Formation of a Conjugated Oxametallacyclohexadiene by Dyotropic Rearrangement of Bis(2-furyl)zirconocene

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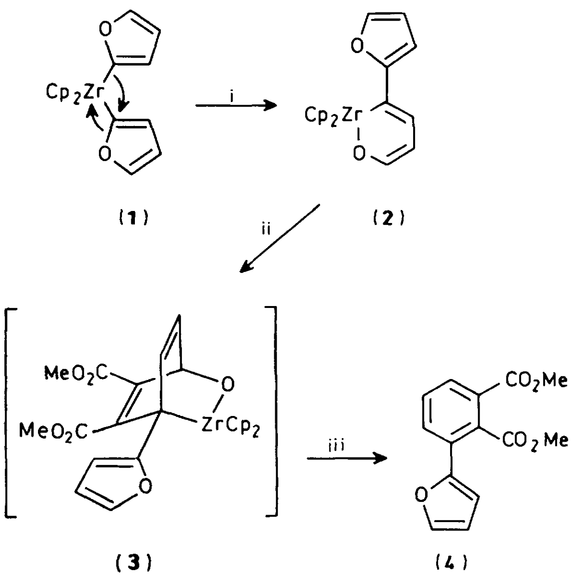
Bis(2-furyl)zirconocene (**1**), obtained from Cp_2ZrCl_2 (Cp = η-cyclopentadienyl) and 2-furyl-lithium, cleanly undergoes dyotropic rearrangement at 185 °C to yield the metallacyclic oxazirconacyclohexadiene derivative (**2**); complex (**2**) reacts with dimethyl acetylenedicarboxylate at 105 °C in a Diels–Alder/*retro*-Diels–Alder reaction sequence to produce $(Cp_2ZrO)_3$ and dimethyl 3-(2-furyl)phthalate (**4**).

In the course of thermally induced intramolecular dyotropic rearrangements two groups (a and b) are concertedly exchanging their relative positions at a connecting pivot (b–c). As a result, a–b–c–d sequences of molecular subunits become converted into d–b–c–a containing frameworks. Pre-formation of three-membered ring structures (*e.g.* $\overline{\text{a–b–c}}\text{–d}$ or $\text{a–}\overline{\text{b–c–d}}$) is enormously effective in decreasing the activation barrier of such coupled pairs of 1,2-migration reactions. While there have been a number of detailed mechanistic studies {using either [Si]–O–CR^1R^2–[Si] or $Cp_2\overline{Zr(X)\text{–}O\text{–}C}R^1R^2$–$ZrCp_2$ (X) (Cp = η-cyclopentadienyl) systems}, little has been done to use dyotropic rearrangements synthetically.[1] We here report a simple variation of the a–b–c–d to d–b–c–a reorganization reaction for constructing a six-membered metallacyclic ring system exhibiting Diels–Alder/*retro*-Diels–Alder activity.

Reaction of bis(η-cyclopentadienyl)zirconium dichloride with 2-furyl-lithium (2 mol. equiv.) in ether[2] gave bis(2-furyl)zirconocene (**1**) [74% isolated yield, m.p. 205—207 °C, correct CH elemental analysis, $^1H/^{13}C$ n.m.r. ($C_6D_6/CDCl_3$): δ 6.11/110.5 (Cp); 2-furyl: 7.39, 6.31, 6.14/107.7, 123.1, 143.9, 206.8]. Complex (**1**) is thermally very stable. It requires a temperature of 185 °C (5 h, solution in toluene) for quantitative rearrangement to the zirconaoxacyclohexadiene (**2**) [87% isolated yield (6.8 g), m.p. (hexane) 69—70 °C, correct CH elemental analysis, $^1H/^{13}C$ n.m.r. (C_6D_6): δ 5.85/111.3 (Cp); 2-furyl: 7.08, 6.23, 5.97/164.6, 139.3, 110.2, 99.8; metallacycle: 7.05, 6.83, 5.29/178.2, 151.7, 127.4, 109.3]. The metallacycle (**2**) reacts cleanly with dimethyl acetylenedicarboxylate in toluene at 105 °C (18 h) to give 'zirconocene oxide,' obtained and identified as the cyclotrimer $(Cp_2ZrO)_3$,[3] and dimethyl 3-(2-furyl)phthalate (**4**). The latter was isolated in 70% yield on a preparative scale after chromatography [M^+ m/z 260.0685 (calc. and obs.); ^1H n.m.r. (C_6D_6): δ 7.06, 6.66, 6.10 (2-furyl), 3.72, 3.38 (CH_3), 7.71, 7.62, 6.88 (ArH); ^{13}C (C_6D_6): δ 51.5, 52.0, 109.2, 112.1, 129.19, 129.24, 130.9, 132.9, 142.5, 143.2, 151.1, 165.7, 169.1 (one signal hidden by solvent resonances); i.r. (film): 1730 cm^{-1}]. Product (**4**) is probably formed *via* Diels–Alder reaction of the metallacycle



Scheme 1. *Reagents and conditions*: i, 185 °C; ii, $MeO_2CC\equiv CCO_2Me$, 105 °C; iii, loss of $(Cp_2ZrO)_3$.

(**2**) to give the bicyclic metal-containing intermediate (**3**) which then undergoes Alder–Rickert type cleavage.[4]

The high activation barrier of the (**1**) → (**2**) rearrangement indicates the absence of any pronounced metal-to-oxygen interaction in the bis(2-furyl)metallocene starting material.[5] Our findings show that a dyotropic rearrangement reaction can nevertheless successfully be used for the construction of, *e.g.*, novel types of metallacycles provided that the usual competition reactions (here *e.g.* aryne metallocene formation *via* β-hydride abstraction[6]) are made sufficiently unfavourable by choosing a suitable σ-ligand combination. Variants of the (**1**) → (**4**) reaction sequence should provide interesting entries for syntheses of highly substituted arene and heterobiarene systems.

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