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TRANSITION METAL COMPLEXATION OF OPTICALLY PURE ANNULATED CYCLOPENTADIENES. FACE SELECTIVITY, THREE-DIMENSIONAL STRUCTURAL FEATURES, AND UTILIZATION FOR ASYMMETRIC HYDROGENATION[1]

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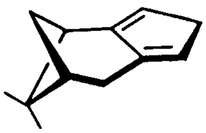
Abstract: The pinene-annulated cyclopentadiene (-)-**1** forms iron carbonyl and dichlorotitanium complexes from its less hindered π surface; the camphor-annulated ligand (+)-**4** exhibits analogous facial selectivity. The utility of complexes **3** and **5** as asymmetric hydrogenation catalysts is evaluated.

Optically active cyclopentadienes have commanded attention recently as ligands to transition metals for the purpose of effecting asymmetric synthesis.[3] However, the results have been generally disappointing, perhaps because only one chiral substituent has been present on the Cp ring. The preceding paper[1] describes new synthetic methodology that makes possible the expedient preparation of two optically pure, annulated cyclopentadienes. Since both of these systems differ from the earlier prototypes by possessing considerably greater conformational rigidity, we have investigated their complexation to iron and/or titanium, as well as the ability of the latter to effect enantioselective hydrogenation.[4]

Heating **1** with 3 mol equiv of $Fe(CO)_5$ in *n*-octane[5] furnished **2** in a disappointing 12.5% yield. The addition of cyclooctene as hydrogen acceptor improved matters to the



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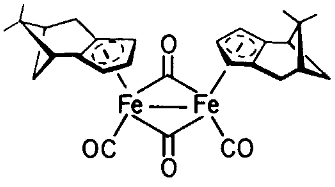

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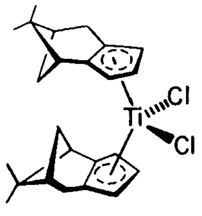

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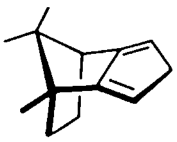

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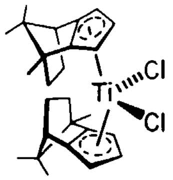

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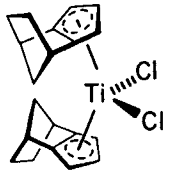

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29.5% level. Subsequently it was found that norbornene serves admirably in this capacity and allows isolation of **2** in 70% yield. Thus, the Cp dicarbonyl hydride mechanistic hypothesis[6] receives added experimental substantiation. X-ray crystallographic analysis of **2** (dark brown crystals, mp 178 °C dec)[7] revealed that coordination to iron occurs from the π-face proximal to the methano bridge and that **2** crystallizes as the cis isomer[8] (Figure 1).

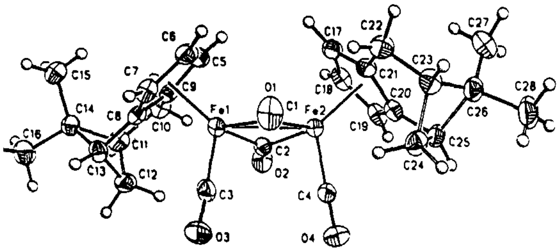


Figure 1. A computer-generated perspective edge view of **2**.

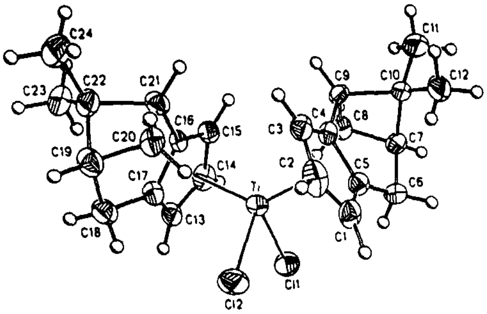


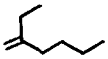
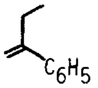
Figure 2. A computer-generated view of **3**.

The cyclopentadienide anions of **1** and **4** reacted with $TiCl_4$ in ether to give major proportions of **3** (39%, deep red crystals, mp 240 °C dec) and **5** (23%, purple brown crystals, mp 175-178 °C), respectively. The three-dimensional features of **3** were determined to be as shown by X-ray analysis (Figure 2).[7] That below-plane complexation had occurred on both ligands in complex **5** was evident by spectral comparison with **3** and **6**.[9,10]

The ability of reduced forms of **3** and **5** to effect enantioselective hydrogenation of 2-ethyl-1-hexene (**7**) and α-ethylstyrene (**8**) is summarized in Table I. In our hands, activation with n-butyllithium[11] proved superior though less reproducible than the Red-Al method.[3n] The data reveal **3** to be an inferior catalyst to **5**, which gives optical yields greatly superior to any previously observed.[3,4] Understandably, the systems do not distinguish the ethyl/n-butyl substituent pair in **7** as well as they do the ethyl and phenyl groups in **8**. Of mechanistic importance is the finding that the asymmetry introduced by **3** is antipodal to that realized with **5**.

Acknowledgment. The generous financial support of the Public Health Service through grant CA-12115 is acknowledged with gratitude.

Table I. Enantioselective Hydrogenation Results.

			% enantiomeric excess (abs. config.)[a]	
Complex	Temp	Method of activation	 (7)	 (8)
3	20°C	Red-Al	0.1 (*R*)	1.7 (*S*)
	20°C	*n*-BuLi	---	2 (*S*)
	-20°C	*n*-BuLi	---	6.9 (*S*)
4	20°C	Red-Al	2.2 (*S*)	14.1 (*R*)
	0°C	Red-Al	---	23.7 (*R*)
	-20°	*n*-BuLi[b]	---	34

[a] The absolute configurational assignments for 3-methylheptane [Burwell, R. L., Jr.; Gordon, G. S., III *J. Am. Chem. Soc.* **1948**, *70*, 3128] and 2-phenylbutane [Lardicci, L.; Menicagli, R.; Salvadori, P. *Gazz. Chim. Ital.* **1968**, *98*, 738] have been culled from the literature. [b] See footnote 4.

References and Notes

(1) This paper represents our 37th contribution to the chemistry of isodicyclopentadienes. For part 36, see preceding paper in this issue.

(2) Author to whom inquiries concerning the X-ray crystal structure analyses should be directed at the University of Delaware.

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(7) Crystal parameters: **2**, $C_{28}H_{30}Fe_2O_4$, orthorhombic $P2_12_12_1$, a = 11.378(3), b = 11.903(3), c = 18.168(5) Å, V = 2461 Å^3, Z = 4, μ = 12.1 cm^{-1}, D (calc) = 1.463 b cm^{-3} crystal size 0.28 x 0.30 x 0.34 mm; of 6111 reflections collected, 4260 with $F_o \geq 4\sigma(F_o)$ were considered observed. R_F = 4.19%, R_{wF} = 4.88%, GOF = 0.984, Δ/σ = 0.09, $\Delta(\rho)$ = 0.64 e Å^{-3}, data/parameter = 10.7. **3**, $C_{24}H_{30}TiCl_2$, orthorhombic, $P2_12_12_1$, a = 7.349(3), b = 14.520(6), c = 20.429(8) Å, V = 2180 Å^3, Z = 4, μ = 6.6 cm^{-1}, D (calc) = 1.332 g cm^{-3}, crystal size 0.20 x 0.20 x 0.42 mm; of 3019 reflections collected, 2180 with $F_o \geq 4\sigma(F_o)$ were considered observed. R_F = 4.39%, R_{wF} = 4.92%, GOF = 0.985, Δ/σ = 0.01, $\Delta(\rho)$ = 0.41 e Å^{-3}, data/parameter = 8.9. For both, Nicolet R3m/μ diffractometer, MoKα radiation, graphite monochromator, T = 293(1) K, data collection to the limit of availability (**2**, $2\theta = 55^{\circ}$; **3**, $2\theta = 45^{\circ}$). Unit cell parameters were derived from the least squares fit of 25 reflections ($21^{\circ} \leq 2\theta \leq 27^{\circ}$). Two octants of intensity data were collected and not merged. No corrections for absorption or decay (each < 1%) were required. In both cases refinement of a multiplicative factor for $\Delta f''$ showed that the reported enantiomorph is unambiguously correct. All computer programs are contained in the SHELXTL program libraries (version 5.1), Nicolet XRD Corp., Madison, WI. Crystallographic parameters have been deposited with the Cambridge Crystallographic Data File, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England and are available from them. Please give a complete literature citation when ordering.

(8) X-ray data are available for this cis and trans forms of the parent Cp complex [Mills, O. S. *Acta Crystallogr.* **1968**, *11*, 620; Bryan, R. F.; Greene, P. T.; Field, D. S.; Newlands, M. J. *Chem. Commun.* **1969**, 1477]. No attempt has been made to assess the dynamic behavior of **2** [see Gansow, O.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1972**, *94*, 2550].

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(10) Most notably, the endo methyl group in **3** (at δ 0.49) and the *endo*-ethano protons in **6** (at δ 1.11) are significantly shielded relative to the uncomplexed ligand,[1] while their exo counterparts are little affected. The same long-range anisotropy is present in **5** ($\delta_{endo\text{-}CH_3}$ = 0.26, $\delta_{exo\text{-}CH_3}$ = 0.91), whose symmetry is also apparent by ^{13}C NMR.

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