[b]</td>
<td><img src="image2" alt="Reaction 2" /></td>
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<tr>
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<td><img src="image3" alt="Reaction 3" /></td>
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<td>$M_n$ 9 300, $M_w/M_n$ 3.0, atactic</td>
</tr>
<tr>
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<td><img src="image4" alt="Reaction 4" /></td>
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<td>65:27:8[e]</td>
</tr>
<tr>
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<td><img src="image5" alt="Reaction 5" /></td>
<td>3</td>
<td>67:23:10[e]</td>
</tr>
</tbody>
</table>

[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.

References


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


