

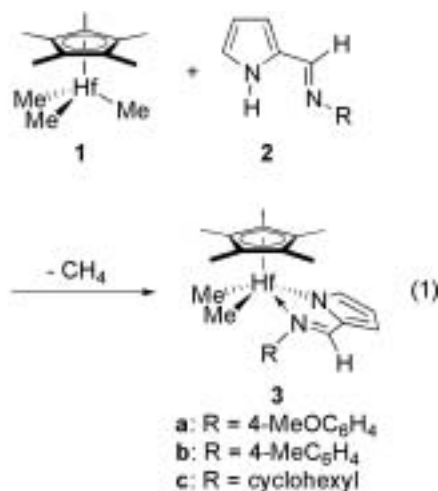
VIII-G Organometallic Chemistry: Synthesis, Characterization, and Catalysts

VIII-G-1 Living Polymerization of 1-Hexene Catalyzed by Half-Metallocene Dimethyl Complexes of Hafnium with Bidentate *N*-Substituted Iminopyrrolyl Ligands

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[*Organometallics* **24**, 3375–3377 (2005)]

We have been interested in iminopyrrolyl ligands as a unique unsymmetrical monoanionic ligand capable of supporting non-metallocene type group 4 metal complexes. As an extension of our continuous interest in the iminopyrrolyl ligand system. We here report the syntheses of half-metallocene type hafnium dimethyl complexes with iminopyrrolyl ligand and their catalytic performance for 1-hexene polymerization upon treated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, giving monodispersed poly(1-hexene) with high isotacticity (up to $[\text{mmmm}] = 90\%$). These complexes were the first hafnium catalyst precursors for stereospecific living polymerization of α -olefin. Non-bridged half-metallocene dimethyl hafnium complexes **3a-c** with *N*-substituted iminopyrrolyl ligands **2a-c** have been synthesized and characterized by NMR spectroscopy as well as X-ray analyses for **3a** and **3b**. These complexes were found to be active catalysts for isospecific living polymerization of 1-hexene upon treated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ below 0 °C.

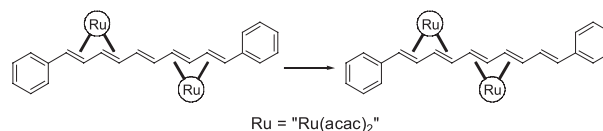


VIII-G-2 Unique Preferential Conformation and Movement of Ru(acac)₂ Fragment(s) Coordinated in an η^4 -*s-trans* Fashion to All Diene Unit(s) of α,ω -Diphenylpolyenes

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α,ω -Diphenylpolyene complexes bearing bis(acetylacetonato)ruthenium(II) of general formula $\text{Ru}_n(\text{acac})_{2n}$ (polyene) [**1**: $n = 1$, polyene = 1,4-diphenylbuta-1,3-diene; **2**: $n = 1$, polyene = 1,6-diphenylhexa-1,3,5-triene; **3**: $n = 2$, polyene = 1,8-diphenylocta-1,3,5,7-tetraene; **4** and **6**: $n = 2$, polyene = 1,10-diphenyldeca-1,3,5,7,9-pentaene; **5**: $n = 3$, polyene = 1,12-diphenyl-dodeca-1,3,5,7,9,11-hexaene] were prepared by reaction of $\text{Ru}(\text{acac})_3$ with the corresponding polyene in the presence of excess amounts of zinc dust. The $\text{Ru}(\text{acac})_2$ fragment(s) in **1–6** coordinated in an η^4 -*s-trans* fashion to each diene unit of the polyene ligands. The Δ - $\text{Ru}(\text{acac})_2$ unit and its counter part Λ - $\text{Ru}(\text{acac})_2$ were assigned to coordinate to the *re*-face and the *si*-face of the diene unit, respectively, on the basis of the crystal structure of complexes **1** and **2** together with the previously reported **3**. The hexaene complex **5** was assumed to have the structure of *anti,anti*- Δ,Δ,Δ -**5a** and its enantiomer *anti,anti*- Λ,Δ,Δ -**5b**. Pentaene complex **4**, in which two ' $\text{Ru}(\text{acac})_2$ ' fragments were bound to C(1)–C(4) and C(7)–C(10) of the pentaene ligand, was isolated. The $\text{Ru}(\text{acac})_2$ fragment of **4** moved over the pentaene in CHCl_3 to settle in the thermodynamically stable **6**, in which two ruthenium fragments located at adjacent positions. Metal migration process, as monitored by decrease of **4**, was found to be first-order for **4**, giving activation parameters (ΔG^\ddagger (25 °C) = 22.5 ± 0.2 kcal/mol; ΔS^\ddagger (25 °C) = -14.2 ± 0.8 cal mol⁻¹ K⁻¹). The negative value of ΔS^\ddagger suggested that the migration of the $\text{Ru}(\text{acac})_2$ fragment is an intramolecular process.



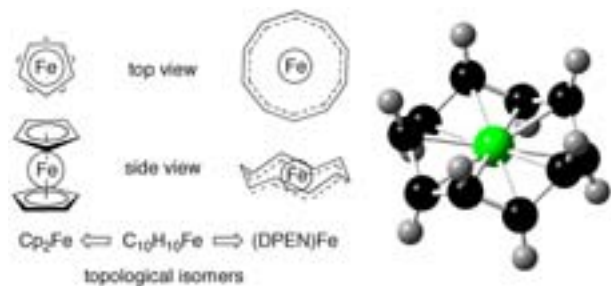
VIII-G-3 A Topological Isomer of Ferrocene: Theoretical Approach for Transition Metal Complexes with Conjugated All Trans Cyclodecapentaene

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Since the discovery of ferrocene in early 1950s, organometallic chemistry of transition metals has been developed extensively in terms of the fundamental bonding, physical properties, and attracting applications as catalysts as well as source for materials. We anticipate that it may be possible to create cyclic polyene coordinating systems, the smallest one being all-trans cyclodeca-1,3,5,7,9-pentaene (DPEN). Thus, by using DFT computation [B3LYP/6-311+G(2d,p) and BP86 level], we examined the capability of all-trans DPEN as a ligand for transition metals. We found that iron(0) and

some other transition metals coordinated by DPEN are stable molecules and unique topological isomers of the corresponding metallocene complexes.



At first, we calculated Fe(0)-DPEN complex. The shape and levels of some orbital interactions including HOMO and LUMO of the iron complex indicate the strong bonding interaction between Fe(0) and DPEN through the aromatic $p\pi$ -electrons of DPEN. Thus, we found on the basis of DFT calculation that DPEN is a potential ligand to hold some transition metals in its center. These complexes are unique topological isomers of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and metallocene derivatives. Computational estimation of general properties of the DPEN complexes is of our interest.