0.1542 nm) showed the four peaks of MCM-41 between 1° and 12° (2θ) A d_{100} spacing of 3.99 nm was observed after calcination. In the synthesis of MCM-41 with C_{14}TMABr, a similar gel composition was made. A d_{100} spacing of 3.50 nm was observed after calcination. In the synthesis of MCM-41 with C_{10}TMABr as surfactant, the molar composition of the gel was SiO_2:TMAOH:C_{10}TMABr:Na_2O:H_2O 1.00:0.09:0.32:0.09:63.45. A d_{100} spacing of 3.03 nm was observed after calcination. In the same way MCM-41 was obtained with TEOS as Si source with the following composition: TEOS:C_{16}TMACl:NaOH:H_2O = 1.00:0.11:0.49:54.09.

In situ hydrolysis of TMA: The calcined MCM-41 samples and Aerosil 380 (Degussa) were equilibrated against a relative humidity of 79.3% at room temperature; thereafter they contained 16–27 wt% of sorbed water. The water-saturated sample was suspended in 270 mL toluene in the reactor, which was flushed with nitrogen and cooled to 273 K under continuous stirring for 1 h. TMA (2.0 M solution in toluene) was diluted in 20 mL toluene and added slowly to the suspension to give a water/Al ratio of 1. The alumoxane-MCM-41 was filtered, washed with toluene, and dried under inert atmosphere. Diffuse reflectance measurements were performed on a Varian Cary 05 UV/Vis/NIR spectrophotometer. Nitrogen sorption isotherms were recorded at 77 K with an Omnisorp 100 CX from Coulter. EPMA measurements were obtained on a JEOL JXA 733 scanning electron microscope using pure SiO_2 and Al_2O_3 as standards. ^{29}Si MAS NMR was performed on a BRUKER AMX 300 spectrometer operating at 59.62 MHz with excitation pulses of 3.5 μs and a spinning frequency of 4 kHz. ^{29}Si CP-MAS NMR was measured with a contact time of 1 ms. ^{27}Al MAS NMR measurements were carried out on a BRUKER MSL 400 with a resonance frequency of 104.26 MHz for Al, excitation pulses of 0.61 μs, and a spinning frequency of 12 kHz.

Catalyst preparation: [{C_2H_4(ind)$_2$}Zr(CH_3)$_2$] (0.036 mmol), obtained from the dichloride [{C_2H_4(ind)$_2$}ZrCl_2] by alkylation with TMA, was added under nitrogen atmosphere to the suspension of in situ prepared alumoxane-MCM-41 (Al/Zr ratios of samples were 360, 180, 90, and 40). Physisorption of MAO (85 g of a 10 wt% solution in toluene, Witco) on the calcined MCM-41 sample (0.77 g) was performed for 3 h at room temperature under inert atmosphere. The suspension was filtered and washed several times with toluene. Chemical analysis of the support shows that only 2.5 mol% of the added Al is anchored to the MCM-41 structure.

Co-oligomerization reactions: The reactions were performed for 75 min in a 600 mL water-cooled batch reactor (Parr) continuously fed with a flow of methane (491 mL min^{-1}), ethene (700 mL min^{-1}), propene (1400 mL min^{-1}), nitrogen (40 mL min^{-1}) and hydrogen (500 mL min^{-1}) at an overall pressure of 0.7 MPa. The solvent and the gases used were carefully dried over a molecular sieve (5 Å, Merck). The gas outlet was monitored by GC to calculate the conversion (methane as internal standard).

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Iterative Nucleophilic and Electrophilic Additions to Coordinated Cyclooctatetraene: An Efficient Route to *cis*-5,7-Disubstituted 1,3-Cyclooctadienes**

Jürgen Heck,* Gerhard Lange, and Oliver Reimelt

Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday

Hitherto, cyclooctatetraene (cot) played only a minor role as a starting material in the stereocontrolled synthesis of *cyclo*-C_8 compounds.[1, 2] From the point of view of synthetic chemistry, cot became more interesting as a complexing ligand.[3] It is usually functionalized by electrophilic substitution[4] and addition,[5] and more recently by photochemical reactions;[6] however, nucleophilic addition has seldom been used thus far despite its synthetic potential.[7, 8] With an iterative method involving nucleophilic and electrophilic additions, *cis*-5,7-difunctionalized 1,3-cyclooctadiene has now been prepared for the first time by a very simple route. These kinds of cyclooctadienes containing two stereogenic centers are representatives of a rare,[9] but remarkable class of compounds that show great synthetic potential with regard to terpenoid *cyclo*-C_8 compounds.

The starting material for our studies of the stereo- and regioselective functionalization of cot is [Ru(Cp)(η^6-cot)]$^+$ (**1**, Cp = cyclopentadienyl), which can be recovered after completion of the reaction cycle (Scheme 1). The first nucleophilic addition of the dimethyl malonate anion to **1** occurs *exo* to the metal center[10] and leads initially, as expected,[11] to the 1,2,3,4,5-η-cyclooctatrienyl complex **2a**, which gradually rearranges to the 1,2,3-η:6,7-η-haptomer **2b**.[12] The thermal stability of **2a** is sufficient, however, to allow, for the most part, its separation from **2b** by chromatographic methods. The stereochemistry of both haptomers can

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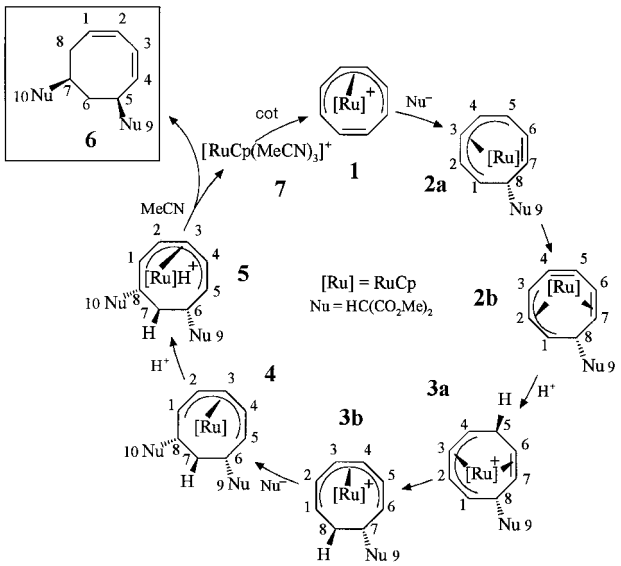

Scheme 1. Reaction cycle for the formation of *cis*-5,7-disubstituted 1,3-cyclooctadiene **6**.

unequivocally be determined by $^1H-{}^1H$ and $^1H-{}^{13}C$ correlation NMR spectra. Essential for the analysis of the ^1H NMR spectra is the coupling of the proton on the C atom that carries the nucleophile (C8): in **2a** this proton couples with neighboring protons of a coordinated and a noncoordinated C=C double bond, and in **2b** the proton on C8 exclusively couples with protons of metal-bound C atoms.

To further functionalize the *cyclo*-C_8 ligand, an electrophilic addition is performed by protonating **2b** with HBF_4, which takes place at position 5. The *cyclo*-C_8 ligand in the product cation **3a** shows 1,2,3,4-η:6,7-η coordination, but rearranges within several days at room temperature to a 1,2,3,4,5,6-η bonding mode (**3b**). The different hapticity of the two isomers is clearly evident from 2D correlation NMR spectra. An important difference between the ^1H NMR spectra of **3a** and **3b** results from the vicinal position of the *endo*-cyclic CH_2 group with respect to the C atom on which the nucleophilic addition in **3b** occurred; only $^1H-{}^1H$ coupling to metal-bound CH units is observed for the CH_2 group in **3a**. Protonation experiments with partially deuterated HBF_4 indicate a metal-assisted 1,5-H migration, as the deuterium atom remains *endo* relative to the Ru center in both **3a** and **3b**.[13]

The second nucleophilic addition is targeted at the terminal C atom of the metal-bound part of the ligand in **3b** farthest away from the first nucleophile. In this way, the 6,8-difunctionalized cyclooctadienyl complex **4** is formed, whose ^1H and ^{13}C NMR spectra have considerably fewer resonance signals than the corresponding spectra of **2a**, **b** and **3a**, **b** (Table 1) due to the local C_s symmetry of the *cyclo*-C_8 ligand. This result proves that the second nucleophile, like the first, is added *exo* to the metal center. It is noteworthy that **4** is formed exclusively even from mixtures of **3a** and **3b** in which the molar amount of **3b** is much less than the molar amount of **4** obtained.

Compound **4** can be protonated to the complex cation **5**, which shows a ^1H NMR spectrum very similar to that of **4**.

Table 1. Selected Spectroscopic data for **2**–**6**.[a]

2a: ^1H NMR (360 MHz, C_6D_6): $\delta = 4.43$ (s, Cp), 3.38 (s, CH_3), 3.27 (s, CH_3), 4.41 (m, 1-H), 4.30 (dd, 2-H), 5.51 (m, 3-H, 6-H), 4.10 (dd, 4-H), 3.66 (t, 5-H), 5.89 (m, 7-H), 3.74 (m, 8-H), 3.31 (d, 9-H); $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): $\delta = 79.6$ (Cp), 169.3, 168.9 (C=O), 51.8, 51.6 (CH_3), 39.1 (C-1), 75.5 (C-2), 99.5 (C-3), 76.4 (C-4), 40.4 (C-5), 129.3 (C-6), 126.6 (C-7), 43.2 (C-8), 60.3 (C-9)

2b: IR (Nujol): $\tilde{\nu} = 1733$ (C=O), 1651 cm^{-1} (C=C); ^1H NMR (360 MHz, C_6D_6): $\delta = 4.34$ (s, Cp), 3.34 (s, CH_3), 3.90 (dd, 1-H), 3.38 (dd, 2-H), 4.57 (dd, 3-H), 5.44 (dd, 4-H), 5.73 (dd, 5-H), 3.86 (dd, 6-H), 2.95 (t, 7-H), 4.48 (m, 8-H), 4.00 (d, 9-H). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): $\delta = 80.5$ (Cp), 58.3 (CH_3) 169.3, 168.9 (C=O), 31.4 (C-1), 78.4 (C-2), 65.3 (C-3), 134.7 (C-4), 136.6 (C-5), 68.5 (C-6), 23.5 (C-7), 40.3 (C-8), 52.1 (C-9). MS (70 eV): *m*/*z* (%): 401 (91) [M^+]

3a: IR (Nujol): $\tilde{\nu} = 1733$ (C=O), 1252–1156 (C–O), 1048 cm^{-1} (BF_4); ^1H NMR (360 MHz, [D_6]acetone): $\delta = 5.59$ (s, Cp), 3.72 (s, CH_3), 3.67 (s, CH_3), 4.79 (t, 1-H), 5.60 (m, 2-H), 5.81 (t, 3-H) 4.56 (m, 4-H), 3.22 (m, 5_{endo}-H), 1.81 (m, 5_{exo}-H), 3.63 (m, 6-H), 3.92 (t, 7-H), 4.17 (m, 8-H), 3.09 (d, 9-H); $^{13}C\{^1H\}$ NMR (50 MHz, [D_6]acetone): $\delta = 83.8$ (Cp), 52.1 (CH_3), 167.7 (C=O), 41.4 (C-1), 90.6 (C-2), 90.9 (C-3), 32.3 (C-4), 17.9 (C-5), 52.3 (C-6), 35.6 (C-7), 33.2 (C-8), 55.2 (C-9), partially deuterized **3a** $\delta = 17.6$ (t, $^1J_{C,D} = 24.6$ Hz, C-5); MS (70 eV) *m*/*z* (%): 401 (18) [M^+][b]

3b: ^1H NMR (360 MHz, [D_6]acetone): $\delta = 5.67$ (s, Cp), 3.73 (s, CH_3), 3.65 (s, CH_3), 6.11 (dd, 1-H), 5.43 (m, 2-H), 6.96 (t, 3-H), 6.84 (dd, 4-H), 6.26 (t, 5-H), 5.42 (m, 6-H), 3.92 (m, 7-H), 1.63 (m, 8_{endo}-H), −0.95 (m, 8_{exo}-H), 3.40 (d, 9-H); $^{13}C\{^1H\}$ NMR (50 MHz, [D_6]acetone): $\delta = 87.2$ (Cp), 52.3 (CH_3), 86.7 (C-1), 85.7 (C-2), 105.6 (C-3), 95.5 (C-4), 83.3 (C-5), 78.0 (C-6), 27.4 (C-7), 32.3 (C-8), 58.0 (C-9); partially deuterized **3b**: $\delta = 27.1$ (t, $^1J_{C,D} = 20.3$ Hz, C-7)

4: IR (KBr): $\tilde{\nu} = 2988$, 2947, 2923, 1729 (C=O), 1228 cm^{-1} (C–O); ^1H NMR (360 MHz, C_6D_6): $\delta = 4.45$ (s, Cp), 3.37, (s,CH_3) 3.35 (s, CH_3), 3.84 (dm, 1-H, 5-H), 4.01 (dd, 2-H, 4-H), 5.63 (t, 3-H), 2.83 (dddd, 6-H, 8-H), 1.30 (dt, 7_{endo}-H), 0.19 (m, 7_{exo}-H), 3.41 (d, 9-H, 10-H); $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): $\delta = 80.2$ (Cp), 61.6 (CH_3), 169.1, 168.8 (C=O), 44.1 (C-1, C-5), 72.3 (C-2, C-4), 103.1 (C-3), 42.9 (C-6, C-8), 27.8 (C-7), 51.6 (C-9, C-10); partially deuterized **4**: $\delta = 27.4$ (t, $^1J_{C,D} = 17.4$ Hz, C-7); MS (70 eV): *m*/*z* (%): 532 (11) [M^+]

5: IR (KBr): $\delta = 3117$ (CH), 2956 (CH), 1732 (C=O), 1244 (C–O), 1058 cm^{-1} (BF_4); ^1H NMR (360 MHz, CD_2Cl_2): $\delta = 5.52$ (s, Cp), 3.76 (s, CH_3), 3.72 (s, CH_3), 3.85 (t, 1-H, 5-H), 5.58 (m, 2-H, 4-H), 7.05 (t, 3-H), 2.66 (m, 6-H, 8-H), 1.24 (m, 7_{endo}-H), 0.27 (m, 7_{exo}-H), 3.36 (d, 9-H, 10-H), −10.6 (s, RuH)

6: IR (Nujol): $\tilde{\nu} = 1742$ (C=O), 1253, 1156, 1024 cm^{-1} (C–O); ^1H NMR (360 MHz, $CDCl_3$): $\delta = 3.761$, 3.754, 3.747, 3.736 (s, 4x3 H, CH_3), 5.84 (m, 1-H), 6.02 (dd, $^3J_{2,3} = 3.3$ Hz, $^3J_{1,2} = 10.7$ Hz, 2-H), 5.95 (dd, $^3J_{3,4} = 11.0$ Hz, $^3J_{2,3} = 3.3$ Hz, 3-H), 5.60 (dd, $^3J_{3,4} = 11.0$ Hz, $^3J_{4,5} = 8.0$ Hz, 4-H), 2.88 (m, 5-H), 1.49 (m, 6-H), 1.26 (m, 6′-H), 2.14 (m, 7-H), 2.30 (m, 8-H), 1.88 (m, 8′-H), 3.47 (d, $^3J_{5,9} = 8.2$ Hz, 9-H), 3.33 (d, $^3J_{7,10} = 7.7$ Hz, 10-H); ^{13}C NMR (50 MHz $CDCl_3$): $\delta = 169.0$, 168.2 (C=O), 57.9, 57.2 (C-9, C-10), 52.4 (CH_3) 132.0, 130.6, 127.8, 126.8 (C-1–C-4), 38.2, 35.5, 31.7, 31.4 (C-5–C-8); MS (70 eV): *m*/*z* (%): 368 (4) [M^+], 336 (5), 305 (8), 276 (13), 236 (17), 189 (20), 176 (49), 133 (21), 117 (89), 105 (100)

[a] Assignment of the NMR signals according to Scheme 1. [b] [M = **3b** – BF_4].

However, with the exception of the signals for 1-H and 5-H, the corresponding resonance signals of the metal-bound parts of the ligands are shifted more than 1 ppm downfield. Moreover a resonance signal is observed at $\delta = -10.6$, which is characteristic for a metal-bound H atom.

When **5** is dissolved in acetonitrile, the *cyclo*-C_8 ligand is cleaved spontaneously. $[Ru(Cp)(MeCN)_3]^+$ (**7**) is formed, which can react with cot to recover **1** again. The organic product was unequivocally identified with the aid of 1D and 2D NMR spectra as isomerically pure *cis*-5,7-disubstituted 1,3-cyclooctadiene (**6**). Compound **6**, which is also formed

when **4** is protonated directly in the presence of acetonitrile, is obtained in 46% yield with respect to the starting cot complex **1**!

Experimental Section

2a,b: A solution of sodium dimethyl malonate (286 mg, 1.8 mmol) in THF (20 mL) was added dropwise to a suspension of **1**-PF_6 (748 mg, 1.8 mmol) in THF (50 mL) at −78 °C. After warming to room temperature the solvent was removed under reduced pressure. The residue was extracted with diethyl ether, and the extract filtered through kieselguhr. After removal of the solvent the product was obtained as a pale yellow powder (yield: 561 mg, 78%). The haptomers **2a** and **2b** were, for the most part, separated by column chromatography (Al_2O_3/5% H_2O, toluene/diethyl ether 1/1). Elemental analysis calcd for $C_{18}H_{20}O_4Ru$ (401.41): C 53.86, H 5.02; found: C 54.12, H 5.18.

3a,b: A mixture of **2a** and **2b** (652 mg, 1.6 mmol) was dissolved in diethyl ether (50 mL) and allowed to react with $HBF_4 \cdot OEt_2$ (54%, 0.23 mL) at −78 °C. After warming to room temperature the mixture was filtered, and the residue washed several times with diethyl ether. The yellow filter residue was dissolved in CH_2Cl_2. The mixture of the products **3a** and **3b** was precipitated with diethyl ether and dried under vacuum (yield: 724 mg, 93%). The composition varied according to the duration of the reaction and the work-up. For the partial deuteration a corresponding amount of HBF_4/H_2O dissolved in D_2O was used instead of $HBF_4 \cdot OEt_2$. Elemental analysis calcd for $C_{18}H_{21}BF_4O_4Ru$ (489.23): C 44.19, H 4.33; found: C 43.49, H 4.38.

4: A solution of sodium dimethyl malonate (223 mg, 1.45 mmol) in THF (20 mL) was added to a suspension of **3a** and **3b** (645 mg, 1.3 mmol) in THF (50 mL) at room temperature. The work-up of the reaction mixture was analogous to that for the synthesis of **2**. Compound **4** was obtained as yellow crystals (yield: 558 mg, 80%). Elemental analysis calcd for $C_{23}H_{28}O_8Ru$ (533.52): C 51.78, H 5.29; found: C 51.63, H 5.60.

5: The protonation was carried out as for **2a,b** (see above). $HBF_4 \cdot OEt_2$ (54%, 0.22 mL) was added to a solution of **4** (613 mg, 1.15 mmol) in diethyl ether (40 mL) at −65 °C. Compound **5** (yield: 581 mg, 82%) was isolated as a yellow powder which slowly decomposed in solution. Elemental analysis calcd for $C_{23}H_{29}BF_4O_8Ru$ (621.34): C 44.46, H 4.70; found: C 44.13, H 4.69.

6: $HBF_4 \cdot OEt_2$ (54%, 0.16 mL, 1.16 mmol) was added to a solution of **4** (617 mg, 1.16 mmol) and acetonitrile (0.2 mL, 3.48 mmol) in diethyl ether (60 mL) at −78 °C. The suspension was warmed to room temperature and filtered. The yellow residue was washed with diethyl ether. After removal of the solvent **6** (yield: 287 mg, 67%) remained as an oil. The extraction residue was also dried under vacuum and identified by ^1H NMR spectroscopy as $[Ru(Cp)(CH_3CN)_3]BF_4$ (**7**). Elemental analysis calcd for $C_{18}H_{24}O_8$ (368.37): C 58.69, H 6.57; found: C 58.87, H 6.91.

Cleavage of **6** from **5**: Acetonitrile (2 mL) was added to a suspension of **5** (56 mg, 0.09 mmol) in diethyl ether (25 mL) at room temperature. The mixture was stirred for one hour, and worked up as in the preparation of **6** from **4**. **6**: 32 mg (97%), **7**: 33 mg (97%).

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[12] a) For isomers which differ only in the order, but not in the number of connectivities of the ligand atoms to the central atom, we suggest the term hapticity isomers (haptomers). We were able to demonstrate the formation of 1,2,3-η:6,7-η-haptomers based on the crystal structure analysis of a vinyl-substituted cyclooctatrienyl Ru complex;[12b] the half-life of **2a** in solution at 60 °C is about 15 h; b) G. Lange, Dissertation, Universität Hamburg, **1996**.

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$Ti_2Nb_6Cl_{14}O_4$: A Unique 2D – 1D Network Combination in Niobium Cluster Chemistry**

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The formation of clusters by metal – metal bonding is characteristic of many compounds with early transition metals in low oxidation states.[1] The most common structural motif in reduced niobium halides and oxides is the cluster unit $[(Nb_6L^i_{12})L^a_6]^{n-}$ (L = F, Cl, Br, O).[2, 3] It is based on an octahedron of Nb atoms surrounded by twelve inner (L^i) and six outer ligands (L^a). In compounds obtained through solid-state synthesis, these units can be present as discrete anions (as in $KLuNb_6Cl_{18}$,[4] $In_2Li_2Nb_6Cl_{18}$,[5] and $Rb_4Al_2Nb_{35}O_{70}$[6]) or link to each other by sharing outer and/or inner ligands to form various polymeric structures (as in

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