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Isodicyclopentadienes and related molecules. 57. Stereocontrolled synthesis of sterically crowded titanocenes of high enantiomeric purity by electrophilic capture of C-silylated ligands with configurational inversion

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of $K[Cp_2Tc(NAr)_3]$ indicates that it is a very symmetrical species, exhibiting a single set of resonances for the imido ligands. The Cp groups also occur as a more simplified set of resonances than would be expected for a fixed $(\eta^1\text{-Cp})_2$ structure. Unlike the room-temperature ^1H NMR spectra of $(\eta^1\text{-Cp})Tc(NAr)_3$, where a single signal for the Cp ligands is observed, the Cp resonances of $K[Cp_2Tc(NAr)_3]$ occur as three separate singlets (295 K; δ 6.44 (1 H), 6.05 (1 H), 5.73 (8 H)). As yet, we cannot explain this pattern. Low-temperature NMR data are similar to those for $(\eta^1\text{-Cp})Tc(NAr)_3$ in that the Cp signals broaden as the temperature is lowered but never separate into a distinguishable pattern. Conversely, raising the temperature to 310 K results in the collapse of the three Cp resonances, into one signal at δ 5.62 (10 H). The potassium in $K[Cp_2Tc(NAr)_3]$ may be exchanged with the PPN cation, and combustion analysis is consistent with formulation as $PPN[Cp_2Tc(NAr)_3]$.[11]

While $(\eta^1\text{-Cp})Tc(NAr)_3$ can be converted to $K[Cp_2Tc(NAr)_3]$ by the action of KCp, the reaction may be reversed by the action of weak acids or protic solvents (Scheme II). Unfortunately, diffractometer-grade crystals of $K[Cp_2Tc(NAr)_3]$ have not yet been obtained.

The work presented here is the first experimental evidence to demonstrate σ-Cp coordination in $CpM(NR)_3$ complexes. It was suggested previously that the cyclopentadienyl ligand in tris(imido)rhenium complexes would be η^1 rather than pentacoordinated, despite several examples of isoelectronic half-sandwich trioxorhenium complexes.[1c] The predicted differences in cyclopentadienyl coordination between the analogous oxo and imido complexes $CpM({=}E)_3$ (M = Tc, Re; E = O, NR) were ascribed to the stronger donor ability of imido over oxo ligands and the marginal ability of the $^{\bullet}ME_3$ fragment to form π bonds.[2,12] While we cannot completely rule out steric interactions forcing η^1 coordination of Cp in $(\eta^1\text{-Cp})Tc(NAr)_3$, examination of space-filling models suggests that there is sufficient space in this complex to allow the Cp ligand to be pentacoordinated.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and a summary of X-ray diffraction data and a ball-and-stick diagram for $(\eta^1\text{-Cp})Tc(NAr)_3$ (12 pages). Ordering information is given on any current masthead page.

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(11) The preparation of $K[Cp_2Tc(NAr)_3]$ is as follows: To a solution of $TcI(NAr)_3$ (100 mg, 0.13 mmol) in THF was added KCp (30 mg, 0.28 mmol). This solution was heated to reflux temperature for 2 min and then cooled to room temperature. The solvent was removed in vacuo and then extracted with benzene (20 mL) and recrystallized with $(TMS)_2O$ to give the product as a dark blue solid (101 mg, 98%). For the purposes of combustion analysis the potassium was exchanged with PPN; however, all other spectral data are quoted for the potassium salt. ^1H NMR (C_6D_6, 295 K): δ 7.03 (s, $C_6H_3Pr^i_2$, 9 H), 6.44 (s, C_5H_5, 1 H), 6.04 (s, C_5H_5, 1 H), 5.73 (s, C_5H_5, 8 H), 3.89 (h, $CHMe_2$, 6 H, ^2J = 6.9 Hz), 1.17 (d, $CHCH_3$, 36 H, ^2J = 6.9 Hz). ^1H NMR (d_8-THF, 310 K): δ 6.90 (m, $C_6H_3Pr^i_2$, 9 H), 5.63 (s, C_5H_5, 10 H), 3.43 (hep, $CHMe_2$, 6 H, ^2J = 6.5 Hz), 0.97 ($CHCH_3$, d, 36 H, ^2J = 6.5 Hz). $^{13}C\{^1H\}$ (D_8-THF, 295 K): δ 140.4 (NC), 124.3 (Ar), 122.4 (Ar), 121.3 (Ar), 104.9 (Cp), 28.9 (CH), 24.0 (CH_3). Anal. Calcd for $C_{82}H_{91}N_4P_2Tc$: C, 76.14; H, 7.09; N, 4.33. Found: C, 75.62; H, 6.59; N, 4.37.

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Stereocontrolled Synthesis of Sterically Crowded Titanocenes of High Enantiomeric Purity by Electrophilic Capture of C-Silylated Ligands with Configurational Inversion[†,1]

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Summary: The complexation of optically active C_1-symmetric annulated cyclopentadienides by $TiCl_4$, $CpTiCl_3$, Cp^*TiCl_3, and related transition-metal halides usually occurs on the less sterically congested π surface. A simple means for inverting this stereoselection to produce the more crowded diastereomer has been developed which proceeds by initial C-silylation (highly stereoselective in favor of the less hindered epimer) and electrophilic capture of the silane with inversion of configuration.

The demand for optically active complexes of the group 4 transition metals has increased significantly over the last several years, in concert with their growing importance in catalytic asymmetric reactions.[3] Full practical exploitation of chiral, C_1-symmetric annulated cyclopentadienide ligands has, however, been limited by their predilection for coordination to a metal atom predominantly or exclusively from a single π surface.[4] This facial selectivity appears

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[†] Dedicated to Professor Harold Shechter on the occasion of his 70th birthday.

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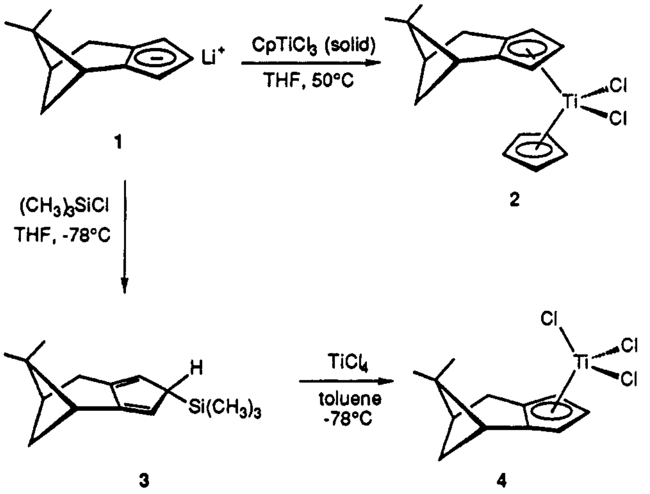
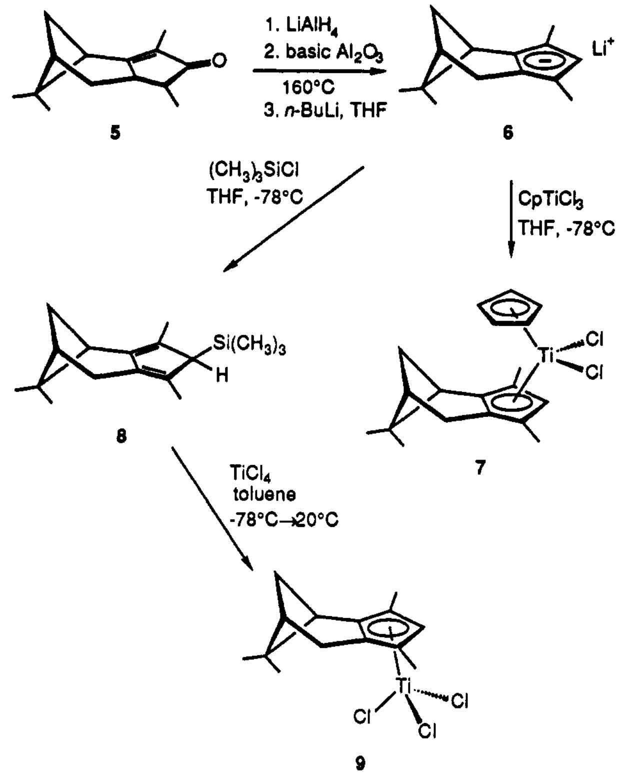
to be controlled by the locus of the lithium counterion and the state of aggregation of the reactive organometallic species.[1,5] When the two surfaces of the cyclopentadienide differ modestly in steric bias, temperature effects suffice to control the direction of complexation.[6] Larger steric imbalances cannot be similarly overridden, and those complexes having the maximum level of nonbonded compression have not routinely been available for study. Presented herein is a simple experimental resolution to this dilemma that takes advantage of the high stereoselectivity of C-silylation in these systems[7] and the strict inversion of configuration[8] that applies to electrophilic condensation of these silanes with titanium chloride reagents.[9]

The most convenient means found for stereocontrolled above-plane complexation of the 1(*R*)-(−)-nopol-derived 1 involves addition of a warm (50 °C) tetrahydrofuran solution of the anion to *solid* CpTiCl$_3$. These conditions provide enantiomerically pure 2 ($[\alpha]^{19}_{D}$ = +817° (c = 0.05, toluene)) in 69% yield after a single recrystallization. Clean stereochemical crossover was realized by first allowing solutions of 1 in cold (−78 °C) tetrahydrofuran to react with chlorotrimethylsilane. Under these conditions, 3 is formed as an 8:1 mixture with its epimer, from which it can be separated chromatographically (71% yield). Proper definition of the newly introduced chiral center in 3 was achieved by Diels–Alder reaction with *N*-phenylmaleimide and independent high-field ^{1}H NMR analysis of the resultant exo and endo adducts. Exposure of 3 to TiCl$_4$ in toluene at −78 °C followed by warming to 25 °C led exclusively to 4 (62%). This reactive brown-black solid exhibits a singlet due to the *syn,endo*-methyl group at δ 0.94,[10] indicating its projection into that region strongly affected by the anisotropy of the titanium atom.[3-6]



For the preparation of 5, (1*R*)-(+)-nopinone (90% ee) was transformed into its morpholine enamine, condensed with 2,4-dibromo-3-pentanone and Fe$_2$(CO)$_9$ in benzene at 60 °C,[11] and exposed to silica gel (88%). Subsequent hydride reduction, dehydration, and metalation provided 6 in high yield. Direct treatment of 6 with CpTiCl$_3$ afforded 7 (*anti-endo*-Me, δ 0.44 (s); *anti-exo*-Me, δ 1.80, d, J = 5.1 Hz) as a red-black solid ($[\alpha]^{20}_{D}$ = −83.3° (c = 0.12, toluene)). In a complementary pair of experiments, 6 was converted to 8 as before (60%) and reacted with TiCl$_4$ in cold toluene. The red-orange 9 so produced was isolated in homogeneous condition after crystallization from toluene (49%, mp 136–138 °C, $[\alpha]^{20}_{D}$ = +26.0° (c = 0.3, toluene)). The upfield methyl resonances for 9 are seen at δ 1.14 (s, syn-endo) and 0.73 (d, J = 9.9 Hz, syn-anti), as expected for the "π-facially inverted" complex.



Further probing of this stereochemical control began with 4-methylthujone (10), as prepared by the condensation of (−)-thujone (62% ee)[12] with formaldehyde, conversion to the tosylate, and hydride reduction according to Brieskorn and Schwack.[13] Palladium(0)-promoted vinylation of its enol triflate[14] gave 11 (69%), which was smoothly transformed into 12 via a Skattebøl rearrangement sequence.[15,16] With the availability of this optically active lithium salt, the opposed influences to its isopropyl substituent and fused cyclopropane ring were manifested upon direct condensation with CpTiCl$_3$ to give predominantly 13 (10:3 mixture with the endo isomer, 63%). The stereochemical character of 13 was easily recognized on the basis of the relatively normal chemical shift of its endo cyclopropyl proton (δ 0.00 in C$_6$D$_6$).

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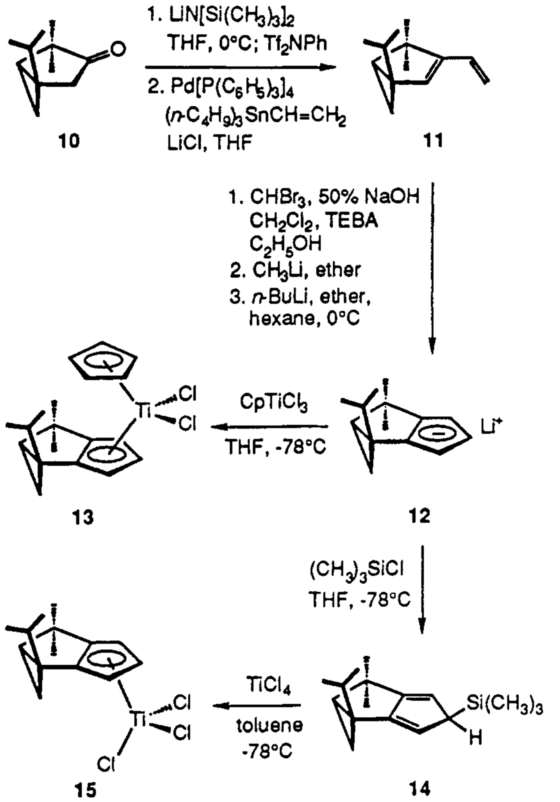

As expected, the silylation of **12** was governed by the same π-facial bias. Admixture of the major silane isomer **14** ($[\alpha]^{20}{}_D = +11.4°$ (c = 1.1, hexane)) with $TiCl_4$ in toluene as before (2 h) with subsequent warming to room temperature (4 h) furnished **15** (70%).[17,18] The powerful deshielding impact of the titanium center in this complex induces a significant downfield shift on the nearby proton of the three-membered ring (δ 0.77).

In summary, this study marks a fundamentally new approach to the preparation from a single precursor of titanocenes that are diastereomeric by virtue of specific π-face complexation. Experiments are in progress to determine the degree to which appreciably enhanced steric compression improves the capacity to function as asymmetric catalysts. The added encumbrance may also provide features more suited to detailed mechanistic clarification.

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[17] As expected, the reactivity of **3**, **8**, and **14** toward more bulky and less electrophilic reagents[9a,c] such as $CpTiCl_3$ and Cp^*TiCl_3 drops off precipitously.

[18] A prototypical procedure follows. A cold (−78 °C) solution of $TiCl_4$ (1.02 g, 5.4 mmol) in toluene (50 mL) was treated slowly with **8** (1.40 g, 5.4 mmol) dissolved in toluene (30 mL) during 30 min. The red mixture was stirred for 1 h at −78 °C and 48 h at room temperature before being concentrated in vacuo. The residue was dissolved in a small quantity of toluene and cooled to −20 °C to provide bright red crystals of **9** (0.90 g, 49%): mp 136–138 °C (toluene); ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (s, 1 H), 3.39 (dd, J = 15.6, 1.9 Hz, 1 H), 3.24 (t, J = 5.1 Hz, 1 H), 2.90 (dd, J = 14.0, 3.6 Hz, 1 H), 2.80 (d, J = 4.9 Hz, 1 H), 2.39 (s, 3 H), 2.36 (s, 3 H), 2.31 (m, 1 H), 1.43 (s, 3 H), 1.14 (s, 3 H), 0.73 (d, J = 9.9 Hz, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 152.3, 139.8, 137.9, 135.5, 124.6, 44.8, 41.0, 40.8, 36.5, 29.6, 29.1, 28.0, 26.7, 16.0 ppm; HRMS m/z ($M^+ - Cl$) calcd for $C_{14}H_{19}Cl_2Ti$ 304.0265, obsd 304.0293; $[\alpha]^{20}{}_D = +26.0°$ (c = 0.3, toluene).

Insertion of Alkynes with Electron-Withdrawing Substituents into a Rhenium–Rhenium Bond. Evidence for an Intramolecular Insertion with a Trans Stereochemistry

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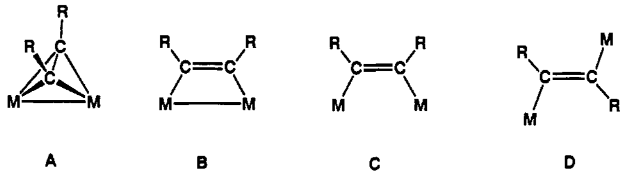
Summary: The reaction of the dirhenium complex $Re_2(CO)_9(NCMe)$ (**1**) with electrophilic alkynes, $R'C{\equiv}CCO_2R$, proceeds by displacement of the NCMe ligand and addition of the alkyne with insertion into the rhenium–rhenium bond to yield the dimetalated olefin complexes $Re(CO)_4[trans\text{-}\mu\text{-}R'C{=}C(CO_2R)]Re(CO)_5$ (R = Me, R′ = H (**2a**), Me (**2b**); R = Et, R′ = CO_2Et (**2c**)) having a trans stereochemistry at the C–C double bond. The carboxylate group is coordinated to one of the rhenium atoms to form a metallacycle. Insensitivity to radical scavengers and the absence of crossover in a reaction of a mixture of labeled and unlabeled reagents indicate that the insertion of the alkyne into the metal–metal bond occurs by an intramolecular process. Crystal data for **2a**: space group $P2_1/n$, a = 6.644 (1) Å, b = 30.005 (8) Å, c = 18.036 (2) Å, β = 96.09 (1)°, Z = 8, 2468 reflections, R = 0.033.

In most polynuclear metal complexes alkyne ligands adopt bridging coordinations and serve as four-electron donors to the metal atoms.[1] In binuclear metal complexes alkynes usually coordinate in the μ-$\perp$ coordination mode A,[2] although there are examples of the μ-$\parallel$ coordination mode B,[3] where the alkyne serves as a two-electron donor. In the absence of a metal–metal bond these complexes are



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