4946 *Organometallics* **1998,** *17,* 4946−4958

Racemic−Meso Interconversion for *ansa*-Scandocene and *ansa*-Yttrocene Derivatives. Molecular Structures of *rac*-$\{Me_2Si[\eta^5-C_5H_2-2,4-(CHMe_2)_2]_2\}ScCl\cdot LiCl(THF)_2$, [*meso*-$\{Me_2Si[\eta^5-C_5H_2-2,4-(CHMe_2)_2]_2\}Y(\mu_2-Cl)]_2$, and *meso*-$\{Me_2Si[\eta^5-C_5H_2-2,4-(CHMe_2)_2]_2\}Zr(NMe_2)_2$

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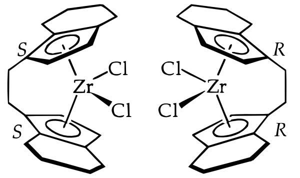
The dilithium bis(cyclopentadienide) species $Li_2\{Me_2Si[C_5H_2-2,4-(CHMe_2)_2]_2\}$ (Li_2Ip) reacts with $ScCl_3(THF)_3$ to afford *rac*-$IpScCl\cdot LiCl(THF)_2$ (**1**) and [*meso*-$IpSc(\mu_2-Cl)]_2$ (**2**) and with $YCl_3(THF)_{3.5}$ to afford *rac*-$IpYCl\cdot LiCl(THF)_2$ (**3**) and [*meso*-$IpY(\mu_2-Cl)]_2$ (**4**). Metalation with both scandium and yttrium chlorides yields the metallocene chlorides in approximately 3:1 racemic:meso ratios. Reaction of IpH_2 with $Zr(NMe_2)_4$ yields exclusively *meso*-$IpZr(NMe_2)_2$ (**9**). Treatment of **1** or **2** with allylmagnesium bromide affords the allyl complexes *rac*-IpSc(η^3-C_3H_5) (**5**) and *meso*-IpSc(η^3-C_3H_5) (**6**) and with crotylmagnesium chloride affords *rac*-IpSc(η^3-C_3H_4Me) (**7**) and *meso*-IpSc(η^3-C_3H_4Me) (**8**). Diastereomerically pure *rac* dichlorometalate compounds (**1** or **3**) or pure *meso* chloro dimers (**2** or **4**) undergo spontaneous isomerization upon dissolution in THF-d_8 with reversion back to a 3:1 racemic:meso ratio. Isomerization of **5** and **6** is observed in THF-d_8, above 55 °C, affording an equilibrium ratio of ∼2:1 racemic:meso isomers. While spontaneous isomerization of **5**, **6**, **7**, or **8** is very slow at room temperature, various salts and Grignard reagents promote isomerization even at room temperature; the isomerizations are not accelerated by light. The proposed mechanism for racemic−meso isomerization involves heterolytic dissociation of one cyclopentadienide ligand from the metal, rotation around that Si−Cp^- bond, and recoordination on the opposite face, effecting net epimerization. X-ray diffraction studies have been performed on *rac*-$IpScCl\cdot LiCl(THF)_2$ (**1**), [*meso*-$IpY(\mu_2-Cl)]_2$ (**4**), and *meso*-$IpZr(NMe_2)_2$ (**9**).

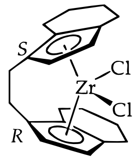
Introduction

The active species in the new metallocene-based polymerizations of α-olefins are 14-electron group 4 metallocenium−alkyl cations, $[Cp_2M-R]^+$ (Cp = variously substituted cyclopentadienyl and M = a group 4 transition metal), with a very weakly coordinating counteranion.[1] The polymerization performance of these catalysts and the less active, isoelectronic neutral group 3 and lanthanide metallocene alkyls Cp_2M-R have been extensively investigated.[2]

Stereo-random enchainment to afford atactic poly(α-olefins) is effected by achiral metallocene catalyst precursors. One type of stereospecific polymerization yielding isotactic polymers[3,4] is best effected using C_2-symmetric *ansa*-metallocenes.[5] In Brintzinger's original reports,[6] ethylenebis(1-indenyl) (EBI) and ethylenebis-(4,5,6,7-tetrahydro-1-indenyl) (EBTHI) derivatives of titanium and zirconium are described. Linking the indenyl ligands results in two possible isomers on metalation: a C_2-symmetric racemic isomer (consisting of the *R,R* and *S,S* enantiomeric pairs) and a C_s-symmetric meso (achiral) isomer.



rac-(EBTHI)ZrCl$_2$



meso-(EBTHI)ZrCl$_2$

When they are combined with methylaluminoxane (MAO), chiral *rac*-(EBTHI)ZrCl$_2$ and *rac*-(EBI)TiCl$_2$ polymerize α-olefins to isotactic polymers. The achiral *meso*-(EBTHI)-ligated metallocenes produce atactic poly-

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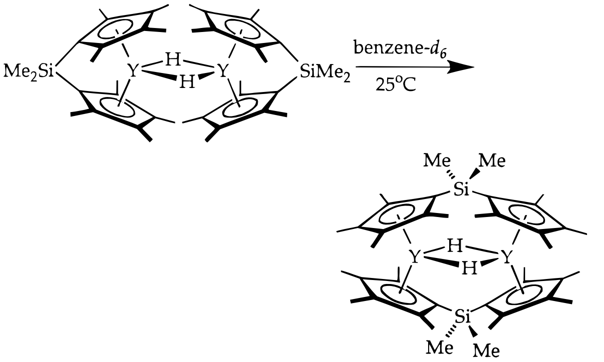
10.1021/om980349j CCC: $15.00

mer. These differences in polymer microstructure obtained with racemic vs meso isomers have been shown to be general for a large number of group 3 or group 4 transition-metal metallocenes.[1]

The racemic isomer, therefore, normally is the desired product of metalation of the ligand. Unfortunately, in most cases some amount of the achiral meso isomer is also formed, necessitating an often tedious separation process. Brintzinger has suggested that the racemic:meso ratios obtained on metalation may be kinetically controlled by the face selection for the attachment of the second cyclopentadienyl ring to the metal.[7] On the other hand, Marks and co-workers have reported that some lanthanide *ansa*-metallocenes bearing a chiral substituent may undergo epimerization to the more stable diastereomer, a process that requires one of the cyclopentadienyl ligands to dissociate from the metal and recoordinate by the other face.[2b,8] Coordinating solvents (THF-d_8 and Et_2O-d_{10}) were found to promote interchange, as did lithium chloride. Similar results were also obtained by Okuda et al. for chiral lanthanocene "ate" compounds containing two linked amido−cyclopentadienyl ligands.[9] Since these promoters are commonly present during the preparation of the *ansa*-metallocene dichlorides, we wondered whether during metalation the racemic:meso ratio is thermodynamically, rather than kinetically, controlled.

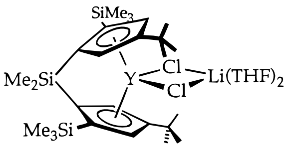
More recently, Jordan et al. have reported that racemic−meso isomerizations take place concurrently with metalations of linked bis(cyclopentadiene) ligands utilizing (reversible) amine elimination reactions for amide complexes.[10] The above studies, along with earlier investigations of photoisomerization reactions of *ansa*-titanocenes and *ansa*-zirconocenes,[5,11] appear to be the only examples of *ansa*-metallocene racemic−meso interconversion reactions.

Numerous examples have been reported, however, of reactions that involve metal−cyclopentadienyl bond rupture. Photochemically induced ring loss from nonbridged titanocenes has been extensively studied.[12] Disproportionation reactions of Cp'_nLnX_{3-n} ($Cp' = \eta^5$-C_5H_5, η^5-C_5Me_5; X = Cl, OR, NR_2, etc.) compounds are well-known[13] and have been used in the synthesis of Cp'_2LnCl derivatives.[13d] Recently, loss of Cp* has been observed from mixed-ring zirconocenes in ethereal solvents.[14] Also, "flyover dimer" complexes formed by linked bis(cyclopentadienyl) ligands when they span two metal centers have been observed to form spontaneously from group 3 *ansa*-metallocene hydride dimers;[15] one example is shown in eq 1.[15a] Thus, there appear to be many pathways available for M−Cp bond rupture and reformation.

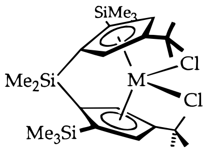


(1)

We have described a ligand system that undergoes metalation with group 3 and 4 transition metals to afford only the desired racemic isomer, thus obviating the need for isomer separation.[2a,16] The yttrocene hydride so obtained, $[rac\text{-}Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2Y(\mu_2\text{-}H)]_2$ ($[BpY(\mu_2\text{-}H)]_2$), is active for the isospecific polymerization of α-olefins.[2a] The sterically demanding trimethylsilyl substituents α to the silylene linker atom direct metalation of the Bp ligand exclusively to the racemic isomer, since in the meso isomer the [$SiMe_3$] substituents would be placed next to one another in the narrow portion of the metallocene wedge.

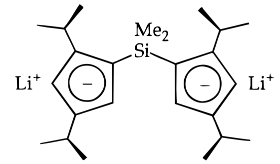


rac-$BpYCl_2Li(THF)_2$



rac-$BpMCl_2$ (M = Ti, Zr)

The dimethylsilylene-linked $Me_2Si\{[C_5H_2\text{-}2,4\text{-}(CHMe_2)_2]_2\}$ ("Ip") *ansa* ligand system utilized in the present study was designed by analogy to Bp. Although molecular mechanics calculations[17] predicted that the isopropyl substituents in the 2-positions should direct coordination preferentially to the racemic isomer, we find instead that metalations of Li_2Ip with scandium



Li_2Ip

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Table 1. X-ray Diffraction Data Collection Parameters for 1, 4, and 9

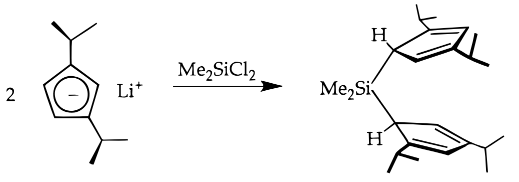
	1	**4**	**9**
empirical formula	$C_{32}H_{54}Cl_2LiO_2ScSi$	$C_{66}H_{94}Cl_2Si_2Y_2$	$C_{28}H_{50}N_2SiZr$
fw	621.64	1192.31	534.01
cryst size (mm)	0.4 × 0.3 × 0.3	0.4 × 0.3 × 0.3	0.5 × 0.3 × 0.3
temp (K)	160	160	293
space group	$P2_1/n$	*Ibam*	$P2_1/n$
cell constants			
a (Å)	12.547(3)	21.060(4)	17.354(3)
b (Å)	19.314(4)	14.254(3)	10.179(2)
c (Å)	14.893(3)	21.754(4)	17.628(4)
β (deg)	96.47(3)		107.43(3)
V (Å^3)	3586.1 (13)	6530 (2)	2970.9 (10)
Z	4	4	4
d (calcd) (g/mL)	1.151	1.213	1.194
2θ range (deg)	3.50−46.0	3.50−55.0	4.0−50.0
index ranges	$0 \le h \le 13, -21 \le k \le 21, -16 \le l \le 16$	$0 \le h \le 27, -18 \le k \le 18, 0 \le l \le 28$	$-20 \le h \le 20, -12 \le k \le 5, -21 \le l \le 21$
rflns collected	10918	8421	16710
no. of indep rflns	4965	3853	5211
R(merge)	0.028	0.046	0.053
GOF(merge)	1.11	1.21	1.04
data/restraints/params	4961/0/568	3840/0/269	5207/0/339
GOF(F^2)[b]	1.514	1.615	1.403
R indices (all data)[c,d]	R1 = 0.0464, wR2 = 0.0691	R1 = 0.0951, wR2 = 0.0816	R1 = 0.0939, wR2 = 0.0716

[a] All structures were obtained on an Enraf-Nonius CAD-4 using Mo Kα radiation ($\lambda = 0.710\,73$ Å). [b] GOF = $\{\sum w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$ (n = number of data, p = number of variables). [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

or yttrium chlorides afford a mixture of racemic and meso isomers. Relatively facile interconversion of these isomers is observed, especially in coordinating solvents such as THF and in the presence of salts such as lithium chloride. We report herein the synthesis and characterization of scandocene and yttrocene compounds with the Ip ligand system together with the results of an investigation of the racemic−meso interconversion process.

Results and Discussion

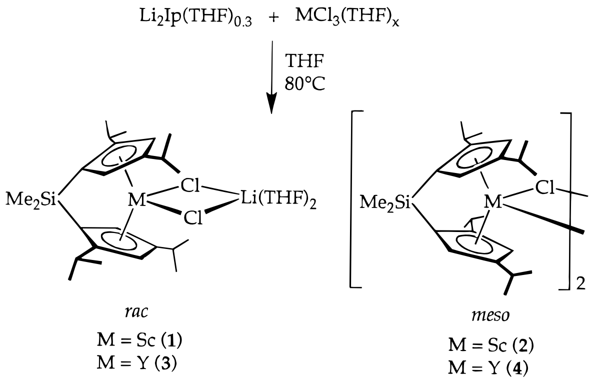
Synthesis and Characterization of Ip-Ligated Scandocene and Yttrocene Compounds. The ligand $Me_2Si[C_5H_2\text{-}2,4\text{-}(CHMe_2)_2]_2H_2$ (IpH_2) is conveniently prepared by the reaction between 2 equiv of $[C_5H_3\text{-}1,3\text{-}(CHMe_2)_2]Li$ and dichlorodimethylsilane in THF solution. This procedure affords IpH_2 as a light yellow oil after Kugelröhr distillation (eq 2). Deprotonation proceeds readily using *n*-butyllithium in petroleum ether, and a white powder is obtained that, after workup with THF, is consistently analyzed (by ^1H NMR) as $Li_2Ip(THF)_{0.3}$.



(2)

Reactions of $Li_2Ip(THF)_{0.3}$ with $ScCl_3(THF)_3$ as well as with $YCl_3(THF)_{3.5}$ in refluxing THF afford mixtures of racemic and meso isomers (Scheme 1). The resulting metallocene chlorides are separated by successive filtration/crystallization cycles. Thus, after a series of heptane washes of the crude product mixture to remove excess THF, separation of the meso from the racemic complexes is accomplished by successive dissolutions of the mixture in heptane or petroleum ether followed by filtration, isolating the mostly insoluble meso chloride-bridged dimer. After two to three iterations of this process, the filtrate is essentially pure *rac*-IpScCl·LiCl-$(THF)_2$ (**1**); this species may then be recrystallized from a cold (−40 °C) pentane solution. The procedure used for the synthesis and separation of the yttrium congeners is identical with that used for the scandium compounds.

Scheme 1



Light yellow plates of **1** were obtained from a concentrated petroleum ether/THF solution upon cooling. Details of the X-ray data collection and solution and refinement of all of the structures presented herein can be found in Table 1. Selected bond distances and angles for all structures can be found in Table 2. The X-ray structure for **1**, shown in Figure 1, reveals the lithium dichloroscandate formulation given in Scheme 1. This formulation is further supported by the presence of coordinated THF (^1H NMR) for solutions of **1**. The Sc−Cp(centroid) distances (2.239(1) and 2.236(1) Å) are at the long end of those normally encountered in scandocene complexes (2.171−2.212 Å),[18] and the Cp−M−Cp angle of 127.9(1)° is within the normal range. Due to the similar solubility properties between **1** and "*rac*-IpYCl" and the presence of coordinated THF (^1H NMR) in the yttrium species, the yttrium congener (**3**) is formulated as a $\{LiCl(THF)_2\}$ adduct as well.

Table 2. Important Bond Lengths (Å) and Bond Angles (deg) Obtained from X-ray Structure Analysis of 1, 4, and 9

feature	**1** (X = Cl)	**4** (X = Cl)	**9** (X = N)
M−Cp(1)[a]	2.239(1)	2.344(1)	2.348(1)
M−Cp(2)[b]	2.236(1)		2.312(1)
M−X(1)	2.496(1)	2.668(2)	2.107(3)
M−X(2)	2.509(1)		2.067(3)
M−C(1)	2.461(2)	2.570(3)	2.573(3)
M−C(2)	2.456(2)	2.625(3)	2.631(4)
M−C(3)	2.618(2)	2.690(3)	2.701(4)
M−C(4)	2.622(2)	2.707(3)	2.714(3)
M−C(5)	2.544(2)	2.587(3)	2.567(3)
M−C(6)	2.479(2)		2.552(3)
M−C(7)	2.539(2)		2.651(3)
M−C(8)	2.601(2)		2.684(4)
M−C(9)	2.604(2)		2.638(4)
M−C(10)	2.471(2)		2.496(3)
Cp(1)[a]−M−Cp(2)[b]	127.9(1)	123.7(2)	122.9(1)
X(1)−M−X(2)	88.14(3)	81.57(4)	95.38(14)
Cp(1)[a]−M−X(1)	108.7(3)	110.2(2)	106.0(1)
Cp(1)[a]−M−X(2)	107.9(3)	111.6(2)	110.8(1)
Cp(2)[a]−M−X(1)	107.9(3)		108.0(1)
Cp(2)[a]−M−X(2)	109.1(3)		110.0(1)

[a] Cp(1) is defined as the centroid of the ring made up of C(1)−C(5). [b] Cp(2) is defined as the centroid of the ring made up of C(6)−C(10).

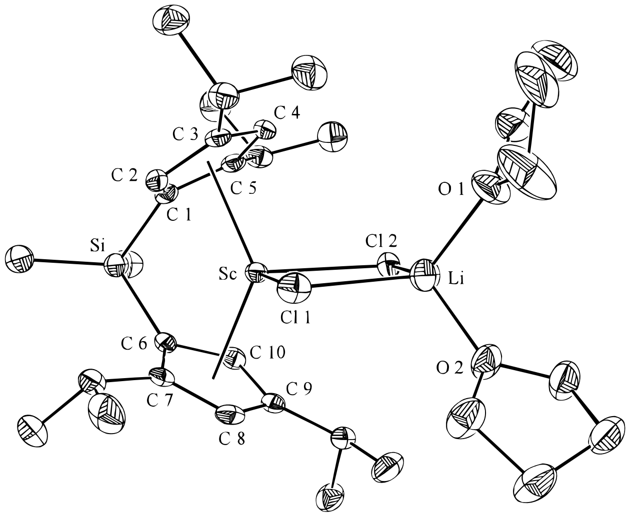


Figure 1. Molecular structure of **1** with selected atoms labeled (50% probability ellipsoids; hydrogens omitted for clarity).

Colorless prisms of *meso*-[IpY(μ_2-Cl)]$_2$ (**4**) were obtained from a pentane solution cooled to −40 °C. An X-ray structure (Figure 2) reveals a dimeric structure. The distances (Table 2) from Y to the centroid of the cyclopentadienyl rings (2.344 (1) Å) is within the range of normal Y−Cp distances (2.279−2.414 Å).[19] The Y−Cl distance (2.668(2) Å) is consistent with a bond from yttrium to a bridging chlorine atom (2.614−2.776 Å) and is significantly longer than those typically found from yttrium to a terminal chlorine atom (∼2.58 Å).[20] The Cp−Y−Cp′ angle is 123.7(1)°, in good agreement with the angles typically observed in other *ansa*-yttrocenes.

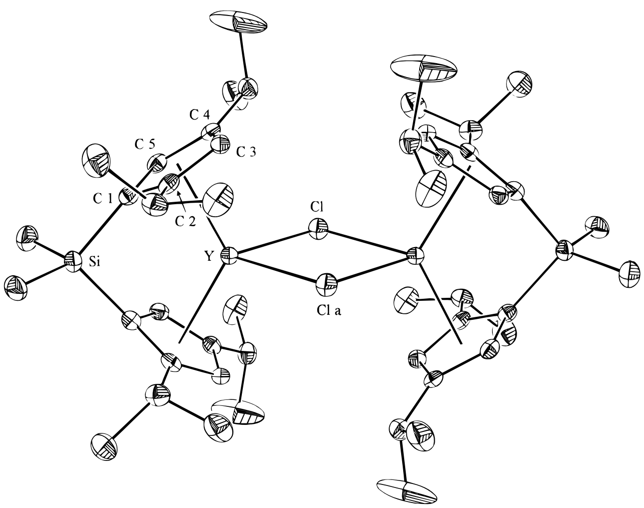
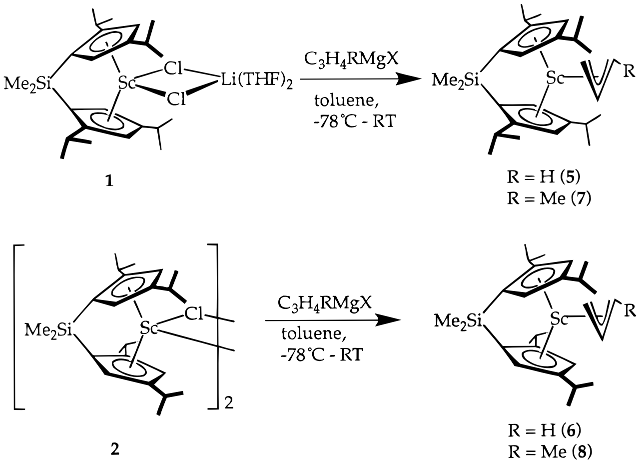


Figure 2. Molecular structure of **4** with selected atoms labeled (50% probability ellipsoids; hydrogens omitted for clarity).

Scheme 2



The lack of coordinated THF in the NMR spectrum of "*meso*-IpScCl" (**2**) and the similarity of its solubility to that of **4** indicate that the scandium meso compound is most likely dimeric also.

Both *rac*-IpSc(η^3-C_3H_5) (**5**) and *meso*-IpSc(η^3-C_3H_5) (**6**) may be synthesized by slowly warming toluene solutions of either **1** or **2**, respectively, from −78 °C to room temperature in the presence of a slight excess of allylmagnesium bromide. Slow warming of these reaction mixtures is necessary because at higher temperatures an excess of the Grignard reagent serves to promote the interconversion of the racemic and meso isomers (vide infra). In the same manner, the crotyl derivatives *rac*-IpSc(η^3-C_3H_4Me) (**7**) and *meso*-IpSc(η^3-C_3H_4Me) (**8**) may be prepared (Scheme 2). An X-ray crystal structure was carried out on a single crystal of **5**.[21]

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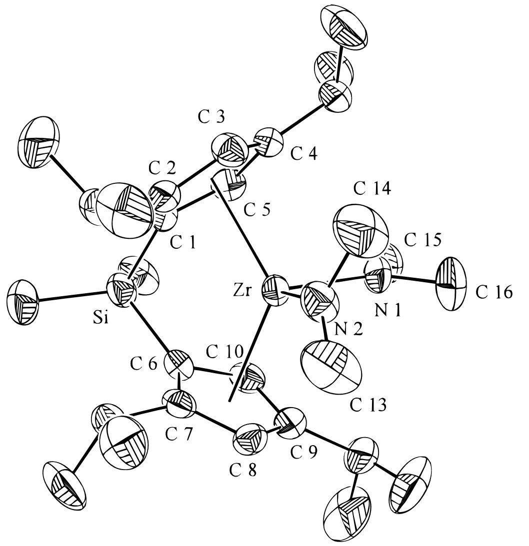
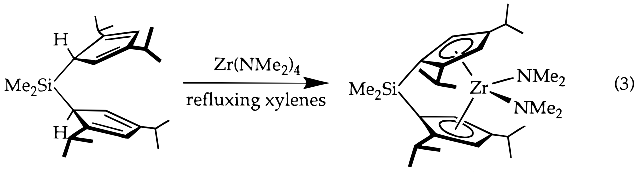


Figure 3. Molecular structure of **9** with selected atoms labeled (50% probability ellipsoids; hydrogens omitted for clarity).

Despite the ease with which IpSc(η^3-allyl) complexes can be synthesized, all attempts to prepare the yttrium analogues by reaction of **3** or **4** with allylmagnesium bromide have failed.

Since initial attempts to synthesize $IpZrCl_2$ by a metathetical reaction between $IpLi_2$ and $ZrCl_4$ or $ZrCl_4(THF)_2$ were unsuccessful,[22] alternative metalation strategies were sought. Using the amine elimination reaction between a bis(cyclopentadiene) ligand and $Zr(NMe_2)_4$, as described by Jordan et al.,[10] reaction of IpH_2 with $Zr(NMe_2)_4$ (eq 3) proceeds cleanly during an overnight reflux at 140 °C in xylenes open to a mercury bubbler.



9

Filtration of the reaction mixture from pentane and cooling at −80 °C for 1 week yield bright orange crystals which are suitable for X-ray diffraction experiments. The meso structure of **9** is shown in Figure 3. ^{1}H NMR spectra show no evidence for formation of the racemic analogue of **9**.

The distances (Table 2) from zirconium to the centroids of the cyclopentadienyl rings (2.348(1), 2.312(1) Å) are longer than those typically observed in zirconocene chloride compounds, which average 2.2−2.3 Å. However, these values are in excellent agreement with the Zr−Cp bond distances in *rac*-$Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}CMe_3)_2Zr(NC_4H_8)_2$ (**10**) (2.357, 2.348 Å), one of the only other structurally characterized *ansa*-zirconocene amides.[10d] Slightly longer M−Cp distances for amido-ligated zirconocenes may be attributable to the larger size of the amide functionality, as well as possible N-to-Zr lone electron pair donation that should serve to lower the electrophilicity of zirconium. The Cp−M−Cp angle in **9** (122.9(1)°) agrees well with the corresponding angle in **10** (122.5°), at the low end of those typically observed in *ansa*-zirconocene compounds. The orientations of the two [NMe_2] ligands, one with the C−N−C plane essentially coincident with the zirconocene equatorial plane (dihedral angle 7.8(3)°), the other with the C−N−C plane close to perpendicular (dihedral angle 66.3(4)°), is as expected for the former amide ligand serving as a one-electron donor, the latter as a three-electron donor, completing the 18-electron count at zirconium. A similar arrangement of phosphide ligands was reported earlier by Baker and co-workers for $(\eta^5\text{-}C_5H_5)_2Hf(PEt_2)_2$.[23] The Zr−N bond lengths in the structure for **9** reveal a difference of only 0.04 Å for the two Zr−N bond lengths (Zr−N(1) = 2.107(3) Å and Zr−N(2) = 2.067(3) Å). Although the shorter Zr−N bond is that for the amide ligand oriented properly for π donation from nitrogen to zirconium, the small difference in bond lengths suggests that the N-to-Zr π bonding is relatively weak. The two amide ligands appear to adopt an arrangement which minimizes unfavorable steric interactions.

The ^{1}H NMR spectrum of **9** in benzene-d_6 at room temperature reveals that one of the two $N(CH_3)_2$ resonances is considerably broadened, presumably due to restricted rotation about the Zr−N bonds. Consideration of the (limiting) static solid-state structure leads to a prediction of three N*Me* signals in a 2:1:1 relative intensity ratio. The broadened signal suggests that the two methyl groups of N1 are at intermediate exchange, reminiscent of the temperature-dependent ^{1}H NMR spectrum for $(\eta^5\text{-}C_5Me_5)_2Hf(H)NMe_2$, which reveals a (steric) rotational barrier for the Hf−N bond of 13.5(10) kcal mol^{-1}.[24] Variable-temperature ^{1}H NMR data were recorded for **9** which revealed a barrier to rotation of 12.7(5) kcal mol^{-1} at 270 K. A Hf−N bond distance of 2.027(8) Å was determined for $(\eta^5\text{-}C_5Me_5)_2Hf(H)NHMe$, where the magnitude of the Hf−N π bonding was shown to be less than ca. 10 kcal mol^{-1}.[24] In view of the close similarity of hafnium and zirconium covalent radii, we may conclude from the longer Zr−N2 distance in **9** (2.067(3) Å) that the Zr−N2 π bonding is even weaker for **9**.

Racemic−Meso Interconversions for IpScCl and IpYCl Complexes. As described above, metalation by reaction of $Li_2Ip(THF)_{0.3}$ in THF solvent with either $ScCl_3(THF)_3$ or $YCl_3(THF)_{3.5}$ invariably yields a 3:1 ratio of the racemic and meso metallocene chlorides. Due probably to the difference in preferred solid-state structures (vide supra), separation of the group 3 compounds is possible in noncoordinating solvents.

When dissolved in THF, diastereomerically pure *rac*-$IpScCl\cdot LiCl(THF)_2$ (**1**) or *rac*-$IpYCl\cdot LiCl(THF)_2$ (**3**) each spontaneously revert back to the 3:1 racemic:meso ratios obtained on metalation. The mechanism operating here is assumed to be analogous to that proposed earlier, i.e.,

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(21) Abrams, M. B.; Yoder, J. C.; Bercaw, J. E. Manuscript in preparation.

(22) Subsequently, a route to the pure *meso*-$IpZrCl_2$ was devised. $IpLi_2(THF)_{0.3}$ and $ZrCl_4(THF)_2$ were refluxed in toluene for 2 weeks, and the resulting mixture of racemic and meso metallocenes was purified by an aqueous HCl workup. Dissolution of the resulting compounds in pentane resulted in precipitation of pure meso−$IpZrCl_2$: Chirik, P. J.; Bercaw, J. E. Unpublished results.

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LiCl-assisted heterolysis of the M$-$Cp bond followed by Si$-$Cp$^-$Li$^+$ bond rotation and recoordination to the opposite face of the cyclopentadienyl ring.[2b,8]

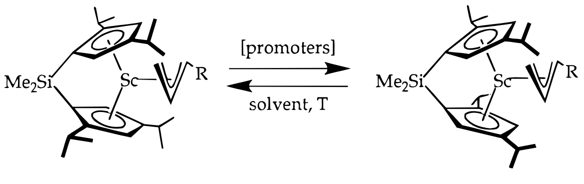
Considering the proposed mechanism for the isomerization of chiral *ansa*-metallocenes, it is perhaps not surprising that the LiCl adducts **1** and **3** undergo spontaneous isomerization in THF-d_8. Not expected, however, was the facile interconversion that is also observed, upon dissolution in THF-d_8, of *meso*-[IpM(μ_2-Cl)]$_2$ derivatives **2** or **4**, with reversion back to a 3:1 racemic:meso ratio observed for each, since they have no obvious source of lithium ion to assist isomerization and to generate the lithium chloride adducts. Moreover, the racemic$-$meso interconversion for these Ip derivatives does not occur in diethyl ether, unlike the system examined by Marks et al.[2b,8] Further, the addition of 1$-$2 equiv of 12-crown-4 to THF-d_8 solutions of **1**, **2**, or **4** does not slow the rate of interchange. Moreover, while addition of 35 equiv of 12-crown-4 to a solution of **4** in THF-d_8 does slow the process, it does not prevent racemic$-$meso interchange. Consistent with Marks' observations, no isomerization is observed for **1**, **2**, or **4** in toluene-d_8 solution.

If the mechanism previously proposed is assumed to be operative for these Ip complexes, then it must be assumed that the meso compounds **2** and **4** are contaminated with LiCl and that the crystal structure obtained for **4** is not representative of the isolated bulk solid. Elemental analyses for chlorine, carbon, and hydrogen in **4** are not mutually consistent and thus do not rule out some lithium chloride contamination.

A THF solution of **2** was stirred for 8 days, and the resulting product mixture was examined by ^{1}H NMR spectroscopy. Heptane washings permitted **2** to be separated from the new product. The heptane-soluble component does indeed prove to be a racemic metallocene derivative, but its ^{1}H NMR spectrum is different from that of **1**, and coordinated THF is not evident. Significantly, when this new product was dissolved in THF, no isomerization to **2** was observed even after 1 week at ambient temperature. Addition of lithium chloride to the THF solution caused an immediate shift in the ^{1}H NMR signals to those of **1**, and isomerization to **2** was then rapid. We tentatively conclude that the heptane-soluble species is [*rac*-IpSc(μ_2-Cl)]$_2$, but all attempts to verify this assignment by independent synthesis have been unsuccessful. The heptane-insoluble species proved to be a (ca. 3:1) mixture of **1** and **2**. The results of these experiments indicate that, of the meso complexes, at least **2** is contaminated with LiCl. In THF solution the racemic and meso isomers are equilibrating, but the equilibrium process is complicated by the presence of dichloro-bridged dimers and lithium chloride adducts for both, the relative amounts of each depending upon the amount of lithium chloride present.

Racemic$-$Meso Isomerizations for IpSc(η^3-allyl) Complexes. While performing variable temperature ^{1}H NMR experiments with allyl compounds **5** and **6**,[21] we discovered that these are also configurationally unstable, although the isomerization reactions are slower and occur only at higher temperatures. In THF-d_8 at 80 °C, both **5** and **6** isomerize to a 2:1 racemic:meso ratio as they decompose. Slower isomerization is observed at 55 °C, whereas no reaction is observed at room temperature after 7 weeks. Addition of 4 equiv of 12-crown-4 to a sample of **6** in THF-d_8 with subsequent heating to 80 °C showed no change in the rate of racemic$-$meso interchange. In Et$_2$O-d_{10} no isomerization is observed at temperatures at or below 55 °C, and only decomposition is observed after heating to 110 °C in toluene-d_8.

The allyl derivatives **5** and **6** provide a system much better suited to mechanistic studies than the chloride compounds (vide supra), since lithium chloride is not added or lost during the interconversion. Moreover, since no isomerization occurs for **5** or **6** at room temperature in any of the solvents examined, any promoting effects of added salts in various solvents could be systematically studied (eq 4).



(4)

R = H (**5**)
R = Me (**7**)
racemo

R = H (**6**)
R = Me (**8**)
meso

To determine their effects on the rate of approach to equilibrium, various reagents were used as promoters to effect isomerization of **5** and **6**. The results of the equilibration experiments are summarized in Table 3.

When *rac*-IpSc(η^3-C$_3$H$_5$) (**5**) was dissolved together with an excess of LiCl in THF-d_8, a variety of species was observed, none of which corresponded to **5** or **6** (^{1}H NMR). Replacing THF-d_8 with toluene-d_8 after 14 h resulted in precipitation of LiCl, and from the ^{1}H NMR spectrum of the soluble complexes it was then evident that epimerization to an ~2:1 ratio of **5** and **6** had taken place with little or no decomposition. Although addition of solid potassium chloride to either **5** or **6** in THF-d_8 results in no detectable dissolution, ^{1}H NMR spectra reveal that isomerization takes place over a period of 10 days, yielding the same ~2:1 ratio of **5** and **6**.

Grignard reagents also promote racemic$-$meso isomerization. Thus, addition of ~16 mol % allylmagnesium bromide to a THF-d_8 solution of **6** resulted in isomerization to a racemic:meso ratio of 1.5:1 after 3 weeks. Also, addition of 10 mol % diallylmagnesium to individual THF-d_8 solutions of **5** and **6** afforded the same ~1.7:1 racemic:meso ratio after 4 weeks. A qualitative test (silver ion) for the presence of halide was negative on a sample of (C$_3$H$_5$)$_2$Mg, indicating that halide is not required for isomerization of **5** and **6**.

A ^{1}H NMR spectrum taken immediately after mixing diallylmagnesium and a THF-d_8 solution of the crotyl compound *rac*-IpSc(η^3-C$_3$H$_4$Me) (**7**) revealed the presence of both racemic allyl complex **5** and racemic crotyl complex **7**, suggesting fast and reversible formation of bis(allyl) scandate intermediates. After a period of approximately 3 h, both meso compounds **6** and **8** were also observed.

The effects of other added salts to solutions of the allyl complexes in less polar solvents were also examined (Table 3). Addition of 30 mol % (n-heptyl)$_4$NCl to a toluene-d_8 solution of **5** results in immediate initiation of isomerization to the meso isomer. After about 6 h a

Table 3. Results of Racemic−Meso Interconversions Carried out with Allyl Derivatives 5−8[a]

compd	solvent	additive	final *rac*:*meso* ratio	reacn time
5 or **6**[b]	THF-d_8		2:1[c]	10 days
6[d]	THF-d_8		(1:6)[c,e]	7 days
5 or **6**[d]	Et_2O-d_{10}		no reacn	5 months
5[f]	toluene-d_8		dec	7 days
7 or **8**[g]	toluene-d_8		2:1[c]	1 day
6	THF-d_8	16 mol % allylMgBr	1.5:1	∼3 weeks
5 or **6**	THF-d_8	10 mol % $allyl_2Mg$	1.7:1	∼6 weeks
7	THF-d_8	50 mol % $allyl_2Mg$	2:1 allyls and 1.3:1 crotyls	7 days
7	Et_2O-d_{10}	$(allyl)_2Mg$[h]	no reacn	5 weeks
5 or **6**	THF-d_8	2 equiv LiCl	2:1	1 day
7	THF-d_8	2 equiv LiCl	2.8:1	3 days
5 or **6**	THF-d_8	KCl[h]	2:1	10 days
5	toluene-d_8	30 mol % $(n\text{-}C_7H_{15})_4NCl$	2:1	6 h
5	cyclohexane-d_{12}	35 mol % $(n\text{-}C_7H_{15})_4NCl$	2:1	3 days
5	THF-d_8	35 mol % $(n\text{-}C_7H_{15})_4NCl$	1.5:1	7 days
5	Et_2O-d_{10}	60 mol % $(n\text{-}C_7H_{15})_4NCl$	(1.6:1)[i]	1 day
5	toluene-d_8	27 mol % $(n\text{-}C_7H_{15})_4NBr$	2:1[c]	1 day
5	cyclohexane-d_{12}	24 mol % $(n\text{-}C_7H_{15})_4NBr$	2:1[c]	2 days
5	THF-d_8	1.1 equiv $LiB(C_6F_5)_4$	2:1	1 day
5	THF-d_8	20 mol % $LiB(C_6F_5)_4$	1.9:1	∼6 weeks
5	THF-d_8	1.5 equiv $NaB(C_6H_3(CF_3)_2)_4$	2.5:1	1 day
5	THF-d_8	20 mol % $NaB(C_6H_3(CF_3)_2)_4$	2:1	∼6 weeks
5	Et_2O-d_{10}	$LiB(C_6F_5)_4$[h]	(8:1)[e]	2 weeks
5	Et_2O-d_{10}	25 mol % $NaB(C_6H_3(CF_3)_2)_4$	no reacn	7 days
5	THF-d_8	1.3 equiv $(n\text{-}C_7H_{15})_4NB(C_6H_3(CF_3)_2)_4$	2:1	∼4 weeks
5	Et_2O-d_{10}	1.1 equiv $(n\text{-}C_7H_{15})_4NB(C_6H_3(CF_3)_2)_4$	no reacn	3 weeks
5	toluene-d_8	$(n\text{-}C_7H_{15})_4NB(C_6H_3(CF_3)_2)_4$[h]	dec	2 weeks

[a] Reactions were carried out at 22 °C unless otherwise specified. [b] 80 °C. [c] The reaction was accompanied by partial decomposition. [d] 55 °C. [e] Reaction was stopped before equilibrium was established. [f] 110 °C. [g] 120 °C. [h] Additive is only partially soluble. [i] Additive reacts with allyl species to make an unidentified compound which is the major component of the reaction mixture.

2:1 equilibrium mixture of **5** and **6** is observed. Following the same procedure, but in the absence of light, resulted in isomerization at qualitatively the same rate. Addition of 35 mol % $(n\text{-heptyl})_4NCl$ to **5** in cyclohexane-d_{12} also initiates isomerization, but at a slower rate; equilibrium is established after ∼3 days. Tetraheptylammonium bromide also promotes racemic−meso isomerizations at about the same rates. These isomerizations promoted by tetraheptylammonium halide salts in hydrocarbon solvents are qualitatively faster than those promoted by allylmagnesium salts in tetrahydrofuran, indicating that halides are more effective in promoting Sc−Cp heterolysis.

When $(n\text{-heptyl})_4NCl$ is added to THF-d_8 or Et_2O-d_{10} solutions of **5**, the ^1H NMR signals for **5** broaden somewhat and/or new signals are present, suggestive of a dynamic equilibrium with a chloroscandate complex. When **5** is titrated with LiCl at −56 °C in THF-d_8, clean conversion to a LiCl adduct with an η^1-C_3H_5 splitting pattern was observed. Formation of the LiCl adduct is complete upon addition of 1 equiv of LiCl, and no further changes are observed in the ^1H NMR spectrum after addition of a second equivalent. Raising the temperature to 25 °C results in the same complex spectrum observed previously. Addition of an excess of LiBr to **1**, **2**, or **4** results in isomerization, qualitatively at the same rate as when no promoter is added, but compounds other than the respective racemic and meso chloride complexes do not build up in detectable levels.

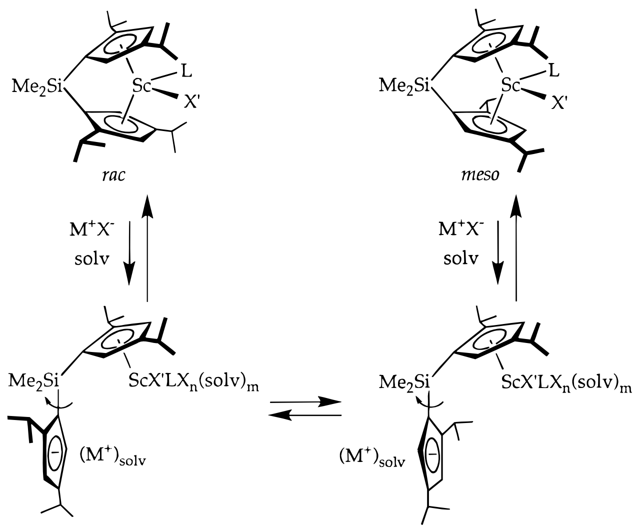
Addition of salts having a small cation and large, weakly coordinating counteranion were also tested as possible promoters. Addition of $LiB(C_6F_5)_4$ to a solution of **5** in THF-d_8 resulted in isomerization to the same 2:1 ratio of **5** and **6**. The analogous isomerization reaction carried out in Et_2O-d_{10} was very slow, either due to the lower basicity of Et_2O as compared to THF or to the lower solubility of $LiB(C_6F_5)_4$ in diethyl ether. The related sodium salt $NaB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ promotes isomerization in THF-d_8 at approximately the same rate as that for $LiB(C_6F_5)_4$. On the other hand, addition of 25 mol % $NaB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ to solutions of **5** in Et_2O-d_{10} (in which the salt is completely soluble) fails to promote isomerization to **6**, even after 1 week at room temperature.

Since salts containing either a large cation with halide or a small cation with a large, weakly coordinating anion promoted racemic−meso isomerization, a salt having a large cation with weakly coordinating anion was also tested. The addition of $(n\text{-heptyl})_4NB(C_6H_3(CF_3)_2)_4$ to samples of **5** was carried out in THF-d_8, Et_2O-d_{10}, and toluene-d_8 (Table 3). Although no reaction was observed in either toluene-d_8 (in which the salt is insoluble) or Et_2O-d_{10}, slow isomerization *was observed* in THF-d_8.

These results suggest that in tetrahydrofuran merely increasing the ionic strength of the solution is adequate to induce interconversion of racemic and meso isomers. In less polar solvents such as diethyl ether, toluene, and cyclohexane, it appears that the assistance of a coordinating anion or a small cation is a further requirement for promotion of isomerization. On the basis of these considerations we propose the general mechanism for racemic:meso interchange shown in Scheme 3.

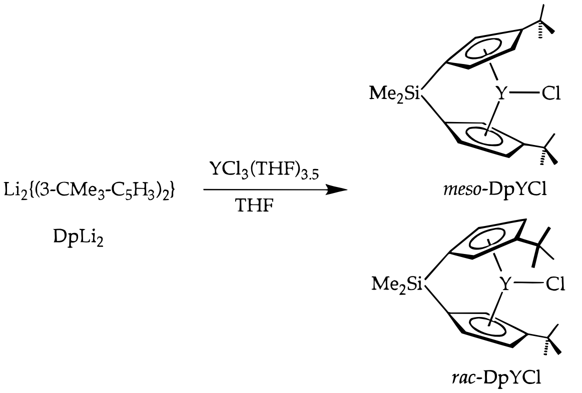
Studies of the Kinetics of Metalation and Attempts To Determine the Generality of *ansa*-Metallocene Ligand Isomerization. Following the metalation reactions of $IpLi_2(THF)_{0.3}$ with both $ScCl_3(THF)_3$ and $YCl_3(THF)_{3.5}$ by ^1H NMR revealed that the meso isomers initially are formed in greater than the thermodynamic concentrations. Thus, after 15 min at 71 °C in THF-d_8, a 1.7:1 racemic:meso ratio of **1** to **2** is observed. Racemic isomer **1** grows to approach the thermodynamic 3:1 racemic:meso ratio within 1 h.

Scheme 3



Similarly, after 15 min at room temperature, $IpLi_2$ metalates to a 1.5:1 racemic:meso ratio of yttrocenes, which converts to the 3:1 thermodynamic ratio immediately upon heating to 71 °C.

The kinetics of metalation of another *ansa*-metallocene were also examined. The ligand $[Me_2Si(\eta^5\text{-}3\text{-}CMe_3\text{-}C_5H_3)_2]Li_2$ ($DpLi_2$) has been shown to coordinate yttrium in THF to yield a 1:1 racemic:meso mixture (eq 5).[25] Upon mixing $DpLi_2$ and $YCl_3(THF)_{3.5}$ in THF-d_8 at room temperature, a 1:1 racemic:meso ratio had already been established. When the reaction was carried out under more controlled conditions, however, a kinetic product mixture was observed. Dissolution of the reagents in THF-d_8 at −78 °C, followed by insertion of the NMR tube into the probe which had been precooled to 227 K, resulted in the observation of a 2:1 racemic:meso mixture of yttrocenes. After the mixture was warmed to room temperature, the ratio initially remained unchanged but after 20 h converted to the 1:1 thermodynamic mixture. Separation of these yttrocenes into diastereomerically pure *rac*- and *meso*-DpYCl has never been accomplished.[26]



(5)

Other *ansa*-metallocene complexes were examined briefly to establish whether racemic−meso interconversions could be promoted. Addition of LiCl to THF-d_8 solutions of pure *meso*-DpScCl did not promote formation of detectable amounts of the racemic isomer. Since the meso isomer is formed exclusively on metalation of $ScCl_3(THF)_3$ with Li_2Dp in toluene solution, it is not clear whether the racemic isomer is thermodynamically or kinetically inaccessible, however. Similarly, both $\{(C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2SiMe_2\}Li_2$ ($BpLi_2$)[2a] and *rac*-$\{(C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}SiMe_3)SiO_2C_{20}H_{12}\}K_2$ (*rac*-$BnBpK_2$)[27] metalate exclusively to the racemic isomer, and perhaps not surprising is the failure of LiCl in THF-d_8 to promote formation of any new isomers.

Using amine elimination followed by treatment with $SiMe_3Cl$, as described by Jordan and co-workers,[10d] a 1:5 racemic:meso mixture of $DpZrCl_2$ isomers may be obtained. A different ratio (racemic:meso = 1.3:1) is obtained by reaction of $DpLi_2$ with $ZrCl_4(THF)_2$ in THF-d_8. Addition of LiCl to either of these mixtures of $DpZrCl_2$ isomers in THF-d_8 does not result in racemic−meso interconversion at room temperature or at 80 °C. Thus, it appears that racemic−meso isomerization for $DpZrCl_2$ is unfavorable in THF-d_8. Curiously, treatment of pure *meso*-$DpZrCl_2$ with methyllithium in diethyl ether has been found to afford a mixture of 33% *rac*-$DpZrMe_2$ and 67% *meso*-$DpZrMe_2$.[28]

Addition of LiCl to diastereomerically pure *rac*-$(EBI)ZrCl_2$ in THF-d_8 does result in isomerization to a 1:1 racemic:meso mixture after 6 days, the same ratio of products obtained when $(EBI)Li_2$ and $ZrCl_4$ are allowed to react for 10 days at room temperature in THF-d_8. There is no doubt in this case, therefore, that thermodynamic control is operating.

Thus, it appears that for group 4 *ansa*-metallocenes, racemic−meso interchange does not occur in some cases. In general, the 16-electron group 4 metallocenes are expected to be less disposed to coordinate salts or donor solvents as compared with their 14-electron group 3 analogues. Also, being less electropositive than the group 3 metals, cyclopentadienyl bonds to group 4 metals are less ionic and thus less readily heterolyzed. These two factors stabilize the M−Cp bonds and discourage isomerization for group 4 metallocenes.

Conclusions

Evidence for the stereochemical isomerization of a variety of *ansa*-metallocene compounds has been observed. Racemic−meso interchange has been established now for scandium and yttrium complexes with the Ip ligand system, for DpYCl, $DpZrMe_2$, and (EBI)-$ZrCl_2$. Moreover, isomerizations have been reported by Marks and Okuda for lanthanide derivatives.[2b,8,9] In addition Brintzinger, Kaminsky, and Bosnich have found that racemic−meso interchange may be promoted photochemically.[11] For the allyl derivatives described here, we have established that the process is promoted by a variety of salts in both ether and hydrocarbon solvents and is not accelerated by light.

A plausible mechanism based on an earlier proposal by Marks et al.[2b] is offered as an explanation of this process (Scheme 3). It involves coordination of anions and/or donor solvents to the metal center with cation assistance to encourage metal−cyclopentadienyl bond heterolysis, rotation about the Si−Cp bond of the detached cyclopentadienide, and recoordination of the

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(25) Bunel, E. E.; Bercaw, J. E. Unpublished results.

(26) It is quite likely that both *rac*- and *meso*-DpYCl are dimeric.

(27) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

(28) Chirik, P. J.; Bercaw, J. E. unpublished results.

opposite face. The facility of the process in toluene and even cyclohexane solution indicates that a donor solvent is not required. The highly ionic nature of the M−Cp bonds in group 3 metallocenes permits metal−cyclopentadienyl bond heterolysis merely by raising the ionic strength of a THF-d_8 solution of **5** or **6** with $(n\text{-}C_7H_{15})_4NB(C_6H_3(CF_3)_2)_4$. Both coordinating anions and small cations also appear to promote racemic−meso interchange. Our observations in some cases of thermodynamic racemic:meso ratios under the reaction conditions commonly used for the synthesis of the metallocene chlorides suggests that the interchange is faster than metalation, such that the composition of the reaction mixture is determined by thermodynamic, not kinetic, control in these cases.

Experimental Section

All air- and/or moisture-sensitive compounds were manipulated using standard high-vacuum-line, Schlenk, or cannula techniques or in a glovebox under a nitrogen atmosphere, as described previously.[29] Argon gas was purified and dried by passage through columns of MnO on vermiculite and activated 4 Å molecular sieves. All solvents were stored under vacuum over titanocene[30] or sodium benzophenone ketyl. The preparations of 6,6-dimethylfulvene,[31] (crotyl)MgCl,[32] and $ScCl_3(THF)_3$ (from Sc_2O_3 (Boulder))[33] were carried out as previously reported. The preparation of $YCl_3(THF)_{3.5}$ was carried out (from Y_2O_3 (Aldrich)) as reported for the scandium derivative.[33,34] *rac*-(EBI)$ZrCl_2$ was prepared by the amine elimination route as reported by Jordan[10a] with subsequent substitution with TMSCl.[10b] *rac*-$[BpYCl]_2$,[2a] *meso*-$[DpScCl]_2$,[35] $LiB(C_6F_5)_4$,[36] $NaB\{C_6H_3(CF_3)_2\}_4$,[37] $TlB\{C_6H_3(CF_3)_2\}_4$,[38] (EBI)Li_2,[5] and (*R*,*S*)-BnBpK_2[39] were prepared according to previous procedures. *n*-Butyllithium and allylmagnesium bromide were purchased (Aldrich) and used as received. Lithium chloride, potassium chloride, and lithium bromide were purchased from Aldrich and dried in vacuo at ≥150 °C for ≥36 h. $(n\text{-heptyl})_4NCl$ was purchased from Aldrich and was dried in vacuo at 120 °C for 6 h. $(n\text{-heptyl})_4NBr$ was purchased from Fluka and dried in vacuo at room temperature for 3 h.

NMR spectra were recorded on General Electric QE300 (300 MHz for ^1H) and Bruker AM500 (500.13 MHz for ^1H) spectrometers. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey. Many of the compounds failed to give satisfactory carbon/hydrogen analyses, even when combusted with added V_2O_5 oxidant. Moreover, in many cases the results were inconsistent from run to run.

Preparation of Isopropylcyclopentadiene. A solution of 6,6-dimethylfulvene (70.5 g, 0.663 mol) in anhydrous ether (200 mL) was slowly added via addition funnel to a well-stirred 25 °C solution of $LiAlH_4$ (0.670 mol) in ether (1 L) in a 3 L flask equipped with air-driven overhead stirrer, efficient reflux condenser filled with dry ice/acetone, and N_2 adapter. The addition required 1 h. The reaction mixture was stirred for 4 h more, after which the excess $LiAlH_4$ was quenched by addition of water (30 mL) using a syringe pump at a rate of 0.4 mL/min. **CAUTION: Reaction is exothermic and produces large amounts of dihydrogen!** NaOH (30 mL, 15% aqueous solution) was then added at a rate of 0.4 mL/min, causing the formation of a pale yellow solution with a granular white solid. After H_2 evolution ceased, water (1 L) was added to the reaction mixture. The product was extracted with ether (2 × 500 mL), the organic layer was washed with water (3 × 1 L), and the ether solution was dried with $MgSO_4$. The solvent was removed *in vacuo*, and the product was distilled at 80 °C and ~40 Torr, yielding 65 g of a pale yellow oil (90%). ^1H NMR ($CDCl_3$): δ 6.5−5.5 (C_5H_5, m (br), 4H total), 3.2 (C_5H_5, m, 1H), 2.8−2.5 ($CH(CH_3)_2$, m (br), 1H), 1.16 ($CH(CH_3)_2$, d, 6H, $J = 8$ Hz).

Preparation of 3-Isopropyl-6,6-dimethylfulvene. Isopropylcyclopentadiene (59.6 g, 0.555 mol), methanol (400 mL), acetone (35 g, 0.603 mol), and pyrrolidine (62 mL, 0.70 mol) were combined in a 1 L flask and stirred for 12 h at 25 °C. The solution was then neutralized with glacial acetic acid (40 mL in 600 mL of water). The product was extracted with ether (4 × 400 mL). The organic layer was washed with water (4 × 600 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, and the yellow oil was Kugelröhr-distilled at 90 °C and 50 Torr, yielding 48.3 g of product (59%). ^1H NMR ($CDCl_3$): δ 6.52 (C_5H_3, m, 1H), 6.45 (C_5H_3, m, 1H), 6.16 (C_5H_3, m, 1H), 2.70 ($CH(CH_3)_2$, sep, 1H, $J = 7$ Hz), 2.16 ($C(CH_3)_2$, s, 6H), 1.18 ($CH(CH_3)_2$, d, 6H, $J = 7$ Hz).

Preparation of 1,3-Diisopropylcyclopentadiene. A solution of 3-isopropyl-6,6-dimethylfulvene (48 g, 0.323 mol) in anhydrous ether (300 mL) was slowly added via addition funnel to a well-stirred 25 °C solution of LAH (0.372 mol) in ether (700 mL) in a 3 L flask equipped with air-driven overhead stirrer, efficient reflux condenser (dry ice/acetone), and N_2 adapter. The addition required 1 h. The reaction mixture was stirred for 4 h more, at which time the excess LAH was quenched by addition of water (20 mL) at a rate of 0.4 mL/min. **CAUTION: Reaction is exothermic and produces large amounts of dihydrogen!** NaOH (30 mL, 15% aqueous solution) was then added at a rate of 0.4 mL/minute, causing the formation of a pale yellow solution with a granular white solid. After H_2 evolution ceased, water (1 L) was added to the reaction mixture and the product was extracted with ether (2 × 500 mL). The organic layer was washed with water (3 × 1 L), and the ether solution was dried with $MgSO_4$. The solvent was removed in vacuo, and the product was distilled at 80 °C and ~15 Torr, yielding 38 g of a pale yellow oil (78%). ^1H NMR ($CDCl_3$): δ 6.05−5.98 (C_5H_4, s (br), 3H total), 3.0−2.3 (C_5H_4, s (br), 1H total), 2.7−2.3 ($CH(CH_3)_2$, m (br), 2H), 1.70, 1.11, 1.07 ($CH(CH_3)_2$, d, 12H total, $J = 7$ Hz).

Preparation of Lithium 1,3-Diisopropylcyclopentadienylide. Dry, degassed toluene (200 mL) and petroleum ether (150 mL) were cannula-transferred onto $^iPr_2CpH$ (24 g, 0.16 mol) in a large swivel frit assembly under argon. ^nBuLi (100 mL, 1.6 M in hexanes, 0.16 mol) was added via cannula over a period of 30 min at 25 °C. The solution was stirred overnight, and the resulting white solid was filtered and washed with petroleum ether (4 × 100 mL). The solid was dried in vacuo, resulting in 22.4 g of a fine white powder (90%). ^1H NMR (THF-d_8): δ 5.37 (C_5H_3, t, 1H, $J = 2$ Hz), 5.33 (C_5H_3, d, 2H, $J = 2$ Hz), 2.73 ($CH(CH_3)_2$, sep, 2H, $J = 7$ Hz), 1.15 ($CH(CH_3)_2$, d, 12 H, $J = 7$ Hz).

Preparation of $Me_2Si[C_5H_3\text{-}2,4\text{-}(CHMe_2)_2]_2$ (IpH_2). In an inert-atmosphere drybox, $(CHMe_2)_2C_5H_3Li$ (19.1 g, 0.12 mol) was transferred to a 200 mL Kjeldahl flask, which was then attached to a swivel frit assembly. THF (175 mL) was transferred into the flask via cannula. The resulting yellow solution was evacuated at −78 °C, and dichlorodimethylsilane (7.4 mL, 0.061 mol) was added by vacuum transfer. The

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solution was warmed from −78 °C to room temperature over a period of 1 h and was stirred overnight at room temperature. The THF was then removed in vacuo, and petroleum ether (100 mL) was added by vacuum transfer. The resulting yellow slurry was stirred for 2 h and filtered, resulting in a yellow supernatant and slightly yellow precipitate. The precipitate was washed twice with fresh petroleum ether, and the combined supernatants were evaporated to leave a yellow oil. The product was Kugelröhr-distilled at 100 °C under dynamic vacuum, affording 20.0 g of a light yellow oil (92% yield). ^{1}H NMR (THF-d_8): δ 6.27, 6.10, 6.03, 5.94, 5.87, 5.74 (C_5H_3, s, 2H total), 2.80 (C_5H_3, d, 1.3H), 2.64, 2.54, 2.40 ($CH(CH_3)_2$, m, 2H total), 1.12, 1.11 ($CH(CH_3)_2$, d, 12H total), 0.08, 0.55, 0.49, 0.45, 0.37 ($Si(CH_3)_2$, s, 3H total).

Preparation of $Me_2Si[C_5H_2\text{-}2,4\text{-}(CHMe_2)_2]_2Li_2(THF)_{0.3}$ ($IpLi_2(THF)_{0.3}$). The Kügelrohr distillate of IpH_2 (20.0 g, 0.056 mol) was weighed into a 200 mL Kjeldahl flask and attached to a swivel frit assembly. The assembly was degassed, and petroleum ether (175 mL) was added via cannula. A 1.6 M solution of *n*-butyllithium (80 mL, 0.13 mol) was added via syringe at 0 °C, affording a light orange solution. After the mixture was stirred overnight at room temperature, the petroleum ether was removed in vacuo to give a viscous orange gel. THF (75 mL) was added by vacuum transfer, and the solution was stirred for 30 min. The THF was then removed, yielding an off-white solid. Petroleum ether (150 mL) was added by vacuum transfer, and the resulting light orange slurry was stirred for 2 h. Filtration yielded a white precipitate which was washed twice with fresh petroleum ether and dried in vacuo to afford a white solid, $IpLi_2(THF)_{0.3}$ (19.6 g, 89% yield). ^{1}H NMR (THF-d_8): δ 5.67 (s, 1H, C_5H_2), 5.62 (s, 1H, C_5H_2), 3.62 (m, overlaps with residual THF-d_7, C_4H_8O), 3.11 (sep (br), 1H, $CH(CH_3)_2$), 2.79 (sep, 1H, $CH(CH_3)_2$, *J* = 7 Hz), 1.77 (m, overlaps with residual THF-d_7, C_4H_8O), 1.14 (d, 12H, $CH(CH_3)_2$, *J* = 7 Hz), 0.35 (s, 3H, $Si(CH_3)_2$).

Preparation of *rac*-IpScCl·LiCl(THF)$_2$ (1) and [*meso*-IpSc(μ-Cl)]$_2$ (2). $IpLi_2(THF)_{0.3}$ (4.00 g, 10.2 mmol) and $ScCl_3(THF)_3$ (3.8 g, 10.3 mmol) were weighed into a 200 mL Kjeldahl flask equipped with a stirbar in an inert-atmosphere glovebox. THF (175 mL) was added, and a reflux condenser and argon inlet adapter were attached to the flask. The resulting slurry was stirred at room temperature until all the ligand had dissolved. The solution was then heated to reflux, resulting in a slightly cloudy, golden solution; after reflux for 3 days, the reaction flask containing the clear, light yellow solution was attached to a swivel frit assembly. The THF was evacuated from the frit assembly, and petroleum ether (100 mL) was added by vacuum transfer. The resulting bright yellow slurry was stirred for 1 h and then filtered, separating the yellow supernatant from a white precipitate. Immediately after filtration, a slightly green microcrystalline solid, subsequently identified as [*meso*-IpSc(μ-Cl)]$_2$, precipitated from the filtrate. This solid was isolated by repeated crystallization/filtration cycles from heptane. Once separated completely from the *meso* compound, hydrocarbon-soluble *rac*-IpScCl·LiCl(THF)$_2$ was recrystallized by cooling a pentane solution to −40 °C. The yield was 3.31 g (55%) for **1** and 0.96 g (22%) for **2**.

rac-IpScCl·LiCl(THF)$_2$: Anal. Calcd for $C_{32}H_{54}Cl_2LiO_2ScSi$: C, 61.91; H, 8.77. Found: C, 62.18, 61.51; H, 8.68, 7.19. ^{1}H NMR (THF-d_8): δ 6.02 (d, C_5H_2, 1H, *J* = 2 Hz), 5.44 (d, C_5H_2, 1H, *J* = 2 Hz), 3.62 (m, THF, overlaps with residual THF-d_7), 3.01 (sep, $CH(CH_3)_2$, 1H, *J* = 7 Hz), 2.84 (sep, $CH(CH_3)_2$, 1H, *J* = 7 Hz), 1.77 (m, THF, overlaps with residual THF-d_7), 1.25 (d, $CH(CH_3)_2$, 3H, *J* = 7 Hz), 1.10 (d, $CH(CH_3)_2$, 3H, *J* = 7 Hz), 1.05 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 0.77 (s, $Si(CH_3)_2$, 3H).

[*meso*-IpSc(μ-Cl)]$_2$: Anal. Calcd for $C_{24}H_{38}ClScSi$: C, 66.26; H, 8.80. Found: C, 72.09, 71.58; H, 10.09, 9.80. ^{1}H NMR (THF-d_8): δ 5.87 (s, C_5H_2, 2H), 5.50 (s, C_5H_2, 2H), 3.01 (sep, $CH(CH_3)_2$, 2H, *J* = 7 Hz), 2.77 (sep, $CH(CH_3)_2$, 2H, *J* = 7 Hz), 1.30 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.07 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.04 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.01 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 0.83 (s, $Si(CH_3)_2$, 3H), 0.63 (s, $Si(CH_3)_2$, 3H).

Preparation of *rac*-IpYCl·LiCl(THF)$_2$ (3) and [*meso*-IpY(μ_2-Cl)]$_2$ (4). A procedure analogous to that of the scandium compounds (**1** and **2**) was followed using $IpLi_2(THF)_{0.3}$ (2.02 g, 5.15 mmol) and $YCl_3(THF)_{3.5}$ (2.05 g, 4.58 mmol). All aspects of the separation procedure are also identical for the yttrium congeners. The yield was 1.74 g (58%) for **3** and 0.51 g (23%) for **4**.

rac-IpYCl·LiCl(THF)$_2$: Anal. Calcd for $C_{32}H_{54}Cl_2LiO_2SiY$: C, 57.81; H, 8.19. Found: C, 56.86, 56.83; H, 8.29, 7.96%. ^{1}H NMR (C_6D_6/THF-d_8): δ 6.57 (s, C_5H_2, 1H), 5.77 (s, C_5H_2, 1H), 3.62 (m, THF, overlaps with residual THF-d_7), 3.47 (sep, $CH(CH_3)_2$, 1H, *J* = 7 Hz), 2.94 (sep, $CH(CH_3)_2$, 1H, *J* = 7 Hz), 1.77 (m, THF, overlaps with residual THF-d_7), 1.39 (d, $CH(CH_3)_2$, 3H, *J* = 7 Hz), 1.33 (d, $CH(CH_3)_2$, 3H, *J* = 7 Hz), 1.25 (d, $CH(CH_3)_2$, 3H, *J* = 7 Hz), 1.20 (d, $CH(CH_3)_2$, 3H, *J* = 7 Hz), 0.81 (s, $Si(CH_3)_2$, 3H).

[*meso*-IpY(μ-Cl)]$_2$: Anal. Calcd for $C_{24}H_{38}ClSiY$: C, 60.18; H, 8.00. Found: C, 43.17, 42.85; H, 6.21, 6.17. ^{1}H NMR (THF-d_8): δ 5.95 (d, C_5H_2, 2H, *J* = 2 Hz), 5.39 (d, C_5H_2, 2H, *J* = 2 Hz), 3.09 (sep, $CH(CH_3)_2$, 2H, *J* = 7 Hz), 2.99 (sep, $CH(CH_3)_2$, 2H, *J* = 7 Hz), 1.33 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.11 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.05 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.04 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 0.76 (s, $Si(CH_3)_2$, 3H), 0.52 (s, $Si(CH_3)_2$, 3H).

Preparation of *rac*-IpSc(η^3-C_3H_5) (5). *rac*-IpScCl·LiCl(THF)$_2$ (0.45 g, 0.76 mmol) was weighed in an inert-atmosphere drybox into a 50 mL Kjeldahl flask which was attached to a swivel frit assembly. Toluene (25 mL) was added by vacuum transfer, and the contents of the flask were stirred at −78 °C. A 1.0 M solution (Et_2O) of allylmagnesium bromide (1.0 mL, 1.0 mmol) was syringed against a strong argon counterflow into the stirred solution at −78 °C. The solution was warmed slowly to room temperature over a period of 10 h, providing an orange solution. Toluene was removed in vacuo, and the resulting solid was washed once with petroleum ether (10 mL) in order to remove residual diethyl ether. Petroleum ether (15 mL) was then added by vacuum transfer, and the orange slurry was stirred for 1 h at room temperature; subsequent filtration separated an off-white precipitate from the orange supernatant. The petroleum ether was then evacuated, leaving 0.24 g of an orange powder (0.54 mmol, 72% yield). Anal. Calcd for $C_{27}H_{43}ScSi$: C, 73.59; H, 9.84. Found: C, 72.92; H, 10.09. ^{1}H NMR (toluene-d_8, 295 K): δ 7.43 (m, CH_2CHCH_2, 1H), 6.67 (d, C_5H_2, 2H, *J* = 2 Hz), 5.17 (d, C_5H_2, 2H, *J* = 2 Hz), 4.46 (d (br), *anti*-CH_2CHCH_2, 1H, coupling unresolved), 3.58 (d (br), *anti*-CH_2CHCH_2, 1H, coupling unresolved), 3.04 (sep, $CH(CH_3)_2$, 2H, *J* = 7 Hz), 2.54 (sep, $CH(CH_3)_2$, 2H, *J* = 7 Hz), 2.5 (s (br), syn-CH_2CHCH_2, 1H), 1.9 (s (br), *syn*-CH_2CHCH_2, 1H), 1.29 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.11 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 1.05 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz), 0.72 (s, $Si(CH_3)_2$, 6H), 0.64 (d, $CH(CH_3)_2$, 6H, *J* = 7 Hz).

Preparation of *meso*-IpSc(η^3-C_3H_5) (6). In an inert-atmosphere drybox, [*meso*-IpSc(μ-Cl)]$_2$ (0.60 g, 1.4 mmol) was weighed into a 50 mL Kjeldahl flask which was then attached to a swivel frit assembly. Toluene (25 mL) was added by vacuum transfer, and the resulting light green slurry was stirred at −78 °C. Allylmagnesium bromide, as a 1.0 M solution in Et_2O (1.7 mL, 1.7 mmol), was added via syringe against a strong argon counterflow. The solution was warmed slowly to room temperature over a period of 10 h, at which time the mixture was orange. This slurry was stirred at room temperature for an additional 4 h. The toluene was removed, and petroleum ether (20 mL) was added by vacuum transfer. The orange slurry was stirred for 1 h and filtered, affording an off-white precipitate and an orange supernatant. After the precipitate was washed four times with fresh portions of petroleum ether, the solvent was removed from the filtrate, leaving a bright orange powder (0.46 g, 1.0 mmol, 75% yield).

Anal. Calcd for $C_{27}H_{43}ScSi$: C, 73.59; H, 9.84. Found: C, 72.99, 72.52; H, 10.25, 10.10. ^1H NMR (Et_2O-d_{10}, 295 K): δ 7.53 (m, 1H, CH_2CHCH_2), 6.78 (d, 2H, C_5H_2, $J = 2$ Hz), 5.27 (d, 2H, C_5H_2, $J = 2$ Hz), 4.03 (d (br), 2H, *anti*-CH_2CHCH_2, coupling unresolved), 3.04 (sep, 2H, $CH(CH_3)_2$, $J = 7$ Hz), 2.36 (sep, 2H, $CH(CH_3)_2$, $J = 7$ Hz), 1.97 (d, 2H, *syn*-CH_2CHCH_2, $J = 9$ Hz), 1.22 (d, 6H, $CH(CH_3)_2$, $J = 7$ Hz), 1.07 (d, 6H, $CH(CH_3)_2$, $J = 7$ Hz), 0.92 (d, 6H, $CH(CH_3)_2$, $J = 7$ Hz), 0.86 (d, 6H, $CH(CH_3)_2$, $J = 7$ Hz), 0.81 (s, 3H ($Si(CH_3)_2$), 0.69 (s, 3H, $Si(CH_3)_2$).

Preparation of *rac*-IpSc(η^3-$C_3H_4CH_3$) (7). In an inert-atmosphere drybox, a 50 mL Kjeldahl flask was charged with *rac*-IpScCl·LiCl(THF)$_2$ (0.43 g, 0.72 mmol) and attached to a swivel frit apparatus. Toluene (~20 mL) was added by vacuum transfer, affording a light yellow slurry. The solution was warmed until all *rac*-IpScCl was dissolved, at which time the solution was cooled back to −78 °C. A standardized 3.2 M solution of (crotyl)MgCl in ether (0.3 mL, 0.96 mmol) was added by syringe against a strong argon counterflow. The reaction flask was warmed to room temperature over 12 h, at which time the solution was dark red. The solution was stirred for 6 h at room temperature and the solvent was removed under vacuum, giving a dark red oil. The oil was dried by washing nine times with fresh portions of heptane followed by drying in vacuo. Extraction with heptane yielded a deep red supernatant and a light orange precipitate, which was washed three times with heptane. The supernatant was dried for 2 h, leaving a dark red paste. Anal. Calcd for $C_{28}H_{45}ScSi$: C, 73.96; H, 9.98. Found: C, 79.53, 79.01; H, 10.19, 11.30. ^1H NMR (THF-d_8, 295 K): δ 6.91 (m, $CH_2CHCH(CH_3)$, 1H), 6.73 (s, C_5H_2, 2H), 5.15 (s, C_5H_2, 2H), 4.6 (s (br), $CH_2CHCH(CH_3)$), 3.11 (sep, $CH(CH_3)_2$, 2H, $J = 7$ Hz), 2.56 (s (br), $CH(CH_3)_2$, 2H), 1.34 (d, $CH_2CHCH(CH_3)$, 3H, $J = 5$ Hz), 1.27 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 1.06 (s (br), $CH(CH_3)_2$, 12H), 0.73 (s, $Si(CH_3)_2$, 6H), 0.69 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz). The $CH_2CHCH(CH_3)$ resonance cannot be located at this temperature.

Preparation of *meso*-IpSc(η^3-$C_3H_4CH_3$) (8). In an inert-atmosphere glovebox, *meso*-[IpScCl]$_2$ (0.34 g, 0.78 mmol) was weighed into a 50 mL Kjeldahl flask which was attached to a swivel frit assembly. Toluene (~20 mL) was added by vacuum transfer, affording a bright yellow slurry. At −78 °C, a 3.2 M solution of (crotyl)MgCl in ether (0.3 mL, 0.96 mmol) was added by syringe against an argon counterflow. The reaction mixture was warmed to room temperature over a period of 12 h and then stirred for an additional 24 h at room temperature, at which time the reaction mixture was dark red. The solvent was removed under vacuum, and the resulting red sludge was washed three times with heptane. Extraction with heptane afforded a dark red supernatant and left a tan precipitate which was washed three times with heptane. The supernatant was dried, affording red crystals. Anal. Calcd for $C_{28}H_{45}ScSi$: C, 73.96; H, 9.98. Found: C, 73.32, 74.10, 73.37; H, 10.21, 10.49, 9.94. ^1H NMR (C_6D_6, 295 K): δ 7.08 (m, $CH_2CHCH(CH_3)$, 1H), 6.70 (s, C_5H_2, 2H), 5.31 (s, C_5H_2, 2H), 5.07 (m, $CH_2CHCH(CH_3)$, 1H), 3.08 (sep, $CH(CH_3)_2$, 2H, $J = 7$ Hz), 2.48 (sep, $CH(CH_3)_2$, 2H, $J = 7$ Hz), 1.39 (d, $CH_2CHCH(CH_3)$, 3H, $J = 6$ Hz), 1.30 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 1.15 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 0.96 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 0.83 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 0.80 (s, $Si(CH_3)_2$, 3H), 0.68 (s, $Si(CH_3)_2$, 3H). The $CH_2CHCH(CH_3)$ resonance cannot be located at this temperature.

Preparation of *meso*-IpZr(NMe$_2$)$_2$ (9). A 100 mL Schlenk flask was charged with $Zr(NMe_2)_4$ (0.5 g, 1.9 mmol) in an inert-atmosphere drybox, and xylenes (~40 mL) was added via pipet. IpH_2 (0.67 g, 1.9 mmol) was then added via pipet, affording a light yellow solution. The flask was attached to a reflux condenser and an Ar inlet valve and was brought to reflux open to a mercury bubbler. The solution darkened to orange over 1 h and after 12 h was black and opaque. At this point, the reaction mixture was cooled and the flask transferred to a swivel frit apparatus with a 100 mL receiver flask. The xylenes were removed under vacuum, and pentane (30 mL) was added to the black residue by vacuum transfer. The resulting black slurry was stirred for 1 h, at which point filtration removed a small amount of jet black precipitate from the yellow/brown supernatant. The pentane was evacuated from the supernatant, leaving a brown oil which was dried for several hours under vacuum. Redissolution of the brown oil in fresh pentane and cooling for 1 week at −80 °C yielded a crop of yellow-orange needles. Additional cooling of the mother liquor after isolation of the first batch of crystals yielded an additional crop of crystals. The total yield was 0.74 g (73%). Anal. Calcd for $C_{28}H_{50}N_2SiZr$: C, 35.92; H, 9.04; N, 20.94. Found: C, 36.17, 36.72; H, 5.35, 5.94; N, 20.77, 21.09. ^1H NMR (C_6D_6): δ 6.46 (d, C_5H_2, 2H, $J = 2$ Hz), 5.67 (d, C_5H_2, 2H, $J = 2$ Hz), 3.18 (s, $N(CH_3)_2$, 6H), 3.01 (sep, $CH(CH_3)_2$, 2H, $J = 7$ Hz), 2.91 (sep, $CH(CH_3)_2$, overlaps with $N(CH_3)_2$), 2.88 (s (br), $N(CH_3)_2$, overlaps with $CH(CH_3)_2$), 1.33 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 1.25 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 1.23 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 1.12 (d, $CH(CH_3)_2$, 6H, $J = 7$ Hz), 0.74 (s, $Si(CH_3)_2$, 3H), 0.54 (s, $Si(CH_3)_2$, 3H).

Generation of *rac*-IpSc(η^1-C_3H_5)·LiCl(THF)$_x$ in Situ. In an inert-atmosphere glovebox, **5** (17.5 mg, 0.0397 mmol) was weighed into an NMR tube with a threaded top. THF-d_8 (0.5 mL) was added by pipet, and the tube was fitted with a septumed screw cap. The solution of **5** was cooled to −56 °C in the NMR probe and the ^1H spectrum acquired. The sample was then ejected from the probe and cooled immediately to −78 °C in a dry ice/acetone bath. The solution of **5** was titrated with a standardized solution of LiCl in THF-d_8 (0.4658 M) added 0.2 equiv at a time through the septum. A ^1H NMR spectrum was acquired at each interval of titration from 0 to 2 equiv, and during this process the tube was never warmed above −56 °C. After the addition of 1 equiv of LiCl, resonances assigned to *rac*-IpSc(η^1-C_3H_5)·LiCl(THF)$_x$ were the only thing visible (besides decomposition product resulting from air leakage into NMR tube) in the ^1H NMR spectra acquired. ^1H NMR (THF-d_8, −65 °C): δ 6.23 (s, 1H, C_5H_2), 6.14 (m, 1H, $ScCH_2CHCH_2$), 5.93 (s, 1H, C_5H_2), 5.24 (s, 1H, C_5H_2), 5.17 (s, 1H, C_5H_2), 3.84 (d, br, 1H, *anti*-$ScCH_2CHCH_2$, $J = 16$ Hz), 3.68 (d, br, 1H, *syn*-$ScCH_2CHCH_2$, $J = 7$ Hz), 3.11 (sep, br, 1H, $CH(CH_3)_2$), 2.88 (sep, br, 1H, $CH(CH_3)_2$), 2.69 (sep, br, 1H, $CH(CH_3)_2$), 2.25 (sep, br, 1H, $CH(CH_3)_2$), 1.31 (d, br, 2H, $ScCH_2CHCH_2$, $J = 7$ Hz), 1.20−0.98 (m, br, 24H, $CH(CH_3)_2$), 0.55 (s, 3H, $Si(CH_3)_2$), 0.53 (s, 3H, $Si(CH_3)_2$).

Preparation of (C_3H_5)$_2$Mg. In an inert-atmosphere glovebox, a 1.0 M solution of allylmagnesium bromide in diethyl ether (5 mL, 5 mmol) was measured into a 100 mL Kjeldahl flask and attached to a swivel frit assembly. The diethyl ether solvent was removed under vacuum and the resulting white paste was dried for 1 h. Dioxane (10 mL) was added by vacuum transfer, affording a slurry with copious amounts of white precipitate. This slurry was stirred for 1 h and then filtered, separating a slightly yellow supernatant from the off-white precipitate. The precipitate was washed once with dioxane, and the filtrate was then dried, affording a sticky yellow powder. Excess dioxane was removed from the product by five cycles of vacuum transfer−evacuation with 5 mL portions of toluene. Subsequently, the product was dried to a free-flowing powder. ^1H NMR indicated less than 0.1 equiv of dioxane present in the final product. ^1H NMR (THF-d_8): δ 6.25 (quin, CH_2CHCH_2, 1H, $J = 11$ Hz), 2.36 (d, 4H, CH_2CHCH_2, $J = 11$ Hz). A small sample was quenched with water and tested negative for halide by the absence of precipitate after addition of silver nitrate.

Preparation of (n-C_7H_{15})$_4$NB{$C_6H_3(CF_3)_2$}$_4$. TlB{$C_6H_3(CF_3)_2$}$_4$ (1.0 g, 0.87 mmol) was dissolved in Et_2O (50 mL) in a 250 mL round-bottom flask. In a separate round-bottom flask, (n-C_7H_{15})$_4$NCl (0.387 g, 0.87 mmol) was dissolved in Et_2O (25 mL). After all species were dissolved, the ammonium salt solution was added to the solution of TlB{$C_6H_3(CF_3)_2$}$_4$ by pipet, immediately forming a fine, white precipitate in the reaction mixture. After the addition was complete, the reaction mixture was stirred for 24 h, at which time the mixture was filtered through Celite and washed three times with Et_2O. The filtrate was a clear, golden solution. The Et_2O was removed in vacuo, and the resulting sticky, yellow solid was dried in vacuo at 100 °C for 12 h. ^1H NMR (CD_2Cl_2): δ 7.73 (d, 2H, o-$C_6H_3(CF_3)_2$, $J = 2$ Hz), 7.57 (s, 1H, p-$C_6H_3(CF_3)_2$), 3.04 (m, 2H, $NCH_2(C_6H_{13})$), 1.60 (s, br, 2H, $NCH_2CH_2(C_5H_{11})$), 1.54−1.27 (m, 8H, $NCH_2CH_2(C_4H_8)CH_3$), 0.88 (t, $N(C_6H_{12})CH_3$, $J = 7$ Hz).

Isomerization of *rac*-IpScCl·LiCl(THF)$_2$ (1), *meso*-[IpScCl]$_2$ (2), *rac*-IpYCl·LiCl(THF)$_2$ (3), and *meso*-[IpYCl]$_2$ (4). A small sample of the appropriate metallocene (~20 mg) was placed in a J. Young NMR tube in an inert-atmosphere glovebox. The appropriate solvent (0.4 mL) was added by vacuum transfer at −78 °C, and the reactions were followed by ^1H NMR until either equilibrium was reached (THF-d_8) or lack of reaction was established (Et_2O-d_{10}, toluene-d_8). Reactions were also carried out in THF-d_8 with added LiBr (~5, equiv).

Preparative-Scale Isomerization of *meso*-[IpScCl]$_2$ (2). In an inert-atmosphere glovebox, **2** (300 mg, 0.069 mmol) was weighed into a 25 mL Kjeldahl flask. This flask was attached to a swivel frit assembly, and THF (10 mL) was added by vacuum transfer at −78 °C. The resulting yellow solution was stirred at room temperature for 8 days, at which time the THF was removed in vacuo. The bright yellow powder was dried and excess THF removed by three successive cycles of vacuum transfer−evacuation with 10 mL portions of heptane followed by filtration, yielding a light yellow precipitate and a bright yellow-green filtrate. Both species were dried in vacuo and isolated in powder form. ^1H NMR of heptane-soluble species (THF-d_8): δ 6.14 (s, br, 1H, C_5H_2), 5.62 (s, 1H, C_5H_2), 2.96 (sep, 1H, $CH(CH_3)_2$, $J = 7$ Hz), 2.81 (s, br, 1H, $CH(CH_3)_2$), 1.22 (d, 3H, $CH(CH_3)_2$, $J = 7$ Hz), 1.17 (d, 3H, $CH(CH_3)_2$, $J = 7$ Hz), 1.06 (d, 3H, $CH(CH_3)_2$, $J = 7$ Hz), 1.04 (d, 3H, $CH(CH_3)_2$, $J = 7$ Hz), 0.76 (s, 3H, $Si(CH_3)_2$).

Isomerization of *rac*-IpSc(η^3-C_3H_5) (5), *meso*-IpSc(η^3-C_3H_5) (6), *rac*-IpSc(η^3-$C_3H_4CH_3$) (7), and *meso*-IpSc(η^3-$C_3H_5CH_3$) (8). A small sample of the appropriate metallocene (~20 mg, 0.045 mmol) was placed in a J. Young NMR tube in an inert-atmosphere glovebox. The appropriate solvent (0.4 mL) was then added by vacuum transfer. In some experiments promoters were also added (Table 3). The NMR tube was either placed in an oil bath at the correct temperature or allowed to sit at room temperature. The reactions were monitored by ^1H NMR until either equilibrium was reached or lack of reaction was established.

Reactions of $ScCl_3(THF)_3$ and $YCl_3(THF)_{3.5}$ with $IpLi_2$. $IpLi_2$ was weighed into a J. Young NMR tube along with 1 equiv of either $ScCl_3(THF)_3$ or $YCl_3(THF)_{3.5}$ in an inert-atmosphere glovebox. In the case of the yttrium complex, THF-d_8 was added by vacuum transfer, and a ^1H NMR spectrum was immediately acquired at room temperature. The reaction mixture was then heated to 71 °C in the NMR probe. The reaction was followed by ^1H NMR for 30 min at which point the thermodynamic product mixture had been achieved. In the case of the scandium complex THF-d_8 was added by vacuum transfer, and the reaction mixture was heated to 71 °C in the NMR probe. The reaction was followed by ^1H NMR for 1 h, at which point the thermodynamic product mixture had been achieved.

Reaction of $YCl_3(THF)_{3.5}$ with $DpLi_2$. $DpLi_2$ (14 mg, 0.045 mmol) and $YCl_3(THF)_{3.5}$ (20 mg, 0.045 mmol) were weighed into a J. Young NMR tube in an inert-atmosphere glovebox. THF-d_8 was added by vacuum transfer at −78 °C followed by immediate warming of the mixture to room temperature. The reaction was followed by ^1H NMR at room temperature for 17 h. All ligand had metalated after 17 h, resulting in a 1:1 racemic:meso ratio. The reaction mixture was then heated to 80 °C for 44 h with no change in the product ratio.

Reaction of $YCl_3(THF)_{3.5}$ with $DpLi_2$ at −46 °C. In an inert-atmosphere glovebox, $DpLi_2$ (9.8 mg, 0.0313 mmol) and $YCl_3(THF)_{3.5}$ (13.7 mg, 0.0313 mmol) were weighed into a J. Young NMR tube. THF-d_8 (0.5 mL) was added by vacuum transfer at −78 °C. The tube was shaken to dissolve the reagents, being careful not to warm the contents. The NMR probe was cooled to −80 °C, and the cold reaction mixture was inserted. The probe was then warmed to −46 °C and a ^1H spectrum was acquired. The sample was warmed to room temreature in the probe, and another ^1H spectrum was acquired. The sample was allowed to stand for 20 h at room temperature, and another ^1H spectrum was acquired. Attainment of the thermodynamic 1:1 racemic:meso ratio was complete after that period.

Preparation of (*R*,*S*)-($C_{12}H_8O_2Si$){C_5H_2-2-$SiMe_3$-4-CMe_3}$_2$ScCl(THF) ((*R*,*S*)-BnBpScCl(THF)). In an inert-atmosphere glovebox, (*R*,*S*)-$BnBpK_2$ (2.0 g, 2.57 mmol) and $ScCl_3(THF)_3$ (0.946 g, 2.57 mmol) were weighed into a 200 mL Kjeldahl flask. A reflux condenser and 180° needle valve were then attached to the flask, and the assembly was evacuated. THF (80 mL) was added by vacuum transfer, and the mixture was heated to reflux for 2 days open to an argon bubbler. The THF was evaporated, resulting in a dark orange, sticky solid. Petroleum ether (~50 mL) was added by vacuum transfer, and the resulting thick slurry was stirred for 1 h, at which time the solvent was evaporated. The reaction flask was then attached to a swivel frit assembly, and Et_2O (100 mL) was added by vacuum transfer. The orange slurry was stirred for 1 h and then filtered to remove KCl. The precipitate was washed once with Et_2O, followed by evaporation of the solvent. Petroleum ether (75 mL) was then added to the filtrate by vacuum transfer, and the resulting mixture was filtered, isolating a tan solid. This solid was washed three times with hexane and then dried, affording 1.12 g of product (51%). Anal. Calcd for $C_{48}H_{56}ClO_3ScSi_3$: C, 68.18; H, 6.67. Found: C, 69.34, 69.83, 69.34; H, 7.19, 8.21, 7.90. ^1H NMR (THF-d_8): δ 7.94 ($C_{20}H_{12}$, d, 1H, $J = 9$ Hz), 7.87 ($C_{20}H_{12}$, d, 1H, $J = 8$ Hz), 7.66 ($C_{20}H_{12}$, d, 1H, $J = 9$ Hz), 7.29 ($C_{20}H_{12}$, t, 1H, $J = 7$ Hz), 7.16 ($C_{20}H_{12}$, m, 2H), 6.54 (C_5H_2, d, 1H, $J = 2$ Hz), 6.42 (C_5H_2, d, 1H, $J = 2$ Hz), 3.62 (m, overlapping solvent resonances), 1.77 (m, overlapping solvent resonances), 1.31 ($C(CH_3)_3$, s, 9H), 0.20 ($Si(CH_3)_3$, s, 9H).

Attempted Isomerizations of *rac*-[BpYCl]$_2$, (*R*,*S*)-[BnBpScCl(THF)], *meso*-[DpScCl]$_2$, and *rac*-(EBI)$ZrCl_2$ with LiCl. A small sample of the appropriate metallocene (~25 mg) was placed in a J. Young NMR tube along with LiCl (~5 equiv) in an inert-atmosphere glovebox. THF-d_8 was added by vacuum transfer, and the corresponding reactions were monitored by ^1H NMR. After 100 h at room temperature without reaction, each sample was heated to 80 °C for several days with no reaction evident by ^1H NMR.

Metalation of $ZrCl_4$ with (EBI)Li_2. In an inert-atmosphere glovebox, (EBI)Li_2 (14.0 mg, 0.0338 mmol) and $ZrCl_4$ (8.6 mg, 0.0369 mmol) were weighed into a J. Young NMR tube. THF-d_8 (0.5 mL) was added by vacuum transfer at −78 °C, affording a slightly cloudy red-orange solution. The mixture was warmed to room temperature and allowed to react for 10 days, at which time the contents were bright yellow. At this point, ^1H NMR indicated the formation of metallocenes in a 1:1 racemic:meso ratio.

Metalation of $ZrCl_4$ with $DpLi_2$. $DpLi_2$ (24 mg, 0.077 mmol) and $ZrCl_4$ (18 mg, 0.077 mmol) were weighed into a J. Young NMR tube in an inert-atmosphere glovebox. THF-d_8 was added by vacuum transfer at −78 °C, affording a slightly cloudy light brown solution upon warming. The reaction was monitored by ^1H NMR and allowed to proceed at room temperature for 48 h. After this time, the reaction mixture was heated to 80 °C for 68 h without change to the racemic:meso ratio (1.3:1).

Structure Determinations for *rac*-IpScCl·LiCl(THF)$_2$ (1), *meso*-[IpYCl]$_2$ (4), and *meso*-IpZr(NMe$_2$)$_2$ (9). A fragment cut from a single crystal under Paratone oil for **1** and **4** was attached to a glass fiber and centered on an Enraf-Nonius CAD-4 diffractometer under a stream of cold N_2 gas. A single crystal mounted in a glass capillary for **9** was centered on an Enraf-Nonius CAD-4 diffractometer at room temperature. Unit cell parameters and orientation matrixes were obtained by least-squares calculations based on the setting angles of 25 reflections with $11.6° < \theta < 12.1°$ for **1**, $12.5° < \theta < 13.1°$ for **4**, and $10.5° < \theta < 11.2°$ for **9**. During the data collection for all samples, three reference reflections were measured every 1 h and showed no significant decay. Two equiv data sets were collected, and no correction was made for decay or absorption for **1** and **9**; absorption corrections by ψ scans were applied to **4**. Lorentz and polarization factors were applied to each, and the two data sets for each case were then merged. Details of the data collection and solution and refinement of the structures can be found in Table 1. Selected bond lengths and angles can be found in Table 2. Structures **1** and **4** were solved by direct methods, which for both revealed all non-hydrogen atom positions (SHELXS). Subsequent difference Fourier maps were successful in finding all hydrogens. In the refinement, all hydrogens in **1** and **4** were freely refined. The structure of **9** was solved by the Patterson method, which revealed most of the heavy atoms, the remaining heavy atoms being revealed in subsequent difference Fourier maps. The hydrogens of **9** were treated as riding atoms in the refinement. All non-hydrogen atoms were refined anisotropically for each of the structures. Full-matrix least-squares refinement on F^2 converged at $R_F = 0.0464$ and GOF(F^2) = 1.514 for **1**, $R_F = 0.0951$ and GOF(F^2) = 1.615 for **4**, and $R_F = 0.0939$ and GOF(F^2) = 1.403 for **9**. The final difference Fourier maps on each of the structures did not reveal any significant features. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation.

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Supporting Information Available: ORTEP drawings showing the complete atom labeling schemes, cell and crystal packing diagrams, and tables of atomic coordinates, complete bond distances and angles, and anisotropic displacement parameters for complexes **1**, **4**, and **9** (26 pages). Ordering information is given on any current masthead page.

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