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General Synthetic Routes to Chiral, Ethylene-Bridged *ansa*-Titanocene Dichlorides[1a]

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Two synthetic routes for the preparation of chiral (1,2-ethylenebis(η^5-3-alkylcyclopentadienyl))titanium dichlorides (**3**) are described wherein the substituent, R, can be a primary, secondary, or tertiary alkyl group. Compounds **3a–d** and **4a–d** are prepared from $TiCl_3 \cdot 3THF$ and the corresponding 1,2-ethylenebis(3-alkyl-1,3-cyclopentadienes) (**8a–d**; R = Me, Et, *i*Pr, *t*Bu) in 80–85% yields. Compounds **8a** and **8b** (R = Me, Et) can be prepared in five steps and in 44 and 24% overall yield, respectively, from 1,2-ethylenebis(1,3-cyclopentadiene) (**5**). Compounds **8c** and **8d** (R = *i*Pr, *t*Bu) can be prepared in two steps and in >90% overall yield from compound **5**. A mixture of *rac*- and *meso*-titanocene dichlorides, **3** and **4**, respectively, is produced on reaction of the dilithium salts of compounds **8** with $TiCl_3$ (the ratio of *rac*:*meso* varies between 1:1.3 and 1:2.0). Isomers **3d** and **4d** may be separated by HPLC or, more conveniently, by flash chromatogaphy on silica gel. Compound **3d** crystallizes in two distinct modifications, both of which were characterized by X-ray crystallography: modification 1, space group $P2_1/c$, $Z = 4$, $a = 11.537$ (4) Å, $b = 13.436$ (6) Å, $c = 13.007$ (4) Å, $\beta = 98.21$ (3)°, $V = 1995$ (1) Å^3, $R = 0.085$ and $R_W = 0.096$ on the basis of 2270 reflections with $I > 3\sigma(I)$; modification 2, space group $P\bar{4}2_1c$, $Z = 8$, $a = 14.443$ (1) Å, $c = 19.249$ (3) Å, $V = 4010$ (1) Å^3, $R = 0.0346$ and $R_W = 0.0355$ on the basis of 1976 reflections with $I > 3\sigma(I)$. The conformations adopted by the ansa ligand in the two modifications are markedly different; it appears that the energy difference between the two conformers is probably low and might be influenced by crystal-packing effects.

Introduction

There has been considerable current interest in the preparation and chemistry of chiral *ansa*-metallocene compounds of the group 4 transition elements. Several examples of this class of compounds have been prepared,[2] among the first of which were based on the ethylenebis(η^5-tetrahydroindenyl) or ethylenebis(η^5-indenyl) ligand system. Metallocene dichlorides derived from these ligands (**1** and **2**, M = Ti, Zr, Hf; Scheme I) function as precursors to highly active, soluble Ziegler–Natta catalysts for the production of isotactic (poly(α-olefins).[3] Despite the enormous potential for compounds of this type (e.g. compounds **1–3**, Scheme I) in olefin polymerization and conceivably in asymmetric synthesis,[4] flexible *and* efficient synthetic routes to this class of compounds have not been developed.

Recently, a paper describing a synthetic approach to analogues of compounds **3** was reported by Brintzinger and co-workers.[2c] As shown in Scheme I, the synthesis of the required (*tetramethyl*)ethylene-bridged ligand was accomplished, in low yield, by reductive coupling of an appropriate 6,6-dimethylfulvene. The metallocene compounds derived from these ligands were produced in less than 50% yield.

Although the route described above is expedient, it seems impractical for the synthesis of these compounds in large quantities. We report here two synthetic routes to the analogous *ethylene*-bridged systems **3** that are more efficient than existing routes to this class of compounds.

Results and Discussion

Initially, we recognized that dienone **7** could serve as a key common intermediate for the synthesis of a number of ethylenebis(3-alkylcyclopentadienes). Addition of an organolithium compound to dienone **7** followed by dehydration of the resulting tertiary allylic diol would provide the desired ligands (Scheme II). In practice, dienone **7** was prepared from ethylenebis(cyclopentadiene) (**5**)[5] in three steps and in 60% overall yield. Hydroboration–oxidation of compound **5** provided an intermediate diol as a single regioisomer in 80–85% crude yield. Although compound **5** exists as a mixture of regioisomers with respect to the position of the ethylene bridge, disiamylborane apparently undergoes selective addition to the less substituted double bond of the 1,3-diene system in a regioselective manner. Oxidation of this diol with use of either PCC or DMSO–oxalyl chloride–triethylamine provided the crystalline diketone **6** in 50–60% yields. While these procedures were suitable for small-scale work, because of the insolubility of the diol in CH_2Cl_2 at low temperatures

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[1] (a) Presented in part at the 3rd Chemical Congress of North America: Collins, S.; Hong, Y. *Abstracts of Papers*, 3rd Chemical Congress of North America, Toronto, Canada, June 1988; American Chemical Society: Washington, DC, 1988; ORGN-49. (b) Ontario Graduate Scholar 1989–1990.

[2] For a review of recent work in the area of group 4, ethylene-bridged, chiral *ansa*-metallocene synthesis see: Brintzinger, H. H. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1988; p 249. See also: (a) Burger, P.; Hund, H.-U.; Evertz, K.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *378*, 153. (b) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H.-H. *Ibid.* **1989**, *369*, 359. (c) Guttmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H.-H. *Ibid.* **1989**, *369*, 343. (d) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Ibid.* **1988**, *342*, 21. (e) Schafer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *Ibid.* **1987**, *328*, 87. (f) Roll, W.; Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *Ibid.* **1987**, *322*, 65. (g) Wild, F. W. R. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H.-H. *Ibid.* **1985**, *288*, 63. (h) Wild, F. W. R. P.: Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *Ibid.* **1982**, *232*, 233.

[3] See inter alia: (a) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617. (b) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (c) Ewen, J. A.; Haspeslagh, L; Atwood, J. L.; Zhang, H. *Ibid.* **1987**, *109*, 6544. (d) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo, P.; Proto, A. *Macromolecules* **1986**, *19*, 2703. (e) Kaminsky, W.; Kulper, K.; Niedoba, S. *Makromol. Chem.* **1986**, *187*, 377. (f) Kaminsky, W.; Kulper, K.; Brintzinger, H.-H. *Angew. Chem.* **1985**, *97*, 507. (g) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

[4] For example, we have investigated the reactions of allyltitanium(III) derivatives of homochiral compound **1** (M = Ti) with aldehydes; only modest enantioselectivity was observed: Collins, S.; Hong, Y.; Kuntz, B. A. *J. Org. Chem.* **1989**, *54*, 4154.

[5] Prepared in ca. 85% yield from Cp_2Mg and 1,2-dibromoethane with use of modifications to the route originally reported: Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159.

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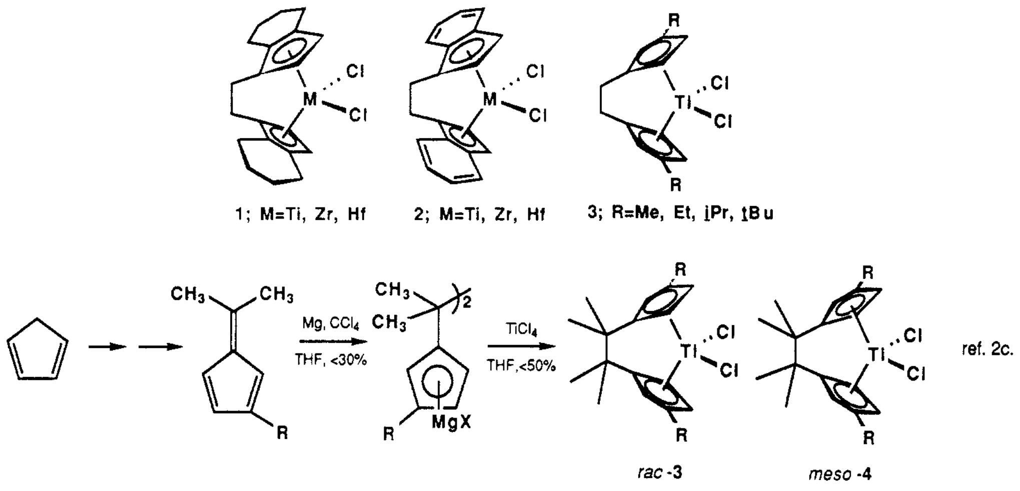
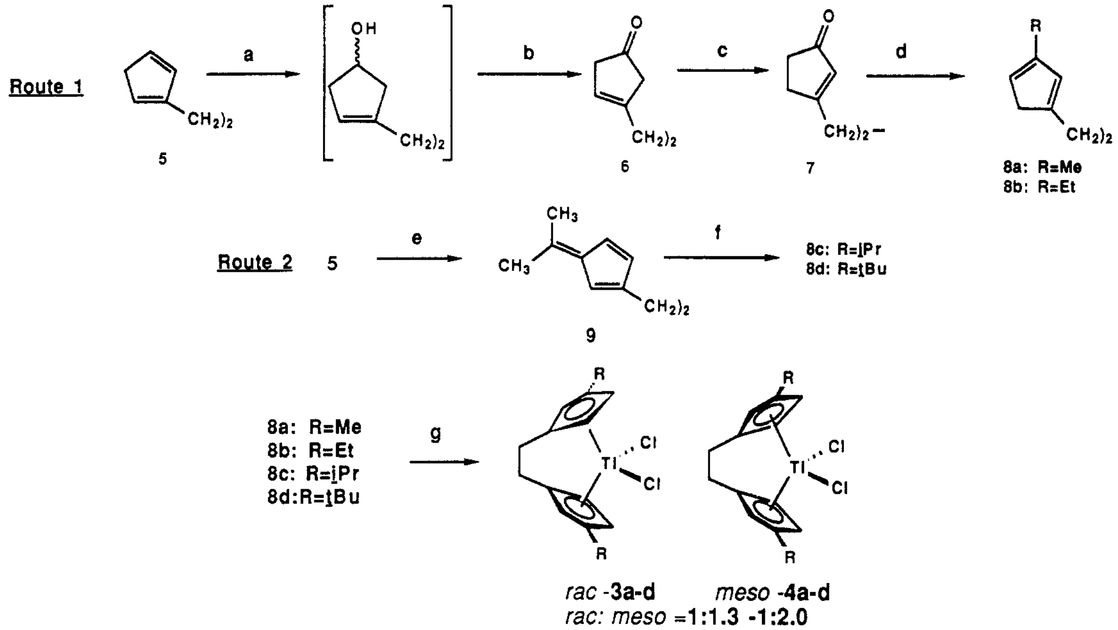
Scheme I



Scheme II[a]



[a] Legend: (a) (1) disiamylborane (2.5 equiv), THF, 0–25 °C, 3 h, (2) 30% H_2O_2, aqueous NaOH, 90–95%; (b) *N*-methylmorpholine *N*-oxide (3.0 equiv), TPAP (30 mol %), 4-Å molecular sieves, CH_2Cl_2, 25 °C, 90 min, 75–80%; (c) 1 N HCl, 1,4-dioxane, 80 °C, 30 s, 95%; (d) (1) MeLi or EtMgBr (2.2 equiv), THF, 0 °C, ~90%, (2) *p*-TSA, Et_2O, 25 °C, 5 min, 60 *or* 35% overall from 7; (e) acetone (excess), pyrollidine, MeOH, 25 °C, 3 h, 95%; (f) $LiAlH_4$ (1.0 equiv), Et_2O, 0–25 °C, 3 h *or* MeLi (2.5 equiv), Et_2O, 0–25 °C, 2 h, quantitative; (g) (1) *n*BuLi (2 equiv), THF, -78 to +25 °C then $TiCl_3$·3THF (1 equiv), -40 °C to reflux, (2) 6 M HCl (2.2 equiv), -40 to +25 °C, O_2, 80–85%.

and that of the diketone **6** in diethyl ether, solvents typically employed in these reactions or during workup, significant decreases in yield on a large scale were obtained. In contrast, the recently developed method[6] with tetrapropylammonium perruthenate as a catalyst and *N*-methylmorpholine *N*-oxide as the oxidant proved superior for large-scale work, reproducibly yielding compound **6** in 75–80% yield. Acid-catalyzed isomerization (1 N HCl, dioxane, 80 °C, 30 s) of compound **6** proceeded cleanly and provided the crystalline dienone **7** in essentially quantitative yield. Addition of methyllithium or ethylmagnesium bromide to dienone **7** (2.2 equiv, THF, 0 °C) followed by dehydration of the resulting diols (catalytic amount of *p*-TSA, 25 °C) provided the ethylenebis(cyclopentadiene) derivatives **8a** and **8b**, in 60 and 35% yields, respectively. A number of dehydrating agents have been examined for this final step with essentially similar results.

Compounds **8c** and **8d** could be more efficiently prepared by using the second route shown in Scheme II. Condensation of acetone with compound **5** according to the method of Little et al.[7] provided crystalline bis(fulvene) **9a** in >90% yield with a regioisomeric purity of >96%. Reduction of **9a** with $LiAlH_4$ provided bis(cyclopentadiene) **8c**, whereas addition of MeLi provided compound **8d** in essentially quantitative yields.[8] The second route outlined in Scheme II is easily adaptable to the synthesis of a wide variety of bis(cyclopentadienes) **8**, where R is a secondary or tertiary alkyl group.

The titanocene dichlorides **3a–d** and **4a–d** were prepared from the dianions of compounds **8a–d** (2.2 equiv of *n*BuLi, THF, 0 °C) and $TiCl_3$·3THF (-40 °C to reflux, 4 h) followed by treatment with HCl (-40 to 25 °C) under aerobic conditions (Scheme II). The isolated yields exceeded 80%.

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(6) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625.

(7) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

(8) See e.g.: (a) Ziegler, K.; Gellet, H. G.; Martin, H.; Schnider, J. *Justus Liebigs Ann. Chem.* **1954**, *589*, 91. (b) Ziegler, K.; Schafer, W. *Ibid.* **1934**, *511*, 101.

Table I. ^{1}**H NMR Chemical Shifts of Cyclopentadienyl Protons for Compound 3a–d and 4a–d**[a]

racemic compd	δ, ppm[b]	meso compd	δ, ppm[b]
3a	6.58 (pt, J = 2.8, 2.1) 6.00 (pt, J = 2.8, 2.5) 5.75 (pt, J = 2.5, 2.1)	**4a**	6.47 (pt, J = 2.8, 2.0) 6.24 (pt, J = 2.8, 2.4) 5.63 (pt, J = 2.4, 2.0)
3b	6.62 (pt, $J \approx$ 2.5) 5.99 (pt, $J \approx$ 2.5) 5.77 (pt, $J \approx$ 2.5)	**4b**	6.51 (pt, $J \approx$ 2.5) 6.25 (pt, $J \approx$ 2.5) 5.63 (pt, $J \approx$ 2.5)
3c	6.69 (pt, $J \approx$ 2.5) 5.54 (pt, $J \approx$ 2.5) 5.37 (pt, $J \approx$ 2.5)	**4c**	6.59 (pt, $J \approx$ 2.5) 5.78 (pt, $J \approx$ 2.5) 5.26 (pt, $J \approx$ 2.5)
3d	6.66 (pt, $J \approx$ 2.5) 6.13 (pt, $J \approx$ 2.5) 6.02 (pt, $J \approx$ 2.5)	**4d**	6.63 (pt, $J \approx$ 2.5) 6.32 (pt, $J \approx$ 2.5) 5.97 (pt, $J \approx$ 2.5)

[a] All spectra were recorded in $CDCl_3$ solution, and shifts are reported with respect to TMS added as an internal standard. [b] pt = pseudotriplet. In the case of compounds **3a** and **4a** the individual coupling constants, shown in parentheses, were measured by appropriate decoupling experiments. All J values are in Hz.

This should be contrasted with the other systems that have been prepared, which are usually produced in less than 50% yield.[2]

The second of the two routes depicted in Scheme II is a very efficient method for the preparation of ligands **8** bearing a secondary or tertiary alkyl group, being more efficient than the method reported recently by Brintzinger et al. for the preparation of the tetramethyl-ethylene- or dimethylsilyl-bridged analogues.[2b,c] However, the first route in Scheme II is quite lengthy and suffers from low yields in the final dehydration step. Efforts to improve on the synthesis of ligands such as **8a** are in progress.

Assignment of stereochemistry to compounds **3a–d** and **4a–d** was problematic in that the separation of diastereoisomers could not be accomplished by fractional crystallization or a variety of other practical, chromatographic techniques. All of the titanocene compounds prepared could be separated on an analytical HPLC column (see Experimental Section), but only in the case of compounds **3d** and **4d** was sufficient resolution observed so as to allow a practical preparative separation. Fortunately, compounds **3d** and **4d** could also be cleanly separated by flash chromatography on silica gel, albeit with some decomposition. An X-ray structure determination of compound **3d** (vide infra) established that the minor product was in fact the desired racemic stereoisomer.

The ^{1}H NMR and ^{13}C NMR spectral characteristics of compounds **3a–d** and **4a–d** are diagnostic for the stereochemistry of the ansa-ligand framework (see Table I and Experimental Section). In particular, the chemical shifts of the cyclopentadienyl protons in compounds **3a–d** and **4a–d** exhibit the same pattern throughout the series. In a mixture of the two isomers, the racemic diastereoisomer *always* has two triplets of equal intensity closely spaced in chemical shift and the remaining signal, also a triplet, is found at lowest field (see Table I). In contrast, the meso isomer has three signals, more or less evenly spaced, with one of the triplets *always* occurring at highest field. This feature appears to be general for this class of compounds.[2]

Table II. Crystal Data for Compound 3d

	modification 1	modification 2
formula	$C_{20}H_{28}Cl_2Ti$	$C_{20}H_{28}Cl_2Ti$
mol wt	387.26	387.26
cryst syst	monoclinic	tetragonal
cell constants		
a, Å	11.537 (4)	14.443 (1)
b, Å	13.436 (6)	
c, Å	13.007 (4)	19.249 (3)
β, deg	98.21 (3)	
V, Å^3	1995 (1)	4010 (1)
space group	$P2_1/c$	$P\bar{4}2_1c$ (No. 114)
Z	4	8
ρ_c, g cm^{-3}	1.289	1.283
$F(000)$	816	1632
λ, Å	0.71073	0.71073
T, K	295	295
μ(Mo Kα), cm^{-1}	7.08	6.88
cryst size, mm	0.28 × 0.30 × 0.31	0.46 (110) × 0.48 (1$\bar{1}$0) × 0.36 (001)
diffractometer	Nicolet R3m	Nicolet R3m
scan method	ω	ω
2θ range, deg	3.5–50.0	3.5–54.0
scan width, deg	1.2	1.2
scan speed, deg min^{-1}	2.93–29.30	2.93–29.30
std rflns	041, 500	080, 0016
std variance, %	±2	±6
transmission factors	0.76–0.86	0.725–0.796
no. of measd data	3875	4720
no. of unique data	3875	2433 (R_{merge} = 0.0324)
no. of obsd data ($I > 3\sigma(I)$)	2270	1976
no. of params	209	321
R^a	0.085	0.0346
$R_w{}^b$	0.096	0.0355
GOF^c	2.41	1.37
$w^{-1} = \sigma^2(F) + aF^2$ (a)	0.00182	0.00045
max residual electron density, e Å^{-3}	0.81	0.26

[a] $R = \sum[||F_o| - |F_c||]/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. [c] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$.

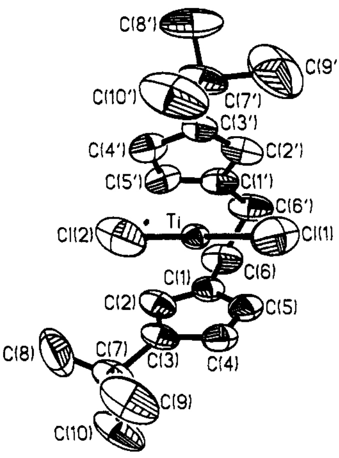

Figure 1. Molecular structure of compound **3d** (space group $P2_1/c$) with 50% probability thermal ellipsoids depicted.

Single crystals of compound **3d** were originally grown by vapor diffusion of hexane into a concentrated benzene solution of this metallocene dichloride. Over the course of several days platelike crystals separated. Most of these had rough exteriors, were somewhat opaque, and appeared to possess interiors with high mosaic spread. Although diffraction was rather limited and diffuse, after several attempts, data collection proved possible. Although crystals grown in this manner were clearly monoclinic, space group $P2_1/c$ (modification 1; relevant crystal data are collected in Table II), most crystals examined gave values of α somewhat deviant from 90° (i.e. for the crystal data reported in Table II α was 89.74 (2)°). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares, with use of Nicolet SHELXTLPLUS software, to an R value of 0.085 (best attempt!). The final atomic coordinates, the isotropic thermal parameters, bond lengths, and selected bond angles are summarized in Tables III, V, and VI, respectively, while an Ortep diagram appears in Figure 1. The large thermal parameters (Table III) are indicative of the limited

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 3d (Space Group $P2_1/c$)

	x/a	*y/b*	*z/c*	*U*(eq)[a]
Ti	7743 (1)	1324.7 (9)	1807.8 (9)	41.5 (4)
Cl(1)	7625 (2)	370 (3)	3304 (2)	109 (1)
Cl(2)	7920 (3)	2850 (2)	2652 (2)	105 (1)
C(1)	6537 (6)	781 (6)	265 (6)	53 (3)
C(2)	6359 (7)	1790 (7)	291 (6)	61 (3)
C(3)	5775 (7)	2045 (6)	1125 (6)	56 (3)
C(4)	5653 (7)	1105 (7)	1691 (7)	62 (3)
C(5)	6131 (7)	377 (7)	1132 (8)	68 (3)
C(6)	7094 (8)	189 (8)	−534 (7)	78 (4)
C(7)	5118 (8)	2997 (7)	1259 (8)	80 (4)
C(8)	5701 (13)	3882 (8)	919 (12)	124 (7)
C(9)	4797 (12)	3031 (10)	2445 (8)	119 (6)
C(10)	3909 (10)	2879 (9)	568 (9)	112 (5)
C(1′)	8830 (7)	403 (7)	752 (6)	62 (3)
C(2′)	9410 (8)	217 (8)	1777 (7)	69 (3)
C(3′)	9930 (6)	1080 (6)	2216 (6)	52 (3)
C(4′)	9666 (7)	1856 (7)	1464 (6)	66 (3)
C(5′)	9006 (7)	1430 (7)	552 (6)	64 (3)
C(6′)	8185 (8)	−361 (8)	25 (7)	81 (4)
C(7′)	10819 (8)	1194 (8)	3209 (7)	77 (4)
C(8′)	11987 (10)	1160 (12)	2919 (9)	122 (6)
C(9′)	10793 (16)	117 (13)	3856 (12)	159 (8)
C(10′)	10484 (13)	1953 (11)	3967 (11)	148 (7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 3d (Space Group $P\bar{4}2_1c$)

	x/a	*y/b*	*z/c*	*U*(eq)[a]
Ti(1)	734.5 (4)	2914.8 (4)	2262.7 (3)	33.8 (2)
Cl(1)	−833.9 (7)	3410.2 (8)	2221.0 (6)	53.6 (3)
Cl(2)	426.7 (9)	1336.9 (7)	2365.0 (6)	59.4 (4)
C(1)	1938 (3)	3657 (3)	2917 (2)	44 (1)
C(2)	1798 (3)	2791 (3)	3235 (2)	41 (1)
C(3)	913 (3)	2766 (3)	3559 (2)	39 (1)
C(4)	489 (3)	3610 (3)	3398 (2)	41 (1)
C(5)	1098 (3)	4154 (3)	2998 (2)	43 (1)
C(6)	2779 (3)	4001 (4)	2536 (3)	57 (2)
C(7)	553 (3)	2072 (3)	4088 (2)	45 (1)
C(8)	1066 (4)	1148 (4)	4060 (3)	65 (2)
C(9)	−490 (4)	1922 (5)	4007 (3)	62 (2)
C(10)	734 (5)	2514 (4)	4805 (3)	62 (2)
C(1′)	1807 (3)	3670 (3)	1518 (2)	45 (1)
C(2′)	933 (3)	3825 (3)	1217 (2)	44 (1)
C(3′)	568 (3)	2982 (3)	949 (2)	46 (1)
C(4′)	1208 (3)	2296 (4)	1138 (2)	48 (1)
C(5′)	1959 (3)	2696 (3)	1492 (2)	47 (1)
C(6′)	2452 (3)	4362 (4)	1832 (3)	55 (2)
C(7′)	−260 (3)	2847 (3)	465 (2)	54 (1)
C(8′)	−874 (4)	3709 (4)	437 (3)	74 (2)
C(9′)	−847 (5)	2017 (5)	682 (4)	77 (2)
C(10′)	137 (6)	2680 (7)	−259 (3)	87 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

diffraction; the C–CH_3 bond lengths within both *tert*-butyl groups are markedly different (e.g. C(7)–C(8), C(7)–C(9), and C(7)–C(10) are 1.464 (16), 1.638 (16), and 1.556 (14) Å, respectively; see Table V). The reason for the anomalous bond lengths exhibited by both *tert*-butyl groups is not immediately apparent; there are no large inter- or intramolecular contacts or evidence of disorder that might account for the unusual geometry observed for the *tert*-butyl groups in this structure. The asymmetric conformation adopted by the ansa ligand with respect to the metal center, as shown in Figure 1, is quite similar to that observed for a tetramethylethylene-bridged analogue, R = 1-phenylcyclohexyl, prepared recently by Brintzinger and co-workers.[2c]

Table V. Bond Lengths (Å) for Compound 3d[a]

	Modification 1		
Ti–Cl(1)	2.351 (3)	Ti–Cl(2)	2.321 (3)
Ti–C(1)	2.387 (7)	Ti–C(2)	2.436 (8)
Ti–C(3)	2.511 (7)	Ti–C(4)	2.412 (8)
Ti–C(5)	2.322 (8)	Ti–C(1′)	2.341 (9)
Ti–C(2′)	2.436 (9)	Ti–C(3′)	2.525 (7)
Ti–C(4′)	2.432 (9)	Ti–C(5′)	2.343 (9)
C(1)–C(2)	1.372 (12)	C(1)–C(5)	1.392 (13)
C(1)–C(6)	1.522 (13)	C(2)–C(3)	1.399 (12)
C(3)–C(4)	1.477 (12)	C(3)–C(7)	1.510 (13)
C(4)–C(5)	1.380 (13)	C(6)–C(6′)	1.549 (13)
C(7)–C(8)	1.464 (16)	C(7)–C(9)	1.638 (16)
C(7)–C(10)	1.556 (14)	C(1′)–C(2′)	1.426 (11)
C(1′)–C(5′)	1.423 (13)	C(1′)–C(6′)	1.517 (13)
C(2′)–C(3′)	1.391 (12)	C(3′)–C(4′)	1.432 (12)
C(3′)–C(7′)	1.538 (11)	C(4′)–C(5′)	1.435 (11)
C(7′)–C(8′)	1.451 (15)	C(7′)–C(9′)	1.677 (20)
C(7′)–C(10′)	1.507 (18)	Cent–Ti	2.098 (8)
Cent′–Ti	2.092 (9)		
	Modification 2		
Ti(1)–Cl(1)	2.375 (1)	Ti(1)–Cl(2)	2.329 (1)
Ti(1)–C(1)	2.398 (4)	Ti(1)–C(2)	2.427 (4)
Ti(1)–C(3)	2.518 (4)	Ti(1)–C(4)	2.431 (4)
Ti(1)–C(5)	2.340 (4)	Ti(1)–C(1′)	2.374 (4)
Ti(1)–C(2′)	2.421 (4)	Ti(1)–C(3′)	2.542 (4)
Ti(1)–C(4′)	2.440 (4)	Ti(1)–C(5′)	2.329 (4)
C(1)–C(2)	1.406 (6)	C(1)–C(5)	1.417 (6)
C(1)–C(6)	1.503 (6)	C(2)–C(3)	1.422 (6)
C(3)–C(4)	1.399 (6)	C(3)–C(7)	1.520 (6)
C(4)–C(5)	1.407 (6)	C(6)–C(6′)	1.525 (7)
C(7)–C(8)	1.526 (7)	C(7)–C(9)	1.528 (7)
C(7)–C(10)	1.542 (6)	C(1′)–C(2′)	1.407 (6)
C(1′)–C(5′)	1.424 (6)	C(1′)–C(6′)	1.493 (7)
C(2′)–C(3′)	1.422 (6)	C(3′)–C(4′)	1.401 (7)
C(3′)–C(7′)	1.529 (6)	C(4′)–C(5′)	1.404 (6)
C(7′)–C(8′)	1.528 (8)	C(7′)–C(9′)	1.526 (8)
C(7′)–C(10′)	1.527 (7)	Cent–Ti	2.106 (4)
Cent′–Ti	2.104 (4)		

[a] Cent and Cent′ are the two centroids of the cyclopentadienyl rings.

In contrast, slow evaporation of a dilute, solution of compound **3d** in isooctane–benzene mixtures under N_2 led to the deposition of "cubic" crystals of this material after about 2 weeks at 25 °C. These crystals were transparent and well-formed and diffracted to a much higher extent than those obtained by the procedure described above. Crystals grown in this manner belonged to the uniquely determined tetragonal space group $P\bar{4}2_1c$ (modification 2, Table II; systematic absences $h00$ ($h = 2n + 1$) and hhl ($l = 2n + 1$)). This structure was solved and refined as described above, but the data quality allowed the location of all hydrogen atoms, which were included in the refinement with isotropic thermal parameters. The final refinement converged with $R = 0.0346$ and $R_W = 0.0355$. Atomic coordinates and isotropic thermal parameters, bond lengths, and selected bond angles are collected in Tables IV, V, and VI, respectively. An Ortep diagram of this structure is depicted in Figure 2; the geometry adopted by the ansa ligand is quite different as the molecule adopts a conformation with approximate C_2 symmetry, which is, however, *not* crystallographically imposed. The extent of the deviation of this structure from ideal C_2 symmetry is seen in, for example, the Ti–Cl(1) and Ti–Cl(2) bond lengths at 2.375 (1) and 2.329 (1) Å, respectively (Table VI). There are no anomalous distances within the *tert*-butyl groups in this structure.

In a recent paper,[2c] it was proposed that the solid-state conformation adopted by the ansa ligand in this class of compounds was determined by the magnitude of steric interactions between the alkyl group at the 3-position of the cyclopentadienyl rings and the chloride ligands bound

Table VI. Selected Bond Angles (deg) for Compound 3d[a]

		Modification 1			
Cl(1)Ti–Cl(2)	95.9 (1)	C(2)–C(1)–C(5)	107.3 (7)	C(2)–C(1)–C(6)	127.8 (8)
C(5)–C(1)–C(6)	124.9 (8)	C(1)–C(2)–C(3)	110.6 (7)	C(2)–C(3)–C(4)	105.5 (7)
C(2)–C(3)–C(7)	127.0 (8)	C(4)–C(3)–C(7)	125.6 (8)	C(3)–C(4)–C(5)	105.7 (8)
C(1)–C(5)–C(4)	110.8 (8)	C(1)–C(6)–C(6′)	108.9 (7)	C(3)–C(7)–C(8)	113.2 (9)
C(3)–C(7)–C(9)	108.5 (8)	C(8)–C(7)–C(9)	115.9 (10)	C(3)–C(7)–C(10)	105.7 (8)
C(8)–C(7)–C(10)	108.8 (9)	C(9)–C(7)–C(10)	104.0 (9)	C(2′)–C(1′)–C(5′)	106.3 (7)
C(2′)–C(1′)–C(6′)	125.9 (8)	C(5′)–C(1′)C(6′)	127.8 (7)	C(1′)–C(2′)–C(3′)	110.8 (8)
C(2′)–C(3′)–C(4′)	106.9 (7)	C(2′)–C(3′)–C(7′)	128.6 (7)	C(4′)–C(3′)–C(7′)	123.6 (7)
C(3′)–C(4′)–C(5′)	108.0 (8)	C(1′)–C(5′)–C(4′)	108.0 (7)	C(6)–C(6′)–C(1′)	105.2 (8)
C(3′)–C(7′)–C(8′)	108.1 (8)	C(3′)–C(7′)–C(9′)	106.2 (8)	C(8′)–C(7′)–C(9′)	100.8 (10)
C(3′)–C(7′)–C(10′)	114.5 (8)	C(8′)–C(7′)–C(10′)	121.7 (10)	C(9′)–C(7′)–C(10′)	103.4 (10)
Cent–Ti–Cent′	127.3 (5)				
		Modification 2			
Cl(1)–Ti(1)–Cl(2)	96.6 (1)	C(2)–C(1)–C(5)	106.2 (3)	C(2)–C(1)–C(6)	128.5 (4)
C(5)–C(1)–Cn6)	125.2 (4)	C(1)–C(2)–C(3)	110.1 (4)	C(2)–C(3)–C(4)	105.8 (3)
C(2)–C(3)–C(7)	128.2 (4)	C(4)–C(3)–C(7)	125.0 (4)	C(3)–C(4)–C(5)	109.5 (4)
C(1)–C(5)–C(4)	108.2 (4)	C(1)–C(6)–C(6′)	107.3 (4)	C(3)–C(7)–C(8)	112.6 (4)
C(3)–C(7)–C(9)	111.2 (4)	C(8)–C(7)–C(9)	110.6 (4)	C(3)–C(7)–C(10)	105.6 (4)
C(8)–C(7)–C(10)	108.2 (4)	C(9)–C(7)–C(10)	108.5 (4)	C(2′)–C(1′)–C(5′)	106.3 (4)
C(2′)–C(1′)–C(6′)	128.3 (4)	C(5′)–C(1′)–C(6′)	125.4 (4)	C(1′)–C(2′)–C(3′)	110.2 (4)
C(2′)–C(3′)–C(4′)	105.5 (4)	C(2′)–C(3′)–C(7′)	128.3 (4)	C(4′)–C(3′)–C(7′)	125.7 (4)
C(3′)–C(4′)–C(5′)	110.1 (4)	C(1′)–C(5′)–C(4′)	107.7 (4)	C(6)–C(6′)–C(1′)	108.9 (4)
C(3′)–C(7′)–C(8′)	111.8 (4)	C(3′)–C(7′)–C(9′)	111.6 (4)	C(8′)–C(7′)–C(9′)	109.1 (4)
C(3′)–C(7′)–C(10′)	106.5 (4)	C(8′)–C(7′)–C(10′)	108.3 (5)	C(9′)–C(7′)–C(10′)	109.5 (5)
Cent–Ti–Cent′	128.8 (3)				

[a] Cent and Cent′ are the two centroids of the cyclopentadienyl rings.

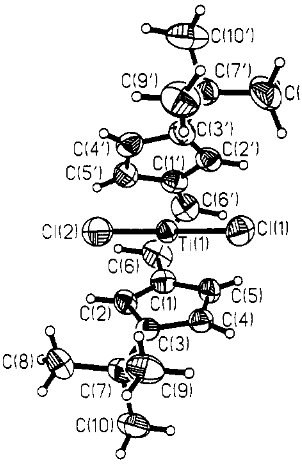

Figure 2. Molecular structure of compound **3d** (space group $P\bar{4}2_1c$) with 50% probability thermal ellipsoids depicted.

to the metal; larger alkyl groups favor a distortion of the ansa ligand toward the conformation depicted in Figure 1 to avoid simultaneous repulsions involving both alkyl groups and the two chloride ligands which would be present in a conformation similar to that depicted in Figure 2.

The results obtained here indicate that both of these conformations are energetically accessible in the solid state for compound **3d**. However, there does not appear to be significant, structural evidence of substantial repulsion between the *tert*-butyl groups and the chloride ligands in the more symmetric structure, as one might have expected, on the basis of the argument presented above. The sums of the angles around C(3) and around C(3′) in modification 1 are 358.1 and 359.1°, respectively, and are 359.0 and 359.5°, respectively, for modification 2. Also, C(7) and C(7′) are 0.314 and 0.230 Å out of the plane defined by C(2)–C(3)–C(4) and C(2′)–C(3′)–C(4′), respectively, in modification 1, whereas the corresponding values are 0.229 and 0.176 Å, respectively, in modification 2. Thus, in the more symmetric structure, the *tert*-butyl groups are closer to the plane of the Cp rings. However, it should be noted that in modification 2 the centroids of the Cp rings are slightly further from the metal than they are in modification 1 (see Table V).

It seems probable that the energy difference between these two conformations in the solid state is probably quite low and that this difference may arise from intermolecular as well as intramolecular contacts. An examination of packing diagrams (see Supplementary Material) of the two modifications was undertaken to determine whether the conformation of the ansa ligand might be influenced by specific, intermolecular interactions within the unit cell. In modification 1, two long-range intermolecular contacts were present—C(4′)···C(10′) at 3.590 Å (x, $^1/_2 - y$, $^1/_2 + z$) and C(5′)···Cl(2) at 3.750 Å (x, $^1/_2 - y$, $-^1/_2 + z$)—that were close to the sums of the van der Waals radii of two CH_3 groups or a CH_3 group and a chlorine atom, respectively. In modification 2, two other interactions—H(10x′)···H(9z′) at 2.48 Å (y, x, z) and H(6y)···Cl(1) at 2.99 Å ($^1/_2 + x$, $^1/_2 - y$, $^1/_2 - z$)—were also present that were close to the sums of the van der Waals radii of hydrogen and chlorine. In general, however, rather inefficient use of space is made within the unit cell in both structures—the shortest intermolecular contacts observed seem insufficient to distort the ligand framework in the manner observed. It is possible, however, that the sum of many long-range repulsions (read crystal-packing forces) may be of sufficient energy to distort the geometry of the ligand in this class of compounds. The room-temperature ^1H NMR and ^{13}C NMR spectra of this compound are consistent with 2-fold symmetry being maintained in solution. Low-temperature NMR spectra did not provide evidence for an asymmetric conformation such as that depicted in Figure 1.

A number of problems remain to be addressed with regard to the efficiencies of the synthetic routes described here. About 60–65% of the titanocene dichloride product consists of the meso diastereoisomers (**4a–d**), which are not useful for asymmetric synthesis or in olefin polymerization.[9] Photoisomerization of the purified meso compound **4d** to racemic **3d** occurs but is accompanied by

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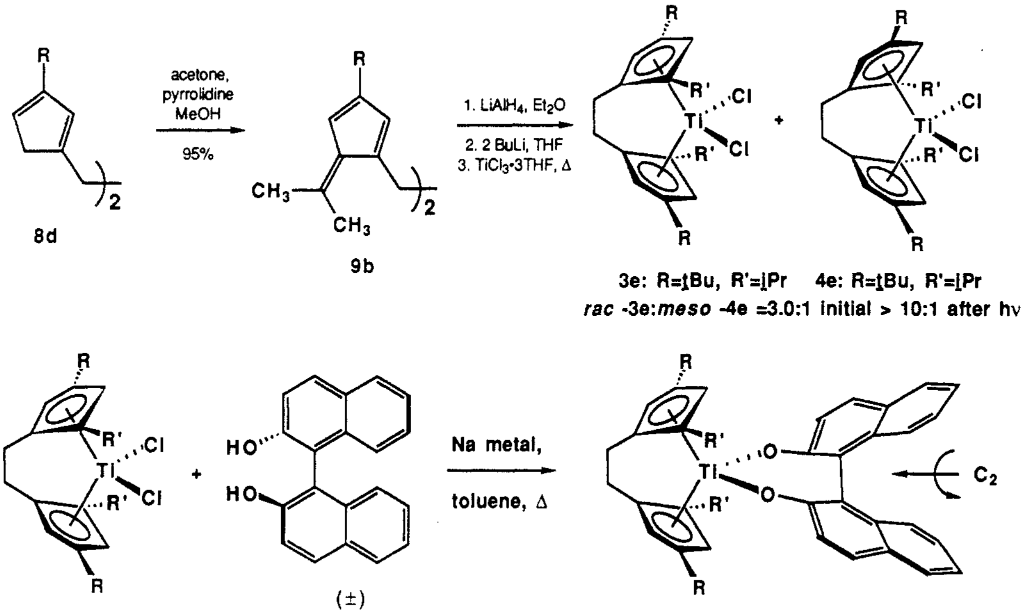
(9) The polymerization of propylene with use of the zirconium analogues of compounds 3 and 4 as catalysts shows some interesting and also unexpected behavior: Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. Manuscript in preparation.

Scheme III



8d 9b 3e 10 (38% yield)

significant decomposition and leads to essentially the same distribution of *meso:rac* as is observed for the synthesis of these compounds from $TiCl_3$ and compounds **8a–d**.[10] This should be contrasted with the virtually complete and clean photoconversion of *meso* to *rac* species observed in the (tetrahydroindenyl)titanium system.[2d,h] The structural difference between the two systems (i.e. **1** vs **3**) is readily appreciated, and it seems clear that introduction of an additional substituent is required to facilitate complete photoisomerization of meso to racemic diastereomers in these ethylene-bridged systems.

Preliminary work has suggested that this hypothesis is indeed correct. Condensation of acetone with ligand **8d** proceeded cleanly to provide the bis(fulvene) **9b** in 95% yield after 1 week at room temperature (Scheme III). Reduction of **9b** with excess $LiAlH_4$ in THF afforded bis(cyclopentadiene) **8e**, which was transformed directly to its dilithio salt. Reaction of this intermediate with $TiCl_3$·3THF produced titanocenes **3e** and **4e** in a combined, overall yield of 38% from fulvene **9b**. The initial ratio of **3e**:**4e** was ~3:1 and improved to >10:1 following photoisomerization in THF solution. The stereochemistry assigned to compound **3e** was readily deduced by reaction of this compound with (±)-binaphthol and Na metal in toluene. A single, cyclic binaphthaloate complex, **10**, was obtained in low yield. The ^{1}H NMR and ^{13}C NMR spectra of this compound (see Experimental Section) were consistent with 2-fold symmetry, a result that is only compatible with compound **3e** being the racemic diastereoisomer.

We are currently studying modifications to the first and second synthetic routes that will allow provision of pure samples of the racemic stereoisomers and will report on this and other chemistry in due course.

Experimental Section

All solvents and reagents were purchased from commercial sources and purified as required. Diethyl ether, THF, toluene, and hexane were distilled under N_2 from sodium and benzophenone. Dichloromethane and HMPA were distilled from CaH_2 under N_2. All reactions were performed under an atmosphere of dry N_2 or Ar. Melting points are uncorrected. Tetra-*n*-propylammonium perruthenate was prepared by the method described in the literature.[6] Solutions of disiamylborane in THF were prepared by the method of Brown and used directly.[11] The compound $TiCl_3$·3THF was prepared by the method of Manzer.[12] Bis(cyclopentadienyl)magnesium was prepared by the method of Lappert.[13] ^{1}H NMR and ^{13}C NMR spectra were obtained with either a Bruker AM-250 or AC-200 spectrometer. Spectral data are referenced to internal TMS. IR spectra were recorded on a Perkin-Elmer 983 instrument and are referenced to polystyrene. Low- and high-resolution mass spectra were collected on a VG-7077F machine at the University of Guelph. Elemental analyses were performed by Guelph Chemical Laboratories or MHW Laboratories. HPLC analyses were performed on a Waters 683 instrument equipped with a Waters 480 UV-vis detector.

Preparation of Ethylenebis(cyclopentadiene) (5).[5] A suspension of bis(cyclopentadienyl)magnesium (30.0 g, 195 mmol) in THF (300 mL) at 0 °C was treated with HMPA (127 mL, 730 mmol). The suspension was then cooled to −78 °C and 1,2-dibromoethane (11.2 mL, 130 mmol) added dropwise by syringe with vigorous stirring. The suspension was then warmed to 0 °C (2 h) and stirred at this temperature for 1 h. The mixture was quenched by the addition of water (75 mL) and diluted with pentane (750 mL). The aqueous phase was separated and extracted with 2 × 40 mL of pentane. The combined organic extracts were washed with water until neutral and dried over $MgSO_4$. Filtration followed by removal of solvents in vacuo provided crude **5**, which could be purified by passage through a short pad of silica gel with pentane as eluent (500 mL). Evaporation of the eluate at 0 °C provided spectroscopically pure **5** (16.4 g, 80%). Compound **5** can be stored at −20 °C under N_2 for several days without significant decomposition but is best stored for extended periods by conversion to the dilthio salt (*n*BuLi, hexane).

Preparation of Ethylenebis[3-(cyclopent-3-en-1-one)] (6). To a freshly prepared solution of disiamylborane in THF (1.0 M, 90.4 mmoL) at 0 °C was added dropwise via syringe compound **5** (6.5 g, 41 mmoL) dissolved in THF (10 mL). The solution was stirred at 0 °C for 1 h and then warmed to room temperature and stirred for 3 h. The solution was placed in a cold water bath and 36 mL of 3 N NaOH added dropwise by syringe. Then 36 mL of 30% H_2O_2 was added dropwise over 1 h via syringe. After the addition was complete, the mixture was diluted with ether (100

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(10) Collins, S.; Hong, Y. Unpublished results.

(11) Brown, H. C. *Organic Synthesis via Organoboranes*; Wiley-Interscience: New York, 1975; p 29.

(12) Manzer, L. *Inorg. Synth.* **1982**, *21*, 137–138.

(13) (a) Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Organomet. Chem.* **1985**, *293*, 271. See also: (b) Eisch, J. J.; Sanchez, R. *Ibid.* **1985**, *296*, C27.

mL) and the aqueous phase saturated with solid NaCl, separated, and extracted with THF–ether (1:1, 4 × 50 mL). The organic extracts were combined, washed with brine (50 mL), dried over $MgSO_4$, and filtered, and the filtrate was concentrated to half volume in vacuo, diluted with 200 mL of toluene, and concentrated in vacuo to ca. 50 mL. An additional 50 mL of toluene was added, and then the solution was concentrated in vacuo overnight to provide crude diol that was sufficiently pure for further use (crude yield 85%). The crude diol was dissolved in 40 mL of CH_2Cl_2 and the solution added dropwise over 10 min to a mixture of tetrapropylammonium perruthenate (1.6 g, 3.4 mmoL), *N*-methylmorpholine *N*-oxide (16.8 g, 144 mmoL), and powdered 4-Å molecular sieves in CH_2Cl_2 (200 mL) at room temperature. A further 3.2 g of the perruthenate catalyst (6.8 mmol) was added in two portions over a period of 1.5 h at room temperature. After 1.5 h, the solution was filtered, washed with water (50 mL), saturated Na_2SO_3 (3 × 20 mL), saturated $CuSO_4$ (3 × 20 mL), and brine (3 × 20 mL) and dried over $MgSO_4$. The mixture was filtered and concentrated in vacuo to provide spectroscopically pure compound **6** (4.9 g, 65% yield from **5**), which could be recrystallized from hexane–acetone; mp 92.5–93.5 °C. IR ($CHCl_3$): 3062, 1745, 1641 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 5.26 (br s, 2 H), 2.81 (br s, 4 H), 2.78 (br s, 4 H), 2.30 (br s, 4 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 216.4, 141.2, 121.2, 44.9, 43.5, 29.3. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.97; H, 7.81.

Preparation of Ethylenebis[3-(cyclopent-2-en-1-one)] (7). Compound **6** (4.75 g, 25 mmol) was dissolved in 100 mL of dioxane and heated to reflux. Then 5.0 mL of 12 N HCl was added in one portion. After 30 s, the solution was diluted rapidly with 100 mL of $CHCl_3$ and the bath was removed. The solution was concentrated in vacuo and then diluted with 150 mL of chloroform. The organic phase was washed with brine until neutral and then dried over $MgSO_4$. Filtration followed by removal of solvent in vacuo provided spectroscopically pure compound **7** (4.5 g, 95%). Recrystallization from hexane–acetone provided compound **7** as pale yellow needles, mp 121.5–123.0 °C. IR ($CHCl_3$): 3067, 1702, 1675 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 5.98 (br s, 2 H), 2.72 (br s, 4 H), 2.64–2.59 (m, 4 H), 2.46–2.41 (m, 4 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 209.0, 179.9, 129.4, 34.9, 31.2, 30.3. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.67; H, 7.69.

Preparation of Ethylenebis[1-(3-methylcyclopentadiene)] (8a). A solution of compound **7** (1.60 g, 8.4 mmol) in THF (400 mL) was added dropwise over 30 min at 0 °C to a solution of MeLi (25.3 mmol) in THF (30 mL). The mixture was stirred at 0 °C for 0.5 h, and then the mixture was quenched by the addition of saturated ammonium chloride (1 mL). The mixture was diluted with ether (50 mL) and washed with brine and the organic phase dried over Na_2SO_4. The organic phase was filtered, and the solvents were removed in vacuo to provide crude diol, which was dissolved in dry ether (200 mL). *p*-Toluenesulfonic acid (60 mg, 0.3 mmol) was added, and after the solution was stirred for 5 min at room temperature, it was washed with saturated $NaHCO_3$ solution (20 mL) and brine (2 × 20 mL) and the organic phase dried over Na_2SO_4. The solution was filtered and concentrated in vacuo. Crude compound **8a** was purified by passing the mixture through a short pad of silica gel with 60 mL of hexane as eluent. The eluate was cooled to −78 °C under Ar, and 5.2 mL of *n*BuLi (2.5 M, 13 mmol) was added dropwise by syringe. The mixture was warmed to room temperature and stirred at room temperature for 2 h. The insoluble dilithium salt of **8a** was filtered under Ar, washed with hexane, and suspended in 50 mL of ether. Two milliliters of brine was added to the mixture at −78 °C and the mixture warmed to room temperature. The mixture was washed with brine and the ether layer dried over Na_2SO_4, filtered, and concentrated in vacuo to provide 1.0 g (65%) of compound **8a** as a pale yellow oil, which was used without further purification to prepare compounds **3a** and **4a**. IR (thin film): 3008, 2973, 2911, 1624, 1517, 1475, 1425 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.0–5.7 (m, 4 H), 2.91–2.72 (br d, 4 H), 2.66–2.26 (m, 4 H), 2.10–1.76 (3 br s, total 6 H).

Preparation of Ethylenebis[1-(3-ethylcyclopentadiene)] (8b). The procedure described above for the preparation of **8a** was followed with use of 2.18 g (11.5 mmol) of compound **7** and 37.2 mL of a solution of ethylmagnesium bromide in ether (0.9 M, 34.4 mmol). Workup and treatment of the crude diol (ca. 80% yield) with *p*-TSA as described above, conversion of the crude cyclopentadiene product to the dilithio salt, filtration, and protonation as described above provided compound **8b** (0.86 g, 35% yield), which was used without further purification to prepare compounds **3b** and **4b**. IR (thin film): 3018, 2970, 2931, 1620, 1521, 1475, 1424 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 6.18–5.76 (m, 4 H), 2.91–2.75 (br d, 4 H), 2.69–2.48 (m, 4 H), 2.48–2.10 (m, 4 H), 1.19–0.99 (overlapping t, 6 H).

Preparation of Ethylenebis[3-(6,6-dimethylfulvene)] (9). A suspension of compound **5** (4.1 g, 26 mmoL) in 95 mL of MeOH at room temperature was treated sequentially with acetone (9.4 mL, 130 mmol) and pyrrolidine (16 mL, 190 mmol). After 2 h at room temperature the mixture was diluted with 100 mL of ether and washed with 2 N acetic acid until the aqueous phase was pH 4. The organic phase was then washed with $NaHCO_3$ until neutral and with brine (2 × 20 mL) and then dried over $MgSO_4$. The solvent was removed in vacuo to provide crude **9**, which was purified by passage through a short pad of silica gel with hexane as eluent (500 mL). The eluate was concentrated in vacuo to provide compound **9** as a bright yellow, crystalline solid (5.8 g, 95% yield; mp 83–83.5 °C) from methanol–dichloromethane. IR ($CHCl_3$): 3100, 3066, 2997, 2932, 2910, 2849, 1640, 1581, 1573, 1476 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 6.57–6.28 (3 overlapping m, 6 H), 2.72 (br s, 4 H), 2.20 (br s, 6 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 146.7, 146.6, 142.1, 132.4, 121.2, 115.1, 29.8, 22.8, 22.7. MS (EI): *m/e* 238 (M^+), 195, 165, 119, 91. Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.46; H, 9.45.

Preparation of Ethylenebis[1-(3-isopropylcyclopentadiene)] (8c). A solution of compound **9** (1.63 g, 6.84 mmol) in 10 mL of ether was added dropwise to a vigourously stirred suspension of $LiAlH_4$ (1.3 g, 3.42 mmol) in 200 mL of ether at room temperature over 30 min. The suspension was stirred at 25 °C for 3 h and then quenched at 0 °C by dropwise addition of water (1.3 mL), 15% NaOH (1.3 mL), and then water (3.9 mL). The mixture was filtered through Celite, washing well with ether. The filtrate was concentrated in vacuo to provide compound **8c** (1.6 g, ca. 100%) as a low-melting solid that was directly employed for the preparation of compounds **3c** and **4c**. ^1H NMR (250 MHz, $CDCl_3$): δ 6.19–5.78 (overlapping multiplets, 4 H), 2.96–2.81 (br d, 4 H), 2.79–2.48 (m superimposed in septet, total 6 H), 1.22–1.09 (two overlapping d, total 12 H).

Preparation of Ethylenebis[1-(3-*tert*-butylcyclopentadiene)] (8d). To a solution of compound **9** (1.56 g, 6.6 mmol) in 50 mL of ether at 0 °C was added 10.7 mL of a solution of methyllithium in ether (1.23 M, 13.2 mmol) dropwise over 30 min. The suspension was warmed to room temperature, and stirred at this temperature until the yellow color dissipated (ca. 2 h). The mixture was quenched with saturated ammonium chloride, filtered, and dried over $MgSO_4$. Removal of the solvent in vacuo provided compound **8d** as a low-melting solid (1.68 g, 95%) that was directly used for the preparation of compounds **3d** and **4d**. ^1H NMR (200 MHz, $CDCl_3$): δ 6.36–5.90 (overlapping m, total 4 H), 3.03–2.98 (br d, 4 H), 2.75–2.67 (m, 4 H), 1.31 and 1.29 (two s, total 18 H).

Preparation of *rac*- and *meso*-(Ethylenebis[η^5-1-(3-methylcyclopentadienyl)])titanium Dichlorides (3a and 4a). To a solution of compound **8a** (278 mg, 1.49 mmoL) in THF (20 mL) at 0 °C was added dropwise by syringe 1.2 mL of a solution of *n*-butyllithium in hexane (2.5 M, 3.0 mmol) over 15 min. The solution was warmed to room temperature and stirred for 30 min, and then $TiCl_3$·3THF (555 mg, 1.49 mmol) was added in one portion at −40 °C. The dark mixture was warmed to room temperature and then heated at reflux for 4 h. The dark green solution was cooled to −40 °C and 200 μL of 6 N HCl added by syringe over 5 min. The green solution was warmed to room temperature and air bubbled through the mixture for several minutes. During this period the solution became dark red. The solution was diluted with 10 mL of ether and passed through a short pad of silica gel, washing with ether. The filtrate was concentrated in vacuo to provide crude compounds **3a** and **4a**, which were further purified by passage through a short column of BioBeads SX-1 with toluene as eluent. The eluate was concentrated in vacuo to provide spectroscopically pure **3a** and **4a** as a crystalline red solid (386 mg, 86%; **3a**:**4a** = 1:1.3). IR ($CHCl_3$): 3093, 2998, 2955, 2924, 2870, 1517, 1446 cm^{-1}. Compound **3a**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.58 (t, *J* = 2.8, 2.1 Hz, 2 H), 6.00 (t, *J* = 2.8, 2.5 Hz, 2 H), 5.75 (t, *J* = 2.1, 2.5 Hz, 2 H), 3.2–3.0 (m, 4 H), 2.33 (s, 6 H); ^{13}C NMR

(50 MHz, $CDCl_3$) δ 137.7, 136.1, 128.6, 116.59, 113.7, 30.8, 16.2. Compound **4a**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.47 (pseudo-t, *J* = 2.8, 2.0 Hz, 2 H), 6.24 (pseudo-t, *J* = 2.9, 2.4 Hz, 2 H), 5.63 (pseudo-t, *J* = 2.4, 2.1 Hz, 2 H), 3.1 (m, 4 H), 2.39 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 136.0, 128.8, 116.62, 113.9, 30.9, 16.3. An analytical sample was obtained by crystallization from hexane–toluene. Anal. Calcd for $C_{14}H_{16}Cl_2Ti$: C, 55.48; H, 5.32. Found: C, 55.80; H, 5.51. Compounds **3a** and **4a** were partly resolved on a 8 mm × 10 cm, 4-μm NovaPak-Phenyl HPLC column (Waters Associates) with hexane–toluene (70:30) as eluent at 2.0 mL/min: compound **3a**, t_R = 4.8 min; compound **4a**, t_R = 5.2 min.

Preparation of *rac*- and *meso*-(Ethylenebis[η^5-1-(3-ethylcyclopentadienyl)])titanium Dichlorides (3b and 4b). The procedure described above was followed with 372 mg (1.74 mmol) of compound **8b**, 1.52 mL (2.5 M, 3.8 mmol) of *n*BuLi in hexane, and 670 mg (1.8 mmol) of $TiCl_3{\cdot}3THF$. Isolation and purification as described above provided crystalline compounds **3b** and **4b** (484 mg, 84% yield; **3b**:**4b** = 1:1.5). IR ($CHCl_3$): 3091, 2998, 2974, 2936, 2872, 1511, 1445, 1428 cm^{-1}. Compound **3b**: ^1H NMR (250 MHz, $CDCl_3$): δ 6.62 (t, 2 H), 5.99 (t, 2 H), 5.77 (t, 2 H), 3.2–3.0 (m, 4 H), 3.0–2.7 (m, 4 H), 1.19 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.2, 137.8, 127.49, 115.2, 113.6, 30.9, 23.6, 13.5. Compound **4b**: ^1H NMR (250 MHz, $CDCl_3$) δ 6.51 (t, 2 H), 6.25 (t, 2 H), 5.63 (t, 2 H), 3.15 (m, 4 H), 2.85 (m, 4 H), 1.20 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.2, 137.6, 127.54, 115.3, 113.8, 31.0, 23.8, 13.6. Anal. Calcd for $C_{16}H_{20}Cl_2Ti$: C, 58.04; H, 6.09. Found: C, 58.07; H, 6.58. Compounds **3b** and **4b** were resolved on the HPLC column described above with hexane–toluene (90:10) as eluent at 2.0 mL/min: compound **3b**, t_R = 6.4 min; compound **4b**, t_R = 7.4 min.

Preparation of *rac*- and *meso*-(Ethylenebis[η^5-1-(3-isopropylcyclopentadienyl)])titanium Dichlorides (3c and 4c). The general procedure outlined above was adopted with 1.40 g (5.77 mmol) of compound **8c**, 4.6 mL (2.5 M, 11.6 mmol) of *n*BuLi in hexane, and 2.15 g (11.6 mmol) of $TiCl_3{\cdot}3THF$. Isolation and purification in the usual manner afforded compounds **3c** and **4c** (1.70 g, 85% yield; **3c**:**4c** = 1:1.8). IR ($CHCl_3$): 3087, 2998, 2962, 2930, 2870, 1507, 1460, 1445 cm^{-1}. Compound **3c**: ^1H NMR (250 MHz, $CDCl_3$) δ 6.69 (t, 2 H), 5.54 (t, 2 H), 5.37 (t, 2 H), 3.50 (septet, *J* = 7.0 Hz, 2 H), 2.3 (m, 4 H), 1.32 (d, *J* = 7.0 Hz, 6 H), 1.12 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 146.1, 137.2, 126.5, 113.8, 112.4, 30.4, 29.2, 24.2, 21.3. Compound **4c**: ^1H NMR (250 MHz, $CDCl_3$) δ 6.59 (t, 2 H), 5.78 (t, 2 H), 5.26 (t, 2 H), 3.57 (septet, *J* = 7.0 Hz, 2 H), 2.4 (m, 4 H), 1.35 (d, *J* = 7.0 Hz, 6 H), 1.13 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 146.0, 136.9, 126.5, 114.2, 112.8, 30.6, 29.4, 24.4, 21.3. Anal. Calcd for $C_{18}H_{24}Cl_2Ti$: C, 60.19; H, 6.74. Found: C, 59.93; H, 7.05. Compounds **3c** and **4c** were resolved on the HPLC column described above, with hexane–toluene (97:3) as eluent at 2.0 mL/min: compound **3c**, t_R = 4.8 min; compound **4c**, t_R = 5.9 min.

Preparation of *rac*- and *meso*-(Ethylenebis[η^5-1-(3-*tert*-butylcyclopentadienyl)])titanium Dichlorides (3d and 4d). Compounds **3d** and **4d** (2.72 g, 86% yield; **3d**:**4d** = 1:2.0) were prepared and isolated as described previously from 1.78 g (6.6 mmol) of compound **8d**, 5.8 mL (14.5 mmol) of 2.5 M *n*BuLi in hexane, and 2.45 g (6.6 mmol) of $TiCl_3{\cdot}3THF$. IR ($CHCl_3$): 3082, 2996, 2958, 2904, 2871, 1502, 1478, 1459, 1446, 1372 (doublet) cm^{-1}. Compound **3d**: ^1H NMR (250 MHz, $CDCl_3$) δ 6.66 (t, 2 H), 6.13 (t, 2 H), 6.02 (t, 2 H), 3.2–3.0 (m, 4 H), 1.34 (s, 18 H); ^{13}C NMR (63 MHz, $CDCl_3$) 149.8, 137.0, 127.1, 114.8, 113.4, 34.8, 30.8, 30.5. Compound **4d**: ^1H NMR (250 MHz, $CDCl_3$) δ 6.63 (t, 2 H), 6.32 (t, 2 H), 5.97 (t, 2 H), 3.15 (br d, 4 H), 1.34 (s, 18 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 149.8, 136.7, 127.1, 115.2, 113.8, 34.5, 31.2, 30.7. Anal. Calcd for $C_{20}H_{28}Cl_2Ti$: C, 62.04; H, 7.29. Found: C, 61.63; H, 7.58. Compounds **3d** and **4d** could be resolved on a Waters NovaPak-CN column (4 μm, 8 mm × 10 cm) with hexane–dichloromethane (80:20) as eluent at 2.0 mL/min: compound **3d**, t_R = 4.7 min; compound **4d**, t_R = 6.5 min. Compounds **3d** and **4d** (300 mg) could be preparatively separated by flash chromatography on 100 g of silica gel (previously deactivated with wet THF) with hexane–toluene (2:1) as eluent. Compound **3d** is the first to elute under these conditions. The total recovery was ca. 60%.

Crystal Structure Determination of Compound 3d. Single crystals of both modifications of compound **3d** were obtained as described in the text. The X-ray studies were carried out with a Nicolet R3m diffractometer. Intensity data were obtained with graphite-monochromated Mo Kα radiation. For further details, consult Table II. Accurate unit cell dimensions for both modifications were determined with use of 25 general reflections (22 < 2θ < 32°) well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements. Absorption corrections to the data were made with use of the ψ-scan method for modification 1 and a face-indexed, analytical treatment for modification 2. The structures of both modificatons were solved and refined by standard Patterson and Fourier methods with use of Nicolet SHELXTLPLUS software and a DEC Microvax II computer. Relevant crystal, collection, and refinement data appear in Table II; atomic coordinates and isotropic thermal parameters for modifications 1 and 2 appear in Tables III and IV, respectively, while bond lengths and selected bond angles for both modifications appear in Tables V and VI, respectively. Anisotropic thermal parameters (Tables S1 and S2), H atom coordinates and isotropic thermal parameters for modification 2 (Table S3), complete lists of bond angles (Tables S4 and S5), packing diagrams, tables of inter- and intramolecular contacts, and structure factor tables for both modifications have been deposited as supplementary material.

Preparation of *rac*- and *meso*-(Ethylenebis[η^5-1-(2-*tert*-butyl-4-isopropylcyclopentadienyl)])titanium Dichlorides (3e and 4e). Preparation of Fulvene 9b. Compound **8d** (378.6 mg, 1.4 mmol) and acetone (2.06 mL, 28 mmol) in 5.0 mL of MeOH were stirred under argon at 0 °C, and pyrrolidine (3.5 mL, 42 mmol) was added via syringe. The mixture was warmed to room temperature and stirred for 7 days at this temperature, at which time the reaction was judged complete by TLC. Workup as described for the preparation of compound **9a** provided spectroscopically pure fulvene **9b** (469 mg, 95%), which was used without further purification. ^1H NMR (200 MHz): δ 6.2 (br d, *J* = 2.1 Hz, 2 H), 5.99 (d, *J* = 2.1 Hz, 2 H), 2.76 (br s, 4 H), 2.10 (s, 6 H), 2.08 (s, 6 H), 1.10 (s, 9 H). ^{13}C NMR (50.3 MHz): δ 153.7, 146.3, 140.6, 137.9, 128.8, 112.6, 32.1, 31.0, 29.8, 25.3, 22.8.

Preparation of Titanocenes 3e and 4e. Fulvene **9b** (1.3 mmol) was reduced with excess $LiAlH_4$ as described in the preparation of compound **8c**. After 48 h at room temperature, workup as described previously provided the bis(cyclopentadiene) **8e** is essentially quantitative yield, which was used directly in the next step.

Compound **8e** (~1.3 mmol) was dissolved in 15 mL of dry THF and the solution cooled to −78 °C under argon. An ethereal solution of methyllithium (1.4 M, 2.0 mL, 28 mmol) was added by syringe at this temperature. The bath was then removed and the mixture warmed to room temperature and stirred for 1 h at this temperature. The suspension was then cooled to −40 °C, and $TiCl_3{\cdot}3THF$ (483.0 mg, 1.3 mmol) was added in one portion. The dark mixture was warmed to room temperature and then heated to reflux. After 2.5 h, the mixture was cooled to −40 °C, quenched by the addition of HCl, and worked up as described for the preparation of compounds **3a** and **4a**. The crude product (with a *rac*:*meso* ratio of 3.0:1 as revealed by ^1H NMR spectroscopy (vide infra)) obtained was purified by passing the material, dissolved in toluene, through a pad of Bio-Beads SX-1, eluting with toluene, and collecting the dark red fraction. After this fraction was concentrated in vacuo, the titanocene products were further purified by flash chromatography on silanized silica gel with hexane as eluent. The eluate, containing the metallocenes, was concentrated in vacuo to provide compounds **3e** and **4e** as purple-red crystals (243 mg, 40%) in a ratio of 3.0:1. Compound **3e**: ^1H NMR (200 MHz) δ 6.37 (d, *J* = 2.6 Hz, 2 H), 5.70 (d, *J* = 2.6 Hz, 2 H), 3.2–3.0 (AA′BB′ multiplet, 4 H), 2.97 (heptet, *J* = 6.7 Hz, 2 H), 1.27 (s, 18 H), 1.18 (d, *J* = 6.7 Hz, 6 H), 1.13 (d, *J* = 6.7 Hz, 6 H). Compound **4e**: ^1H NMR (200 MHz) δ 6.42 (d, *J* = 2.4 Hz, 2 H), 6.29 (d, *J* = 2.4 Hz, 2 H), 3.17 (br s, 4 H), 2.97 (heptet, *J* = 6.7 Hz, 2 H), 1.43 (d, *J* = 6.7 Hz, 6 H), 1.24 (s, 18 H), 1.08 (d, *J* = 6.7 Hz, 6 H).

The mixture of titanocenes was dissolved in 5.0 mL of dry THF in a Schlenk tube and the solution placed adjacent to a water-cooled glass immersion well, containing a Hanovia 125-W mercury lamp, that was placed in a tall, cylindrical glass vessel containing a filter solution of aqueous $Na_2Cr_2O_7$. The solution was stirred under N_2 while being irradiated for 18 h at room temperature. THF was then removed in vacuo to provide nearly pure compound **3e** (ratio of **3e**:**4e** > 10:1) in essentially quantitative yield. Compound **3e**: ^{13}C NMR (200 MHz) δ 153.6, 142.4, 133.8, 121.9, 109.7, 35.0, 30.1, 29.6, 28.9, 25.1, 21.1; IR ($CHCl_3$) 3083, 2995, 2960, 2871, 1460, 1390, 1386, 1363, 1359, 1300, 1261, 1227, 1102, 1020, 923, 796 cm^{-1}; High-resolution mass spectrum (*m*/*e*): calculated for $C_{26}H_{40}{}^{35}Cl_2{}^{48}Ti$, 470.198$_6$; found (EI), 470.197$_4$.

Preparation of Binaphtholate Complex 10. Sodium metal (50 mg, 2.2 mmol) was heated to reflux, with vigorous stirring, in 20 mL of dry toluene under argon until the sodium melted. The resulting suspension was cooled to 80 °C with stirring, and titanocene **3e** (100 mg, 0.21 mmol) and (±)-binaphthol (63.0 mg, 0.22 mmoil) were added in one portion. The mixture was heated at 80 °C for 80 min and then cooled and diluted with petroleum ether. The mixture was filtered through dry Celite, washing with dry ether. The filtrate was concentrated in vacuo, and the crude product obtained was purified by flash chromatography on silanized silica gel with toluene–petroleum ether (1:3) as eluent. A single, dark purple-red band eluted under these conditions, which was collected, and the solvents were removed in vacuo to provide spectroscopically pure compound **10** (50 mg, 34% yield) as a purple-red, microcrystalline solid. ^1H NMR (200 MHz): δ 7.77 and 7.71 (overlapping, broad doublets, J = 8.6 Hz, total 4 H), 7.25 (d, J = 8.6 Hz, 2 H), 7.12 (br t, J = 8.6 Hz, 2 H), 6.94 (br t, J = 8.6 Hz, 2 H), 6.81 (d, J = 8.6 Hz, 2 H), 5.76 (d, J = 2.4 Hz, 2 H), 5.20 (d, J = 2.4 Hz, 2 H), 3.58 (AA′ portion of AA′BB′ multiplet, 2 H), 3.24 (heptet, J = 7.0 Hz, 2 H), 3.13 (BB′ portion of AA′BB′ multiplet, 2 H), 1.39 (overlapping doublets, J = 7.0 Hz, total 12 H), 1.17 (s, 18 H). ^{13}C NMR (200 MHz): δ 165.8, 154.2, 137.6, 135.3, 132.6, 128.5, 128.1, 127.2$_4$, 127.1$_8$, 124.9, 121.7, 120.8, 117.6, 112.4, 105.9, 33.7, 29.8, 29.2, 29.1, 24.7, 23.3. IR ($CHCl_3$): 3060, 2998, 2957, 2925, 2868, 1611, 1589, 1498, 1457, 1421, 1389, 1385, 1363, 1361, 1357, 1328, 1272, 1244, 1140, 1125, 1071, 1047, 994, 952, 877, 849, 839, 818 cm^{-1}. High-resolution mass spectrum (*m*/*e*): calculated for $C_{46}H_{52}O_2{}^{48}Ti$, 684.344$_7$; found (EI), 684.344$_3$.

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Supplementary Material Available: Tables of H atom coordinates and isotropic thermal parameters for modification 2, anisotropic thermal parameters, and all bond angles, packing diagrams, and a list of nonbonded contacts for both modifications (11 pages); tables of structure factors for both modifications (22 pages). Ordering information is given on any current masthead page.

Cyclopentadienylniobium and -molybdenum Phosphorodithioate Complexes. X-ray Crystal Structures of $CpNbCl_3(S_2P(OPr^i)_2)$, $CpNbCl(\mu\text{-}Cl)_2Nb(S_2P(OPr^i)_2)Cp$, and *cis*-$Cp'Mo(CO)_2(S_2P(OPr^i)_2)$

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Reaction of $CpNbCl_4$ (Cp = η-C_5H_5) with $(Pr^iO)_2P(S)(SH)$ in the presence of NEt_3 yields $CpNbCl_3(S_2P(S_2Pr^i)_2)$ (**1**). Reduction of **1** with Na/Hg affords the Nb–Nb-bonded complex $CpNbCl(\mu\text{-}Cl)_2Nb(S_2P(OR)_2)Cp$ (**2**). In refluxing toluene, $(Pr^iO)_2P(S)(SH)$ with $[Cp'Mo(CO)_3]_2$ (Cp′ = η-C_5H_4Me) gives *cis*-$Cp'Mo(CO)_2(S_2P(OPr^i)_2)$ (**3**). Oxidation of **3** with I_2 affords $Cp'MoI_2(CO)(S_2P(OPr^i)_2)$ (**4**). The crystal structures of **1**–**3** are compared. For **1**, triclinic, $P\bar{1}$, a = 7.122 (3) Å, b = 11.365 (4) Å, c = 12.532 (4) Å, α = 77.38 (3)°, β = 89.08 (3)°, γ = 72.87 (3)°, V = 944.5 (8) Å^3, Z = 2, and $R(F)$ = 7.85%. For **2**, triclinic, $P\bar{1}$, a = 7.251 (3) Å, b = 12.386 (5) Å, c = 13.988 (5) Å, α = 102.66 (3)°, β = 103.56 (3)°, γ = 94.66 (3)°, V = 1180.0 (8) Å^3, Z = 2 and $R(F)$ = 2.70%. For **3**, orthorhombic, *Pbca*, a = 12.703 (3) Å, b = 16.706 (4) Å, c = 18.398 (4) Å, V = 3904.4 (17) Å^3, Z = 8, and $R(F)$ = 3.49%.

Introduction

Increasingly, phosphorodithioates, $S_2P(OR)_2$ (R = alkyl), are becoming recognized as ligands of synthetic utility.[1,2] These ligands are of interest, in part, due to their use as catalyst additives[3-5] and sequestering agents.[6,7] Phosphorodithioate complexes are generally very soluble. Additionally, the RO groups within the ligand may be varied to engender desirable properties, such as crystallinity or oil solubility.

Although many simple $M(S_2P(OR)_2)_n$ species have been prepared,[1,2] fewer organometallic phosphorodithioate complexes have been characterized[8-25] and only rarely

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