

SUPPORTING INFORMATION

Axial Chiral Metallocenes by Two-Fold Ring-Closing Metathesis

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General Considerations

All metathesis reactions, isolation and crystallization of **3** were carried out under an inert atmosphere using standard Schlenk techniques. Complexes **1** and **4**¹, catalysts **G1**² and **G2**³ were prepared by the reported methods. Hexanes (POCH) refers to the hydrocarbon fraction with boiling range 65-80 °C. EI (70 eV) mass spectra were recorded on an AMD-604 spectrometer. GC/MS analyses were performed on a Varian Saturn 2100T chromatograph, equipped with a DB-5 capillary column (30 m) and an ion trap detector. Analysis conditions: 60-300 °C, 3 min at 60 °C, 10 °C/min, hold time 10 min, injector 280 °C, detector 220 °C, Ar.

Representative procedure for ring-closing metathesis reactions

A solution of catalyst **G2** (0.0655 g, 0.077 mmol) in toluene (18 mL) was added to a solution of complex **1** (0.324 g, 0.628 mmol) in toluene (22 mL). The resulting solution was stirred at 40 °C for 5 days. EI-MS of the crude reaction mixture indicated that the substrate was not completely consumed, therefore another portion of catalyst **G2** (0.0646 g, 0.076 mmol) in toluene (18 mL) was added and the stirring and heating at 40 °C was continued for 5 days. The volatiles were removed under vacuum, and hexane (30 mL) was added to the solid residue. The resulting suspension was filtered through a short pad of Al₂O₃ and concentrated. Complex **3** was further purified by column chromatography (hexanes) on Al₂O₃ and crystallization at -78 °C. Yield: 0.145 g, 50%, green solid. MS (EI, 70 eV) *m/z* (⁵⁸Ni) 460 (M⁺, 100%), 406 (22, M-C₄H₆), 404 (8, M-C₄H₈), 352 (7, M-C₈H₁₂). HRMS: Calc. for

¹ D. Vos, A. Salmon, H-G. Sammler, B. Neumann and P. Jutzi, *Organometallics* 2000, **19**, 3874.

² P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100.

³ M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953.

$C_{30}H_{42}^{58}Ni$: 460.26400, found 460.26556. Elemental analysis: Found: C, 78.55; H, 9.1. Calc. for $C_{30}H_{42}Ni$: C, 78.1; H, 9.2. Crystals suitable for X-ray measurements were obtained from hexanes at $-78^{\circ}C$.

Under similar conditions with catalyst **G1**, complex **2** ($M = Ni$) was isolated as a green oil. MS (EI, 70 eV) m/z (^{58}Ni) 488 (M^+ , 100%), 447 (62, $M-C_3H_5$), 406 (45, $M-C_6H_{10}$), 364 (9), 287 (69), 246 (42), 204 (60).

GC/MS data for RCM reactions of complex **4** employing catalyst **G2**

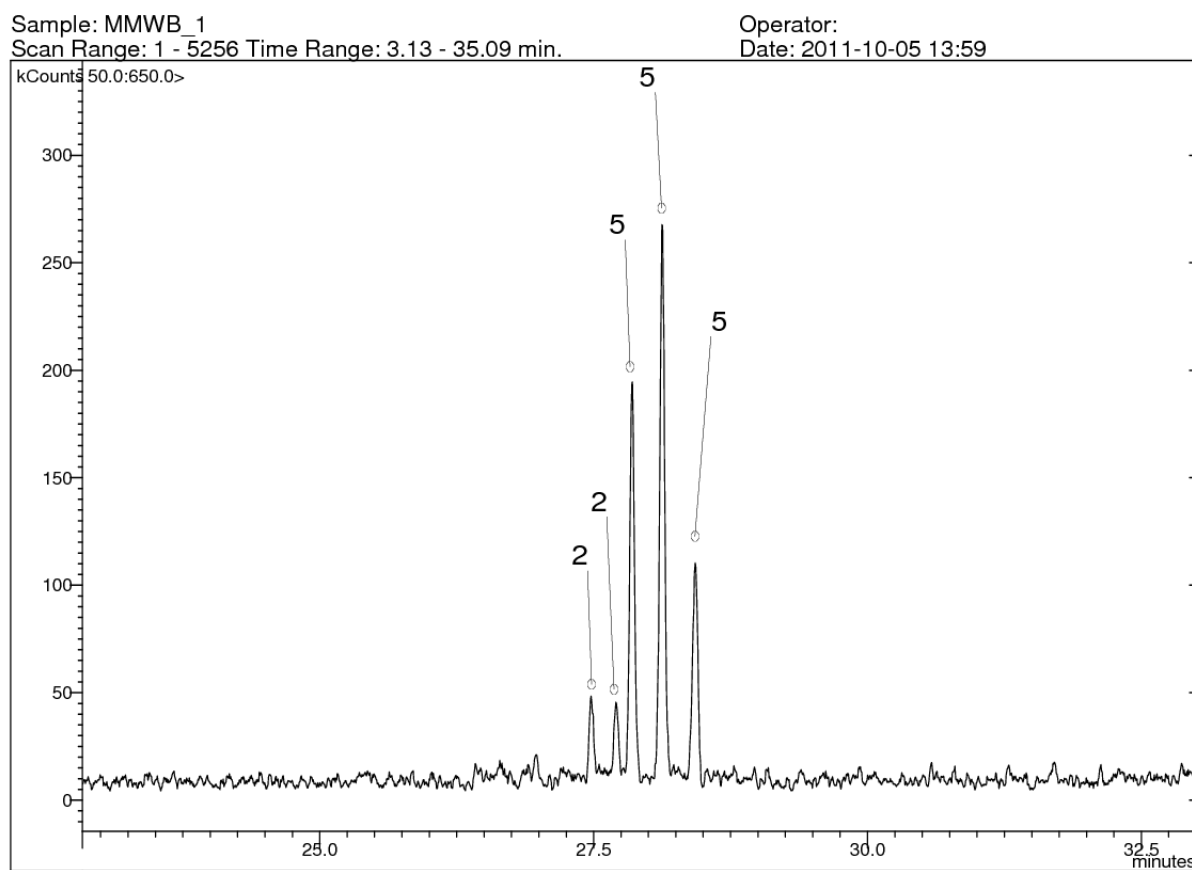


Figure S1. GC/MS chromatogram of the crude reaction mixture.

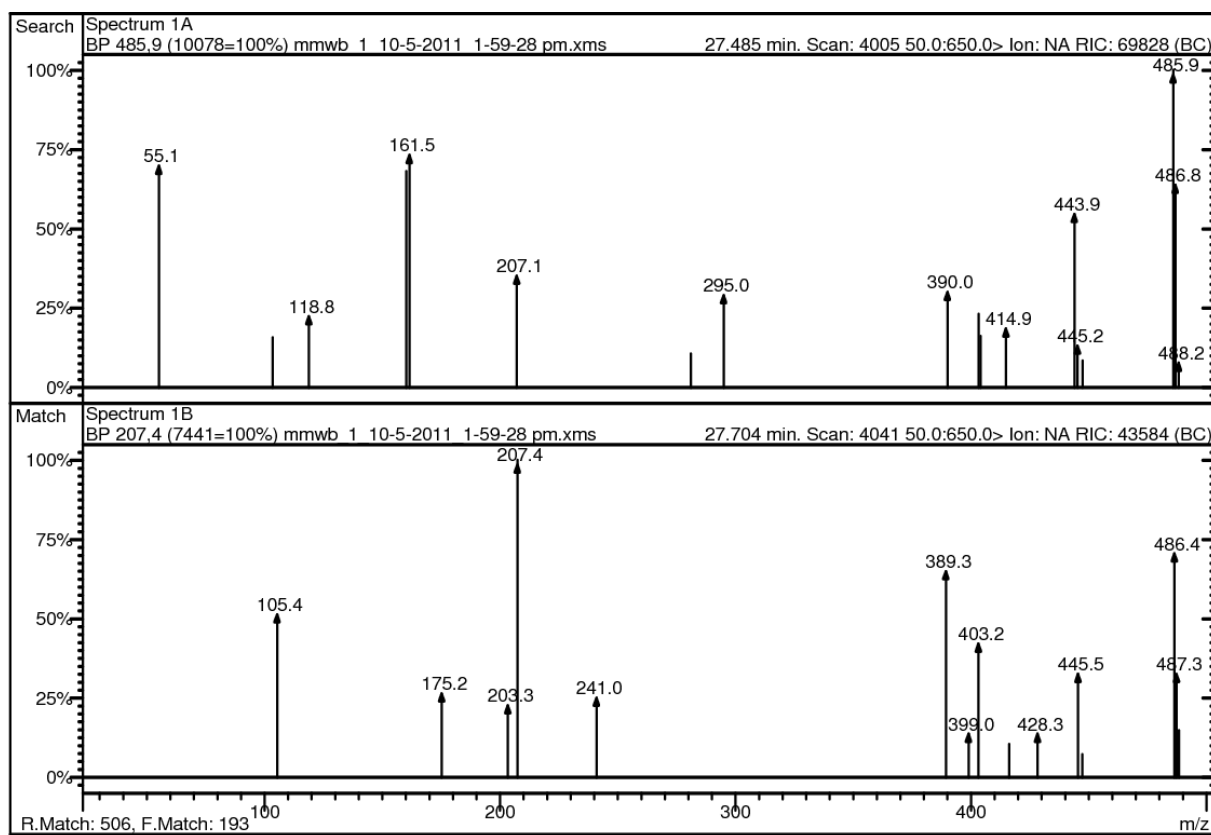


Figure S2. Mass spectra of isomers of complex **2** (M = Fe), retention times: 27.485 and 27.704 min.

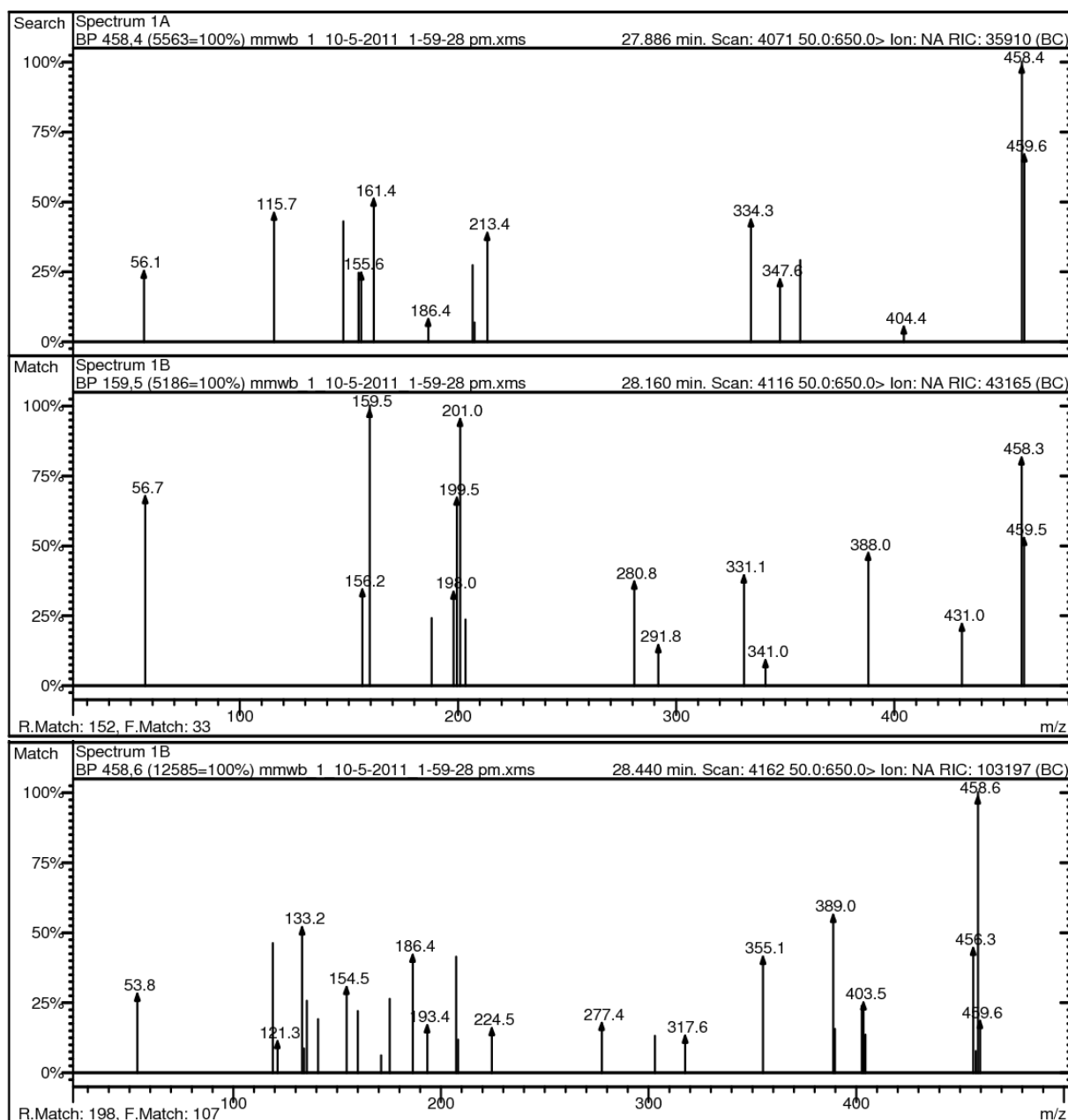


Figure S3. Mass spectra of isomers of complex **5**, retention times: 27.886, 28.160 and 28.440 min.

MS Data

MS(EI) (m/z) of **2** (M = Fe) at 27.485 min. (rel. int. - %): 486.6 (63), 485.9 (100), 445.2 (13), 443.9 (55), 414.9 (19), 403.3 (23), 390 (30), 295 (29), 207.1 (35), 161.5 (73), 160.2 (68), 118.8 (22), 103.5 (15.6), 55.1 (70).

MS(EI) (m/z) of **2** (M = Fe) at 27.704 min. (rel. int. - %): 487.3 (32), 486.4 (71), 445.5 (33), 428.3 (14), 403.2 (42), 399 (14), 389.3 (65), 241 (25), 207.4 (100), 203.3 (23), 175.2 (26), 105.4 (51).

MS(EI) (m/z) of **5** at 27.886 min. (rel. int. - %): 459.6 (67), 458.4 (100), 356.9 (29), 347.6 (22), 334.3 (44), 213.4 (39), 206.7 (27), 186.4 (10), 161.4 (51), 155.6 (25), 147.4 (43), 115.7 (46), 56.1 (25).

MS(EI) (m/z) of **5** at 28.160 min. (rel. int. - %): 459.5 (53), 458.3 (82), 431 (22), 388 (47), 341 (10), 331.1 (39), 291.8 (14), 280.8 (37), 201 (95), 199.5 (67), 198 (34), 188 (24), 159.5 (100), 156.2 (34), 56.7 (68).

MS(EI) (m/z) of **5** at 28.440 min. (rel. int. - %): 459.6 (18), 456.3 (100), 458.6 (43), 404.3 (14), 403.5 (25), 389 (56), 355.1 (41), 317.6 (13), 303 (12), 277.4 (18), 224.5 (16), 207 (41), 193.4 (16), 186.4 (42), 175.3 (26), 160 (22), 154.5 (31), 140.8 (19), 133.2 (52), 121.3 (11), 119.1 (46), 53.8 (28).

Elemental analysis: Found: C, 79.0; H, 9.4. Calc. for C₃₀H₄₂Fe: C, 78.6; H, 9.2.