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(.eta.1-Cp)Tc(NAr)3: synthesis and structure

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ized previously[2,4,15] the A_1 mode of 1 is 2.5 cm^{-1} lower in energy. Although small, this difference corroborates the suggestion that the Cd centers of 1 are more electron rich than would be expected for Cd^{2+}.

Hence, the bonding can be formulated as shown in Chart Ib. An appropriately hybridized Cd^+ coordinated to three Lewis bases has a single remaining valence function containing one electron. The $Co(CO)_3$ fragment is isolobal with CH and can form three two-center two-electron bonds to the individual Cd^+ centers. This model assumes no direct Cd–Cd bonding. Note that for a neutral ligand L, LCd^+ is analogous to LAu and the question of direct Cd–Cd bonding in 1 is similar to that posed by compounds containing adjacent LAu fragments.[16]

One of the drawbacks of metal clusters as substituents is their relatively fragile framework and the consequent necessity of working under conditions in which the cluster does not degrade. It is amusing then to note that this drawback is an advantage here; i.e., $(CO)_9Co_3(\mu_3\text{-CCOOH})$ serves not only as a source for the ligands that bridge the Cd–Cd edges but also as a thermal source of the $Co(CO)_3$ metal fragment that caps the Cd_3 triangle.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. W.C. thanks the department for a Reilly Fellowship.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, anisotropic thermal parameters, and fractional coordinates for hydrogen atoms (12 pages). Ordering information is given on any current masthead page.

OM9203035

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[15] Sturgeon, R. L.; Olmstead, M. M.; Schore, N. E. *Organometallics* 1991, *10*, 1649.

[16] Alvarez, S.; Rossell, O.; Seco, M.; Valls, J.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* 1991, *10*, 2309.

(η^1-Cp)Tc(NAr)$_3$: Synthesis and Structure

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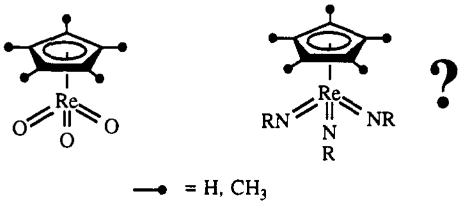
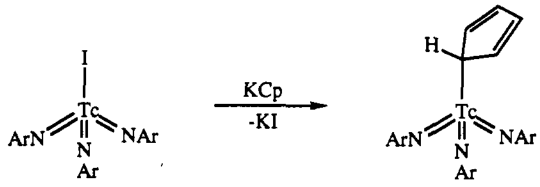
Summary: The reaction of KCp with $TcI(NAr)_3$ (Ar = 2,6-diisopropylphenyl) rapidly forms (η^1-Cp)$Tc(NAr)_3$. A single-crystal X-ray determination confirmed the η^1 nature of the cyclopentadienyl ligand. When $TcI(NAr)_3$ is treated with an excess of KCp, a second cyclopentadienyl group is added to the metal, giving $K[Cp_2Tc(NAr)_3]$.

Synthetic procedures for the synthesis of Cp^*ReO_3 and other derivatives (i.e. $CpReO_3$, $(C_5Me_4Et)ReO_3$, and $(C_5H_4Me)ReO_3$) are well established.[1] This, however, is not the case for the analogous imido complexes. In fact, two separate research groups have reported unsuccessful attempts to form complexes of the type $(C_5R_5)Re(NR)_3$:

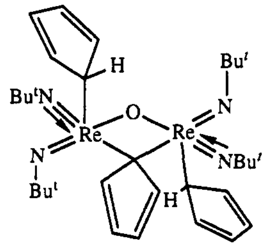


Herrmann et al. reported several attempts to react $(Me_3SiO)Re(NBu^t)_3$ with a variety of cyclopentadienyl (NaCp, TlCp, $CpSnBu_3$) and pentamethylcyclopentadienyl (KCp^*, Cp^*MgCl, $LiCp^*$) sources. All attempts failed to give the desired tris(imido)cyclopentadienylrhenium product, and in most cases no reaction was observed. It was thought that reacting bulky ring-transfer reagents with such a highly sterically hindered $(Me_3SiO)Re(NBu^t)_3$ may be preventing these reactions from taking their desired course.[2] Wilkinson and co-workers, using a less encumbered metal complex, obtained more encouraging results. Treatment of $ReCl(NBu^t)_3$ with NaCp resulted in a facile reaction and the eventual isolation of the oxo-bridged dimer.[3]

Scheme I. Synthesis of (η^1-Cp)Tc(NAr)$_3$[a]



[a] Ar = 2,6-diisopropylphenyl.



When a THF solution of $TcI(NAr)_3$[4] is treated with 1 equiv of KCp, a rapid reaction occurs, forming $CpTc(NAr)_3$ and KI (Scheme I). The ^1H NMR spectrum of the reaction mixture is consistent with the formation of $CpTc(NAr)_3$ in near-quantitative yield.[5] This green complex

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[1] (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 383. (b) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* 1984, *3*, 1313. (c) Herrmann, W. A.; Taillefer, M.; de Méric de Bellefon, C.; Behm, J. *Inorg. Chem.* 1991, *30*, 3247–3248. (d) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* 1987, *6*, 1165–1182. (e) Herrmann, W. A. *J. Organomet. Chem.* 1986, *300*, 111. (f) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* 1991, *113*, 6527–6537.

[2] Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* 1990, *9*, 489–496.

[3] (a) Danopoulos, A. A.; Wilkinson, G.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* 1991, 181–182. (b) Saboonchian, V.; Danopoulos, A. A.; Gutierrez, A.; Wilkinson, G.; Williams, D. J. *Polyhedron* 1991, *10*, 2241–2253.

[4] Bryan, J. C.; Burns, C. J.; Sattelberger, A. P. *Isotope and Nuclear Chemistry Division Annual Report FY 1990*; Report No. LA-12143-PR; National Technical Information Service, U.S. Department of Commerce: Washington, DC, 1990; pp 40–41.

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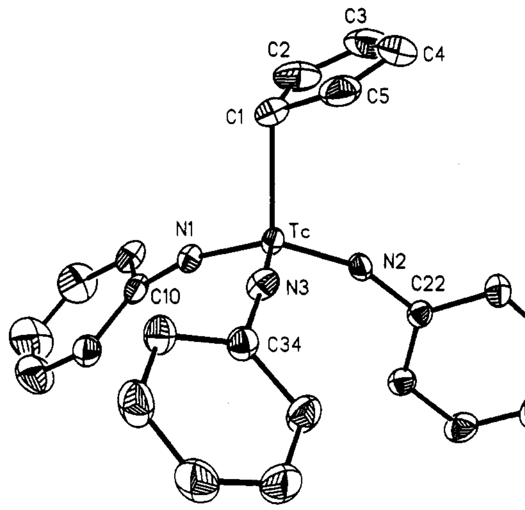
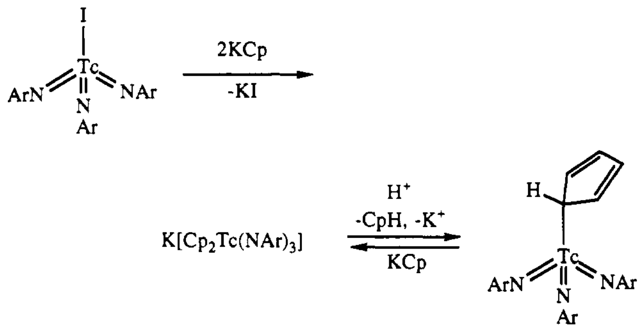


Figure 1. ORTEP drawing of $(\eta^1\text{-Cp})Tc(NAr)_3$ with isopropyl groups omitted. Selected bond lengths (Å) and angles (deg) are as follows: Tc–N(1), 1.753 (2); Tc–N(2), 1.761 (2); Tc–N(3), 1.748 (2); Tc–C(1), 2.156 (3); C(1)–C(2), 1.482 (4); C(2)–C(3), 1.342 (5); C(3)–C(4), 1.431 (4); C(4)–C(5), 1.341 (4); C(5)–C(1), 1.462 (4); N(1)–Tc–N(2), 113.2 (1); N(1)–Tc–N(3), 111.9 (1); N(2)–Tc–N(3), 113.5 (1); N(1)–Tc–C(1), 105.2 (1); N(2)–Tc–C(1), 109.7 (1); N(3)–Tc–C(1), 102.4 (1); Tc–N(1)–C(10), 166.2 (2); Tc–N(2)–C(22), 157.3 (2); Tc–N(3)–C(34), 162.0 (1); Tc–C(1)–C(2), 108.3 (2); Tc–C(1)–C(5), 106.9 (2).

is air- and water-stable and may be purified by column chromatography.

At room temperature the ^{1}H NMR of $CpTc(NAr)_3$ exhibits a single resonance attributed to the Cp hydrogens and one set of resonances for the three imido ligands. As the temperature was reduced, no significant changes were observed in the NMR signals of the imido ligands. However, the Cp resonance (δ 6.70) broadens significantly but never separates into a distinct pattern as the temperature was reduced to 220 K.[6]

Scheme II. Synthesis of $[(\eta^1\text{-Cp})_2Tc(NAr)_3]K$



The η^1 nature of the cyclopentadienyl ligand in $(\eta^1\text{-Cp})Tc(NAr)_3$ was conclusively demonstrated by X-ray crystallographic analysis (Figure 1).[7] Only minor deviations from tetrahedral geometry were observed in the coordination environment of the technetium atom. The cyclopentadienyl carbons are nearly planar, with the maximum deviation being for C(1) at 0.015 Å. The carbon–carbon bonds vary systematically in length around the Cp ring, consistent with a localized cyclopentadiene structure. One point worthy of note is that all of the imido ligands are not structurally equivalent; one deviates significantly from the average parameters of the other two. The two similar imido ligands have Tc–N bond distances of 1.753 (2) Å (Tc–N(1)) and 1.748 (2) Å (Tc–N(3)). The Tc–N(2) bond is significantly longer at 1.761 (2) Å. Also, the Tc–N(2)–C(22) angle is significantly smaller at 157.3 (2)° than either of the Tc–N(1)–C(10) (166.2 (2)°) and Tc–N(3)–C(34) (162.0 (2)°) angles (see Figure 1). This may indicate that the imido ligand containing N(2) is not bound as strongly to technetium as the other two imido ligands.[8]

The rhenium analog of $(\eta^1\text{-Cp})Tc(NAr)_3$, $(\eta^1\text{-Cp})Re(NAr)_3$, is obtained from the treatment of $ReI(NAr)_3$ with 1 equiv of KCp.[9] The reactions of $TcI(NAr)_3$ or $ReI(NAr)_3$ with KCp* give immediate color changes; the products appear to be the result of electron transfer rather than metathesis.[10]

When a excess of KCp is reacted with $TcI(NAr)_3$, an air-sensitive blue complex which can be formulated as $K[Cp_2Tc(NAr)_3]$ is obtained (Scheme II).[11] The ^{1}H NMR

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(5) The preparation of $(\eta^1\text{-Cp})Tc(NAr)_3$ is as follows: To a solution of $TcI(NAr)_3$ (100 mg, 0.13 mmol) in THF (15 mL) was added KCp (15 mg, 0.14 mmol). The mixture was stirred for approximately 1 h, after which the solvent was removed in vacuo. The residue was then extracted with hexamethyldisiloxane ($(Me_3Si)_2O$; 15 mL) and filtered through Celite. Evaporation of the $(Me_3Si)_2O$ gave the product as a green solid (86 mg, 94%). If required, the product can be further purified by column chromatography with silica gel, using chloroform as an eluent. ^{1}H NMR (C_6D_6, 295 K): δ 6.97 (s, $C_6H_3Pr^i_2$, 9 H), 6.70 (s, C_5H_5, 5 H), 3.59 (hep, $CHMe_2$, 6 H, ^3J = 7.2 Hz), 1.08 (d, $CHCH_3$, 36 H, ^3J = 7.2 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ 141.3 (NC), 127.1 (Ar), 122.7 (Ar), 122.7 (Ar), 113.2 (Cp), 28.7 (CH), 23.7 (CH_3). Anal. Calcd for $C_{41}H_{56}N_3Tc$: C, 71.39, H, 8.18, N, 6.09. Found: C, 70.70; H, 7.97; N, 5.89.

(6) This has been observed for other η^1-Cp complexes. For example: (a) Galakhov, M. V.; Bakhmutov, V. I.; Barinov, I. V. *Magn. Reson. Chem.* **1991**, *29*, 506–508. (b) Bitterwolf, T. E.; Gambaro, A.; Gottardi, F.; Valle, G. *Organometallics* **1991**, *10*, 1416–1420. (c) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 751–760. (d) Bakar, W. A.; Davidson, J. L.; Lindsell, W. E.; McCullough, K. J. *J. Chem. Soc., Dalton Trans.* **1990**, 61–71. (e) Fildes, M. J.; Knox, Selby A. R.; Orpen, A. G.; Turner, M. L.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1680–1682. (f) Wright, M. E.; Hoover, J. F.; Glass, R. S.; Day, V. W. *J. Organomet. Chem.* **1989**, *364*, 373–379. (g) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105–119. (h) Adams, H.; Bailey, N. A.; Bannister, C.; Faers, M. A.; Fedorko, P.; Osborn, V. A.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 341–348. (i) Lawless, G.; McNally, G.; Manning, A. R.; Cunningham, D.; McArdle, P. *Polyhedron* **1986**, *5*, 1741–1746. (j) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983–996. (k) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *Aust. J. Chem.* **1985**, *38*, 273–291. (l) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250–255. (m) Wright, M. E.; Nelson, G. O.; Glass, R. S. *Organometallics* **1985**, *4*, 245–250. (n) Priester, W.; Rosenblum, M.; Samuels, S. B. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 525–537. (o) Fabian, B. D.; Labinger, J. A. *J. Organomet. Chem.* **1980**, *204*, 387–392. (p) Howell, J. A. S.; Rowan, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 503–510. (q) Campbell, A. J.; Fyfe, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 8387–8391. (r) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 7523–7524.

(7) Crystal data for $(\eta^1\text{-Cp})Tc(NAr)_3$: dark green, rhombahedral, 0.55 × 0.59 × 0.62 mm; M_r = 689.9; space group $P2_1/n$; a = 12.843 (7) Å; b = 15.762 (7) Å; c = 19.198 (7) Å; β = 106.11 (4)°; V = 3734 (3) Å^3; Z = 4; d_{calc} = 1.226 g/cm^3; Siemens R3m/V diffractometer; 203 K; Mo Kα radiation (λ = 0.710 73 Å); scan method 2θ–θ; data collection range 4.0–55.0°; total number of data measured 9195; number of independent reflections 8614 (R_{int} = 3.70%); number of observed reflections 6831 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of R = 0.0303 and R_w = 0.0417; GOF = 1.04. From final difference Fourier maps, residual electron densities of 0.63 and −0.58 e/Å^3 were present.

(8) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(9) Spectral data for $ReI(NAr)_3$ are as follows. ^{1}H NMR (C_6D_6, 295 K): δ 7.04 (m, $C_6H_3Pr^i_2$, 9 H), 3.61 (hep, $CHMe_2$, 6 H, ^3J = 6.9 Hz), 1.10 ($CHCH_3$, d, 36 H, ^3J = 6.9 Hz). Anal. Calcd for $C_{36}H_{51}N_3IRe$: C, 51.54; H, 6.13; N, 5.01. Found: C, 51.08; H, 6.39; N, 4.86. Spectral data for $(\eta^1\text{-Cp})Re(NAr)_3$ are as follows. ^{1}H NMR (CD_2Cl_2, 295 K): δ 7.08 (m, $C_6H_3Pr^i_2$, 9 H), 6.45 (s, C_5H_5, 5 H), 3.39 (hep, $CHMe_2$, 6 H, ^3J = 6.8 Hz), 1.04 ($CHCH_3$, d, 36 H, ^3J = 6.8 Hz). Anal. Calcd for $C_{41}H_{56}N_3Re$: C, 63.37; H, 7.26; N, 5.41. Found: C, 63.59; H, 6.64; N, 5.18.

(10) Reaction mixtures contained significant amounts of pentamethylcyclopentadiene dimer: Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141–152. Pentamethylcyclopentadiene dimer has been observed as the product of reactions resulting from electron transfer rather than metathesis: Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882–1993.

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.

Acknowledgment. This work is supported by the Laboratory Directed Research and Development program at Los Alamos National Laboratory. We also thank James M. Mayer for helpful discussions and Paul H. Smith for assistance with space-filling models.

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.

[12] Szyperski, T.; Schwerdtfeger, P. *Angew. Chem.* **1989,** *101,* 1271; *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1288.

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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Received July 24, 1992

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.

[1] Isodicyclopentadienes and Related Molecules. 57. Part 56: Bauer, W.; O'Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991,** *113,* 1093.

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