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Regioselective Homo- and Codimerization of α -Olefins Catalyzed by Bis(2,4,7-trimethylindenyl)yttrium Hydride

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Summary: The novel dimeric bis(2,4,7-trimethylindenyl)yttrium hydride $[(\text{Ind}')_2\text{Y}(\text{m-H})]_2$ (**3**) has been prepared from $(\text{Ind}')_2\text{Y}(\text{m-Cl})_2\text{Li}(\text{THF})_2$ (**1**) via the alkyl complex $(\text{Ind}')_2\text{YCH}(\text{SiMe}_3)_2$ (**2**). The hydride **3** is a catalyst that effects the regio- and stereoselective homodimerization of a range of α -olefins at 80 °C as well as head-to-head codimerization of styrene with other α -olefins.

Over the past decade, metallocene-based olefin polymerization catalysts have become important single-site alternatives to the heterogeneous Ziegler-Natta systems.^{1,2} Two types of 14-electron metallocene systems can be distinguished: cationic group 4 metal complexes of the type $[\text{Cp}_2\text{MR}]^+ \text{1a,c-f,2}$ and neutral group 3 metal or lanthanide complexes Cp_2LnR .^{1a,3,4} The latter are extremely efficient catalysts for the polymerization of ethene, but in contrast to the cationic group 4 congeners, they are largely ineffective for the polymerization of α -olefins (mainly due to deactivation through allylic C-H activation of the substrate).^{4,5} Only the recently developed *ansa*-metallocenes of the group 3 metal yttrium, such as $\text{Me}_2\text{Si}[\text{C}_5(\text{SiMe}_3)(\text{CMe}_3)\text{H}_2]_2\text{YR}$, give slow formation of polymers of α -olefins in moderate yield.^{4b,c,e}

Here we describe the synthesis of the first alkyl and hydride compounds of a bis(indenyl)yttrium system, with 2,4,7-trimethylindenyl as ancillary ligand. Again,

this system polymerizes only ethene,⁶ but it also proved to be an efficient catalyst for regioselective homodimerization of a broad range of α -olefins and for the head-to-head codimerization of various α -olefins with styrene. This codimerization is also observed for olefins with heteroatom functionalities and for α -olefins that do not undergo homodimerization under these conditions. These dimerization reactions are of special interest for use in organic synthesis.⁷

The bis(indenyl)yttrium system is accessible through reaction of $(2,4,7\text{-Me}_3\text{C}_9\text{H}_4)_2\text{Li}(\text{Ind}'\text{Li})^8$ with $\text{YCl}_3(\text{THF})_{3.5}$ in tetrahydrofuran to give the bis(indenyl)yttrium complex $(\text{Ind}')_2\text{Y}(\text{m-Cl})_2\text{Li}(\text{THF})_2$ (**1**).⁹ Treatment of **1** with $\text{LiCH}(\text{SiMe}_3)_2$ in toluene yields the alkyl complex $(\text{Ind}')_2\text{YCH}(\text{SiMe}_3)_2$ (**2**). Hydrogenolysis of **2** in cyclohexane for 24 h gives the first bis(indenyl)yttrium hydride complex, $[(\text{Ind}')_2\text{Y}(\text{m-H})]_2$ (**3**). Crystallization of **3** from benzene at room temperature affords crystals suitable for X-ray analysis (Figure 1).¹⁰ The structure consists of two bis(indenyl)yttrium units with a racemic-like rotamer conformation of the indenyl ligands which are

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(9) Synthesis of $(2,4,7\text{-Me}_3\text{C}_9\text{H}_4)_2\text{Y}(\text{m-Cl})_2\text{Li}(\text{THF})_2$ (**1**). A 2.24 g (5.00 mmol) amount of $\text{YCl}_3(\text{THF})_{3.5}$ was suspended in 100 mL of THF, and 1.67 g (10.00 mmol) of $(2,4,7\text{-trimethylindenyl})\text{lithium}$ was added at -80 °C. The mixture was continuously stirred and warmed to room temperature over 2 h. Stirring was continued for 2 h to form a clear solution. After removal of the solvent in vacuo, the residue was treated with 80 mL of toluene/THF (10/1), stirred, and allowed to settle, after which the solution was decanted. Concentration to 35 mL and cooling to -30 °C gave 2.40 g (76%) of pale yellow crystalline **1**. ¹H NMR (benzene-*d*₆): δ 1.31 (m, 8H, THF), 2.35 (s, 6H, 2-CH₃), 2.63 (s, 12H, 4,7-CH₃), 3.50 (m, 8H, THF), 6.28 (s, 4H, 1,3-CH), 6.89 (s, 4H, 5,6-CH). ¹³C NMR (benzene-*d*₆): δ 16.11 (2-CH₃); 19.88 (4,7-CH₃); 25.25 (THF); 68.21 (THF); 100.27 (1,3-C); 121.52 (5,6-C); 128.29, 128.79, 131.09 (2,4,7,8,9-C). Anal. Calcd for C₃₂H₄₂Cl₂LiO₂Y: H, 6.77; C, 61.45; Y, 14.22. Found: H, 6.82; C, 61.50; Y, 14.15.

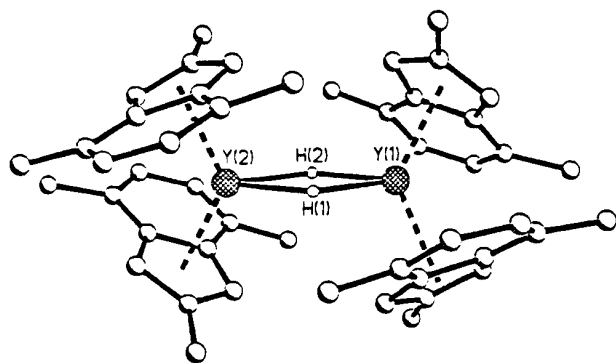


Figure 1. Molecular structure of $[(2,4,7\text{-Me}_3\text{C}_9\text{H}_4)_2\text{Y}(\text{m-H})]_2 \cdot 0.5\text{C}_6\text{H}_6$ (**3**). Selected bond distances (Å) and angles (deg): Y1-H1, 2.12(6); Y1-H2, 2.09(4); Y2-H1, 2.12(4); Y2-H2, 2.14(7); Cen1-Y1, 2.357(4); Cen2-Y1, 2.348(4); Cen3-Y2, 2.343(4); Cen4-Y2, 2.368(4); H1-Y1-H2, 65.0(20); H1-Y2-H2, 64.3(20); Cen1-Y1-Cen2, 132.40(4); Cen3-Y2-Cen4, 131.87(4). All hydrogen atoms, except the two bridging hydrides, and the benzene molecule are omitted for clarity. All unlabeled atoms are carbon.

twice hydride-bridged to form a dimer with overall D_2 symmetry. The dihedral angle for the equatorial planes of the individual yttrocene units of the dimer is approximately 46.9° . Apparently, substantial overlap with the spherically symmetric hydrogen 1s valence orbitals is maintained, despite the skewed arrangement of the yttrocene frontier orbitals. The dimeric structure is retained in solution, based upon the presence of a 1:2:1 triplet ($d = 2.69$ ppm; $^1J_{\text{Y-H}} = 32.7$ Hz) for the hydride ligands in the ^1H NMR spectrum of **3**, due to coupling with two equivalent ^{89}Y nuclei ($I = 1/2$; 100% natural abundance).^{4b,d-g} The dimeric nature is also supported by the appearance of three singlets (relative intensity 1:1:1) for each of the three different CH_3 environments, consistent with slowly rotating or nonrotating, equivalent trimethylindenyl ligands.

Reactions of **3** in benzene at 80–100 °C with a 20–50-fold molar excess of the α -olefins **4a–d** yield dimeric products at modest rates with little concomitant oligomerization (Table 1). An induction time (15–30 min) to break up the dimeric structure of **3** to form the active catalyst is followed by a gradual full conversion of the monomers in 2–24 h, depending on the substrate.¹¹

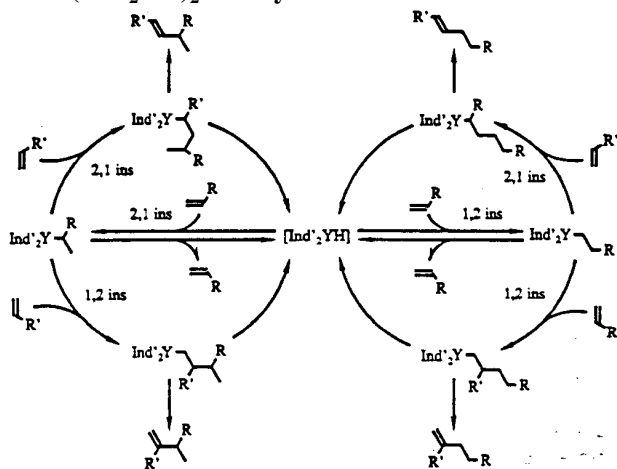
For 1-hexene (**4a**) and 3-methyl-1-butene (**4b**) regular head-to-tail coupling (>98% selectivity) is observed by sequential 1,2-insertion followed by *b*-H abstraction (Scheme 1) to yield 80–90% dimers and 9–17% trimers.^{7a,c-g} For trimethylvinylsilane (**4c**) and styrene (**4d**) the homodimerization gave the unusual head-to-head coupling products (>92% selectivity), as shown in Table 1. Despite the well-known electronic preference of trimethylvinylsilane,^{12,13b} and styrene¹⁴ for 2,1-insertion, the reactions presumably proceed via initial 1,2-

Table 1. Homodimerization of α -Olefins Catalyzed by **3**¹¹

entry	substrate $\text{CH}_2=\text{CH-R}$	product(s)	yield (%)	reaction time ^a (h)
R				
1	4a <i>n</i> Bu		(80) ^b	2
2	4b <i>i</i> Pr		(90) ^c	24
3	4c SiMe ₃		<i>trans</i> -(48), <i>cis</i> -(24) (26)	2
4	4d Ph		<i>trans</i> -(87), <i>cis</i> -(5) (6)	6

^a Time required for full conversion, ^b +17% of the trimer. ^c +9% of the trimer.

Scheme 1. Proposed Mechanism of $(\text{Ind}'_2\text{YH})_2$ -Catalyzed α -Olefin Dimerization



insertion into the Y-H bond, followed by a second insertion in the opposite manner, and a *b*-hydrogen abstraction. For higher styrene concentrations substrate inhibition of the homodimerization and an increase in relative formation of the branched dimer *trans*-1,3-diphenyl-1-butene (6% at 20-fold and 15% at 100-fold molar excess) is observed. This suggests that the electronic preference for 2,1-insertion is still present but that the sterically hindered 2,1-insertion product of styrene into the Y-H bond is slow to insert a second

(11) NMR-tube reactions of $[(2,4,7\text{-Me}_3\text{C}_9\text{H}_4)_2\text{Y}(\text{m-H})]_2 \cdot 0.5\text{C}_6\text{H}_{12}$ (**3**) with α -olefins. The reactions were studied in sealed NMR tubes with 3–9 mmol of **3** and a 20–50-fold molar excess of α -olefin (or α -olefin and styrene in the ratio 2/3) in 0.5 mL of benzene- d_6 . The resulting solutions were heated to 80 °C and were monitored by ^1H NMR spectroscopy after 10 min and 2, 6, 12, 24, and 48 h. After full conversion the reaction mixture was quenched with methanol and passed over a glass filter. The yield and the nature of the different products were determined by NMR spectroscopy and GC-MS analysis. Reported yields are based on the initial amount of the α -olefin.

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(10) Crystal data for **3**: $\text{C}_{48}\text{H}_{54}\text{Y}_2 \cdot 0.5\text{C}_6\text{H}_6$, $M_r = 847.83$, monoclinic, $P2_1/n$, $a = 12.387(1)$ Å, $b = 21.854(1)$ Å, $c = 16.322(1)$ Å, $\beta = 106.998(5)^\circ$, $V = 4225.4(5)$ Å³, $Z = 4$, $D_c = 1.333$ g cm⁻³. Data were collected on an Enraf-Nonius CAD-4F diffractometer at 130 K with $\text{I}(\text{Mo K}\alpha)$ radiation) = 0.710 73 Å. The structure was solved by a combination of Patterson and difference Fourier methods. All non-hydrogen atoms were refined anisotropically. The two bridging hydrogen atom positions were refined with bond restraints and isotropic thermal displacement parameters. The other hydrogen atoms were included in the final refinement in riding mode. Final refinement on F^2 converged at $R_w(F^2) = 0.1871$ for 6430 reflections with $F^2 > 0$ and 498 parameters; $R(F) = 0.0763$ for 4412 reflections with $F \geq 4.0 \sigma(F)$.

substrate molecule. In this case *b*-hydrogen elimination and 1,2-reinsertion into the Y-H bond is preferred for a productive sequential reaction (Scheme 1). In contrast to styrene, **4c** does not show substrate inhibition, presumably due to a more rapid insertion/*b*-hydrogen elimination equilibrium (as was observed before).^{4f} The proposed mechanism was also supported by stoichiometric reactions of **4c** and **4d** with group 3 metallocene hydrides, which exclusively give the 2,1-insertion products.¹⁵




Similarities in the reactivity of styrene and trimethylvinylsilane and their reversible insertion into M-H bonds have been described before for scandium,^{4f} zirconium,^{1f,13,14d} and tantalum hydrides^{14e} and in hydrosilylation reactions with palladium^{14a} and neodymium¹⁶ catalysts. For scandium the stable head-to-head double-insertion product (C₅Me₄SiMe₂NtBu)Sc(CHPhCH₂CH₂-CH₂Ph)PMe₃ has been observed.^{5a}

The α -olefins **4g-j**, containing sulfur or oxygen atoms, 3,3-dimethyl-1-butene (**4e**), and allylbenzene (**4f**) are not homodimerized by **3** to any appreciable extent under the applied conditions. In the reaction of **3** with **4f** CH activation took place and the catalytically inactive allyl complex Ind₂Y(*h*³-CH₂CHCHPh) was detected. Reactions of **3** with **4g-j** yield the formation of stable alkyl complexes which lead to catalyst deactivation, as reported earlier for other yttrocene and cationic zirconocene systems.¹⁷

We also observed that the Ind₂Y system catalytically codimerizes styrene and α -olefins (Table 2). Reaction of styrene with **4a-c** in the presence of **3** (3 mmol of **3**, 50-fold molar excess of α -olefin and styrene in the ratio 2/3) in benzene at 80–100 °C gives the codimer *trans*-1-phenyl-4-alkyl-1-butene as the dominant product together with small amounts of homodimers and traces of co-oligomers. The codimerization is likely to proceed via initial 1,2-insertion of the α -olefin into the Y-H bond followed by a 2,1-insertion of styrene into the Y-C bond of the primary alkyl intermediate and subsequent *b*-H abstraction. A related but inverted sequence (initial 2,1-insertion of styrene followed by ethene insertion) was proposed for the Ni-catalyzed hydrovinylolation of styrene to give 3-phenyl-1-butene.¹⁸ Linear cross-coupled products were recently found in the codimerization of styrene with cycloienes by Ti aryloxides,¹⁹ through a sequence involving a Ti^{II}/Ti^{IV} redox mechanism.

The hydride **3** can also codimerize styrene with the α -olefins **4e-j**, which, as mentioned above, are not readily homodimerized. For instance, the sulfur- and oxygen-containing olefins **4g-j** readily form head-to-

Table 2. Codimerization of α -Olefins and Styrene to *trans*-1-Phenyl-4-alkyl-1-butenes Catalyzed by **3**¹¹

entry	substrate	CH ₂ =CH-R	conversion(%) ^a of CH ₂ =CH-R	yield(%) ^b of Ph-CH=CH-CH ₂ -CH ₂ -R	reaction time (h)
		R			
5	4a	<i>n</i> Bu	100	88 ^c	18
6	4b	<i>i</i> Pr	98	96 ^d	24
7	4c	<i>t</i> Bu	14	93	48
8	4e	SiMe ₃	100	92 ^e	6
9	4f	CH ₂ Ph	98	90 ^f	24
10	4g	CH ₂ S- <i>t</i> Bu	68	94	48
11	4h		92	98	24
12	4i		98	99	48
13	4j		45	96	48

^a The reaction mixtures contain 5–30% (except entry 7) dimer of **4d**, based on the initial amount of **4d**. ^b The yield based on the converted amount of CH₂=CHR. ^c +6% dimer of **4a**, +3% cotrimer, *trans*-1-phenyl-4-butyl-1-decene. ^d +4% dimer of **4b**. ^e +6% dimer of **4c**. ^f +4% dimer of **4f**.

head codimers with styrene. However, for these less reactive α -olefins the required reaction time is significantly longer, and concomitant formation of styrene homodimer is observed.

In conclusion, the first bis(indenyl)yttrium hydride complex (Ind₂YH)₂ (**3**) has been obtained. It provides us with a catalyst that can effect a broad range of homo- and co-dimerizations of α -olefins and that tolerates the presence of substituents and functionalities in the monomers. Presently, studies are in progress to obtain a thorough understanding of the mechanistic aspects of olefin conversions with this and related systems, together with efforts to extend the range of application of this novel catalyst.

Acknowledgment. W.P.K. thanks the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral grant.

Supporting Information Available: Text giving experimental details describing the synthesis of **1-3** and details of the structure determination of **3** and tables of crystal data, as well as information regarding α -olefin dimerizations and NMR and GC-MS analyses for the dimers (20 pages). Ordering information is given on any current masthead page.

OM970983H

(15) The high activation energy to break up dimeric **3** requires reaction temperatures of 80 °C or more. At this temperature rapid further reaction of the primary 2,1-insertion products of **4c** or **4d** took place and no intermediates were detectable. We therefore investigated stoichiometric reactions of trimethylvinylsilane and styrene with the bis(pentamethylcyclopentadienyl) group 3 metal hydrides [Cp*₂Ln(*m*-H)]₂ (Ln = La, Y), which are dimeric but more reactive. These reactions yielded complexes of the type Cp*₂LnCH(R)CH₃ (R = SiMe₃, Ph). Full results of these investigations will be published separately.

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