The structure of FN_3 has recently been determined experimentally by Christen et al. (private communication). The N_3 moiety is slightly bent (170.9°), the FN bond is 1.444 Å, and the FN_aN_b angle is 103.8° in agreement with our conclusions. They have also fully optimized the structure (including the $N_aN_bN_c$ angle) using ab inito molecular orbital calculations, which concur with our results.

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Registry No. FN_3, 14986-60-8; FNO_3, 7789-26-6.

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Stereochemistry of PtO_2-Catalyzed Hydrogenation of [Ethylenebis(indenyl)]zirconium Dichloride

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[Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]MX_2 (M = Ti, Zr; X = Me, Cl) complexes,[1] in the presence of methylaluminoxanes, are highly active homogeneous catalyst precursors for the stereospecific polymerization[2,3] and hydrooligomerization[4] of α-olefins. The tetrahydroindenyl complexes are prepared by catalytic hydrogenation of the corresponding indenyl derivatives under 100 bar of H_2 in the presence of a PtO_2 catalyst.[1] We are interested in preparing stereochemically defined substituted analogues of these catalysts, and thus it was necessary to establish unambiguously the stereochemistry of the hydrogenation reaction.[5] The stereochemistry of catalytic hydrogenations of coordinated ligands is highly dependent on the metal center; participation of the metal center has been demonstrated for Zr,[6] Fe,[7] and Ni[8] systems. For nickelocene,[8] it was shown that catalytic hydrogenation in the presence of Raney nickel, Pd/C, or $(PPh_3)_3RhCl$ occurs stereospecifically from the sterically hindered endo face of the cyclopentadienyl ring. In this paper, we report deuterium-labeling studies that establish that the PtO_2-catalyzed hydrogenation of [ethylenebis(indenyl)]zirconium dichloride occurs with cis stereochemistry at the exo face of the indenyl ligand.

Catalytic deuteration of [ethylenebis(indenyl)]zirconium dichloride (**1**) with PtO_2 under 100 bar of D_2 in CH_2Cl_2 was carried out according to the published procedure[1] to give [ethylenebis(4,5,6,7-tetradeuterio-1-indenyl)]zirconium dichloride (**3**). The ^1H and ^2H NMR spectra of the nondeuteriated and deuteriated dichloride derivatives (**2** and **3**, respectively) are presented in Figure 1. The ^1H NMR spectrum of **3** consists of four doublets (J_{HH} = 5.5–5.8 Hz) corresponding to eight protons of the tetradeuterioindenyl ligand (Figure 1b). Resonances corresponding to the other eight protons are barely discernible in the ^1H NMR spectrum but can be clearly observed in the ^2H NMR spectrum (Figure 1c). Integration of the resonances of 1.57 and 2.57 ppm in the ^1H NMR spectrum of **3** reveals a small amount (<8%) of residual hydrogenation.[9] A molecular ion peak at m/z 432 in the mass spectrum confirmed that eight deuterium atoms were incorporated into the indenyl ligands. A DEPT[10] experiment provided evidence against scrambling processes and confirmed that each carbon of the tetradeuterioindenyl ligand is bonded to only one protium atom.

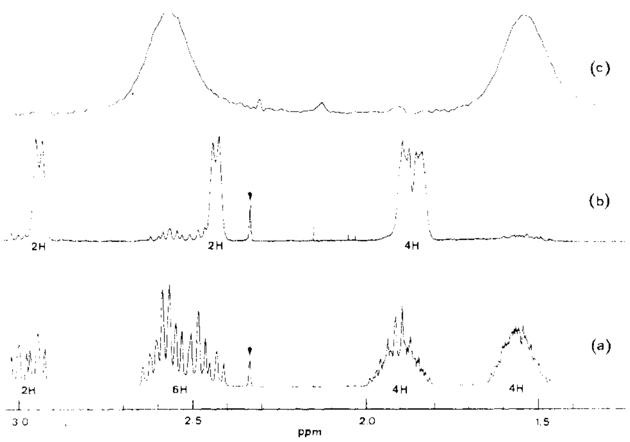

Figure 1. ^1H and ^2H NMR spectra. (a) ^1H NMR spectrum of **2** ($CDCl_3$); (b) ^1H NMR spectrum of **3** ($CDCl_3$); (c) ^2H NMR spectrum of **3** ($CDCl_3$). Arrows indicate peaks due to an impurity.

The loss of multiple couplings upon deuteration and the good peak separation of the remaining four resonances of **3** allowed us to assign the chemical shifts of all eight protons of the tetradeuterioindenyl ligand by homo decoupling and difference NOE experiments (Figure 2). These experiments, carried out in C_6D_6 due to larger peak separations in that solvent, took advantage of the small allylic coupling (J = 0.7 Hz) between the cyclopentadienyl proton at 6.35 ppm (assigned as H3) and the proton appearing at 3.14 ppm (assigned as H4). Once H4 was assigned, assignments of the remaining protons followed straightforwardly. Peak assignments are given in Table I.

To confirm the cis stereochemistry of the hydrogenation reaction and establish that hydrogenation occurs at the exo face of the indenyl ligand, difference NOE experiments were carried out on the deuteriated dichloride and dimethyl derivatives (**3** and **5**) and the nondeuteriated dimethyl derivative **4**. The dimethyl derivatives were prepared as previously described;[11] the ^1H NMR spectra of these compounds are given in Table I.

Irradiation of the cyclopentadienyl resonance of **3** at 5.26 ppm (corresponding to H2) led to enhancement of one resonance at 2.16 ppm (10.3%) corresponding to H7 of the opposite ring. A similar result was obtained for **5**; irradiation of the resonance at 5.13 ppm (H2) led to enhancement of the resonance at 1.98 ppm (11.7%). These results confirm that H7 is in the endo position. The endo disposition of the remaining protons was established by irradiation of the methyl resonance of **5**; irradiation at –0.1 ppm led to enhancement of 3 resonances at 2.82 (17.8%), 1.69 (10.2%), and 1.61 ppm (8.6%) corresponding to H4, H6, and H5, respectively. Similar experiments on the fully hydrogenated dimethyl derivative **4** led to similar results; no enhancements were observed for those resonances that disappear upon deuteriation (centered at 2.67, 2.25, and 1.42 ppm), providing further support for a cis hydrogenation mechanism.

These labeling studies clearly establish the stereochemistry of catalytic hydrogenation of [ethylene-bridged bis(indenyl)]zirconium dichloride with PtO_2. Exo-face hydrogenation implies that

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Table I. NMR Data

solvent	chem shift (mult, integ) 2	chem shift (mult, integ) 3	assignt[a]
$CDCl_3$	6.35 (d, 2 H)	6.35 (d, 2 H)	H3
	5.63 (d, 2 H)	5.63 (d, 2 H)	H2
	3.12 (s, 4 H)	3.12 (s, 4 H)	bridge
	2.96 (dt, 2 H)	2.96 (d, 2 H)	H4 (endo)
	$\left.\begin{matrix}2.6\\2.4\end{matrix}\right\}$ (m, 6H)	2.45 (d, 2 H)	H7 (endo)
	$\left.\begin{matrix}1.95\\1.88\end{matrix}\right\}$ (m, 4 H)	1.90 (d, 2 H) 1.87 (d, 2 H)	H5 (endo) H6 (endo)
	1.57 (m, 4 H)		
C_6D_6	6.35 (dd, 2 H)	6.35 (d, 2 H)	H3
	5.26 (d, 2 H)	5.26 (d, 2 H)	H2
	3.14 (dt, 2 H)	3.14 (d, 2 H)	H4 (endo)
	2.46 (s, 4 H)	2.46 (s, 4 H)	bridge
	2.38 (m, 2 H)		
	2.16 (m, 2 H)	2.16 (d, 2 H)	H7 (endo)
	1.90 (m, 4 H)	1.91 (d, 2 H)	H5 (endo)
		1.82 (d, 2 H)	H6 (endo)
	1.34 (m, 4 H)		
solvent	**chem shift (mult, integ) 4**	**chem shift (mult, integ) 5**	**assignt[a]**
C_6D_6	6.17 (d, 2 H)	6.17 (d, 2 H)	H3
	5.13 (d, 2 H)	5.13 (d, 2 H)	H2
	2.82 (dt, 2 H)	2.82 (d, 2 H)	H4 (endo)
	2.67 (dt, 2 H)		
	2.36 (s, 4 H)	2.36 (s, 4 H)	bridge
	2.25 (m, 2 H)		
	1.98 (m, 2 H)	1.98 (d, 2 H)	H7 (endo)
	$\left.\begin{matrix}1.80\\1.50\end{matrix}\right\}$ (m, 6 H)	1.69 (d, 2 H) 1.61 (d, 2 H)	H6 (endo) H5 (endo)
	1.42 (m, 2 H)		
	-0.10 (s, 6 H)	-0.10 (s, 6 H)	CH_3

[a] Atom-labeling scheme is given in Figure 2.

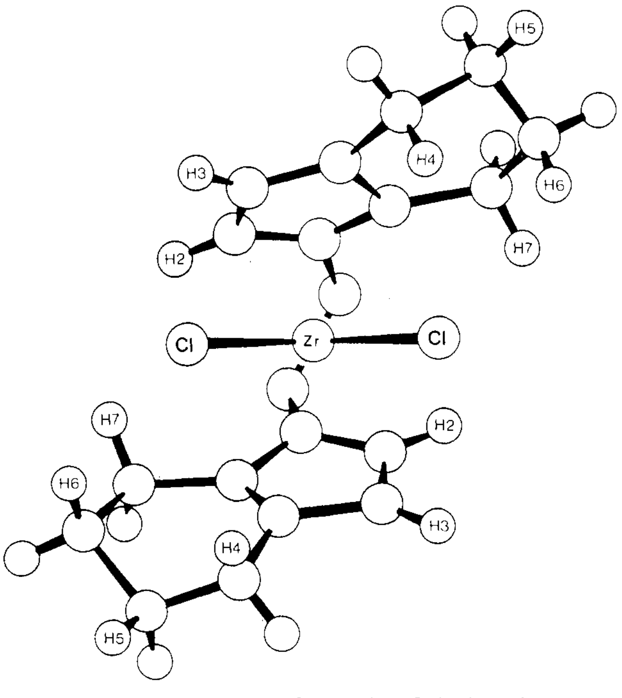

Figure 2. Atom-labeling scheme for **2** and **3**. Only the endo protons of the tetradeuterioindenyl ligand are labeled.

under these conditions, the zirconium center is not involved in intramolecular hydrogenation of the indenyl ligand.

Experimental Section

[Ethylenebis(idenyl)]zirconium dichloride, [ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride,[1] and [ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]dimethylzirconium[11] were prepared as described in the literature. All solvents were distilled under nitrogen prior to use: toluene and THF from Na/K alloy/benzophenone, CH_2Cl_2 from P_2O_5, and Et_2O from $LiAlH_4$. Benzene-d_6 was stirred over Na/K alloy and vacuum-transferred prior to use. PtO_2 and methyllithium were obtained from Fluka and used as received. NMR spectra were carried out on a Bruker AM-300 WB at room temperature; chemical shifts are reported in ppm relative to TMS. Deuterium (99%) was obtained from L'Air Liquide Belge and used as received.

[Ethylenebis(4,5,6,7-tetradeuterio-1-indenyl)]zirconium dichloride (3) was prepared from **1** according to the literature procedure,[1] using deuterium instead of hydrogen. A 0.5-L stainless steel autoclave was pressure tested at 100 bar with H_2 overnight, evacuated, and charged with 2.49 g (5.95 mmol) of **2**, 0.16 g (0.7 mmol) of PtO_2, and 50 mL of CH_2Cl_2 under flowing nitrogen. The autoclave was sealed, submitted to several vacuum/N_2 purge cycles, and pressurized to 95 bar with D_2. The autoclave was shaken for 40 min at room temperature and depressurized, and the reaction mixture was transferred, in air, to a 1000-mL round-bottom flask. A total of 400 mL of CH_2Cl_2 was added and the mixture filtered through a medium frit to give a clear yellow solution. Removal of solvent in vacuo, followed by recrystallization of the residue from 125 mL of toluene, afforded **3** as pale yellow crystals (1.09 g 42%). Mass spectrum: $M^+ = 432$, with expected isotopic distribution. ^1H NMR: presented in Table I. ^{13}C NMR (DEPT, C_6D_6): 119.18 (+), 108.2 (+), 28.17 (-), 23.35 (+, two overlapping three-line signals of equal intensity, $J_{CD} = 17$ Hz), 21.6 (+, two overlapping three-line signals of equal intensity, $J_{CD} = 17$ Hz). (+/- in parentheses refers to the phase of the signal.) Homo decoupling (C_6D_6): Irradiation of resonance at 3.14 ppm caused the doublet of doublets at 6.35 ppm to collapse to a doublet. Irradiation of resonance at 1.91 ppm caused doublet at 3.14 ppm to collapse to a singlet. Irradiation at 1.82 ppm caused doublet at 2.16 ppm to collapse to a singlet. Difference NOE (C_6D_6): Irradiation of the resonance at 2.16 ppm led to enhancement of resonances at 5.26 (14.8%) and 1.82 ppm (13.8%). Irradiation of resonance at 5.26 ppm lead to enhancements at 2.16 (10.3%) and 6.35 ppm (20%). Irradiation of the resonance at 3.14 ppm led to enhancements at 6.35 (7.9%) and 1.91 ppm (15.1%).

[Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]dimethylzirconium (4) was prepared as previously described.[11] Compound **2** (0.951 g, 2.23 mmol) was suspended in 100 mL of Et_2O in a 150-mL Schlenk tube, and the mixture was cooled to -50 °C. To this suspension under nitrogen was added 3.3 mL of a 1.7 M Et_2O solution of methyllithium. After the reaction flask was covered with aluminum foil, the suspension was allowed to warm to room temperature and was stirred for 2 h. Evacuation of the ether solvent afforded a powdery white residue, which was treated with 100 mL of hexane, the mixture was allowed to stir at room temperature for 1 h. The resulting suspension was filtered through Celite on a medium frit and the residue extracted with an additional 50 mL of hexane to give a colorless solution. This solution was concentrated to 75 mL and placed in a -40 °C freezer overnight to afford **4** as colorless microcrystals (0.662 g, 1.717 mol). NMR data are given in Table I.

[Ethylenebis(4,5,6,7-tetradeuterio-1-indenyl)]dimethylzirconium (5) was prepared from **3** by the procedure of **4**. ^1H NMR data are presented in Table I. Difference NOE (C_6D_6): Irradiation of resonance at 5.13 ppm led to enhancements at 1.98 (11.7%) and 1.69 ppm (1.3%). Irradiation of resonance at -0.1 ppm led to enhancements at 2.82 (17.8%), 1.98 (2.5%), 1.69 (10.2%), and 1.61 ppm (8.6%).

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Registry No. **1**, 112243-78-4; **2**, 112243-79-5; **3**, 112088-04-7; **4**, 112243-80-8; **5**, 112088-05-8; PtO_2, 11129-89-8.

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Hydroxide-Assisted Stereospecific Isomerization of a *trans*-Dichloro Bis Chelate of Ruthenium(II)

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A few years ago we reported our early work on complexes of ruthenium(II) with 2-(phenylazo)pyridine (Azpy);[1] three geometric isomers of $[Ru(Azpy)_2Cl_2]$ were isolated and characterized.

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