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Synthesis, Structural Characterization, and Reactivity of Novel Zirconium(IV) Complexes Containing the Tropidinyl Ligand**

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Cyclopentadienyl (Cp) and bis(cyclopentadienyl) complexes have played an enormous role in the development of fundamental and practical organometallic chemistry.^[1] The use of metallocene catalysts for Ziegler–Natta polymerization of alkenes,^[2] one of the most important recent advances in the latter area, has generated interest in the synthesis of ligands that are isoelectronic with Cp but might confer different properties (e. g., different rates or selectivities) on the derived metal complexes.

The conception of the Cp group as a delocalized three-electron anionic allyl ligand combined with a two-electron neutral alkene ligand raises the possibility of combining the allyl group with other two-electron donors to give complexes that would be isoelectronic with, but less symmetrical than, Cp complexes. However, allyl complexes of early transition metals often have low thermal stability.^[3, 4] We therefore sought a system in which an anionic allyl ligand is connected by two bridges to a neutral two-electron donor,^[5] in the hope that this would make the derived organometallic materials more robust. We now report the execution of this idea in the synthesis of complexes derived from the readily available bicyclic molecule tropidine (1-H, Scheme 1). The advantages of 1 are that 1) the ligand derived



Scheme 1. Synthesis of 2 from tropine.

from it has separate 2σ - and 4π -electron donor sites, 2) the presence of the two-carbon bridge helps to localize the allyl functionality in a specific part of the molecule and prevents loss of the ligand by β -hydride elimination (Bredt's rule),^[6-8] and 3) the ligand lacks groups that allow easy deactivation by cyclometallation (intramolecular C-H activation). To our knowledge, this is the first report of coordination of this ligand to a transition metal center.

Tropidine (1-H) can be readily obtained by dehydration of tropine under strongly acidic conditions (Scheme 1).^[9] The allylic position was deprotonated by treating the bicyclic compound with a strong base such as *tert*-butyllithium at low temperature.^[10] Subsequent addition of trimethyltin chloride to the lithium salt of the tropidinyl (trop) anion (1-Li) yields the stannylated compound 1-SnMe₃ in good yield. Addition of two equivalents of 1-SnMe₃ to a solution of $ZrCl_4 \cdot 2THF$ in dichloromethane gave the desired disubstituted zirconium complex [(trop)₂ZrCl₂] (2) in 59% yield (Scheme 1). Other methods involving reaction of 1-H or the corresponding silylated derivative with Zr^{IV} precursors such as [Zr(NMe₂)₄], [Zr(OtBu)₄], or [Zr(CH₂Ph)₄] did not give the expected product, even at elevated temperature. Similarly, addition of the trop anion to Zr^{IV} starting materials led only to mixtures of unidentified complexes.

The ¹H NMR spectrum of **2** in CD_2Cl_2 shows a very simple pattern, which suggests that the complex may have C_2 symmetry. The solid-state structure was solved on a single crystal by direct methods^[11] and expanded with Fourier techniques^[12] (Figure 1).^[13] Surprisingly, the complex has a C_1 -symmetric

structure in which the trop ligands are rotated by 76.86° with respect to one other. The trop ligand labeled C1, C2, C3, C8, N1 is bound symmetrically to the metal center. In contrast, the other trop ligand is unsymmetrically bound to zirconium, as evidenced by different bond lengths for Zr1-C9 and Zr1-C11. The Cl1-Zr1-Cl2 bond angle of 100.89(3)° is slightly more obtuse than the corresponding angle of 97.1° $[Cp_2ZrCl_2]$.^[14] The in Zr1-Cl1 and Zr1-Cl2 bond lengths of 2.5051(8) and 2.5089(8) Å, respectively, are somewhat longer than that of 2.44 Å zirconocene dichloin ride.[14]



Figure 1. ORTEP plot of **2**. Selected bond lengths [Å] and angle [°]: Zr1-Cl1 2.5051(8), Zr1-Cl2 2.5089(8), Zr1-Cl 2.537(3), Zr1-C2 2.518(3), Zr1-C3 2.523(3), Zr1-C9 2.493(3), Zr1-C10 2.595(3), Zr1-C11 2.595(3), Zr1-N1 2.353(3), Zr1-N2 2.369(3); Cl1-Zr1-Cl2 100.89(3).

The discrepancy between the solid-state structure and the observed ¹H NMR spectrum led us to investigate the fluxional behavior of **2**. A series of variable-temperature ¹H NMR (300 MHz) spectra were collected. These revealed strongly fluxional behavior, which resolved into a spectrum exhibiting nonequivalent trop ligands at -90 °C. The spectrum at -90 °C is consistent with the X-ray structure. The decoalescence of the central allylic protons at -48 °C indicates a free energy barrier for rotation of the trop ligands of 19 kcalmol⁻¹.

We carried out some preliminary reactivity studies on 2. Addition of two equivalents of methyllithium gave the yellow dimethylzirconium complex $[(trop)_2 ZrMe_2]$ (3, Scheme 2). As in the dichloride 2, a simple pattern was observed in the room-temperature ¹H NMR spectrum of 3. In contrast to 2, however, no decoalescence of the signals was observed when 3 was cooled to the freezing point of dichloromethane.

Complex 3 was characterized by X-ray crystallography.^[13] As in 2, the trop ligands are related by no symmetry element, but are rotated with respect to one another by 87.71° , more than 10° greater than in 2. We are unsure why the energy barrier for rotation of the trop ligands in 3 is substantially lower than that in the corresponding dichloride 2. The Zr-trop bonds are also longer than those in 2. The Zr-Me bond lengths and the Me-Zr-

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Scheme 2. Ligand-substitution reactions of 2.

Me bond angle are 2.316(2) and 2.315(2) Å, and 95.75(9)°. These values are similar to those reported for dimethylzirconocene [2.280(5) Å and 2.275(5) Å, 95.6(12)°].^[15] Complex **3** was unstable when placed under prolonged dynamic vacuum, and an uncharacterized white powder formed.

Addition of two equivalents of benzylmagnesium chloride to 2 gave the expected bis(benzyl)zirconium derivative 4. The NMR spectrum shows apparent C_2 symmetry, but a recently determined X-ray structure of $4^{[13]}$ shows nonequivalent trop ligands analogous to those in 2 and 3. When only one equivalent of methyllithium or benzylmagnesium chloride was added to 2, a 1:1 mixture of 2 and the corresponding bis(alkyl)zirconium derivative was obtained.

Protonolysis of 3 with *tert*-butyl alcohol at room temperature gave the yellow complex 5 in quantitative yield. Treatment of 3 with *tert*-butylamine did not yield the corresponding *tert*-butylamido complex. Heating the reaction mixture to 77 °C led to decomposition of 3 prior to formation of the desired product 7. The latter could, however, be prepared in 95% purity (92% yield) by protonation of 3 with one equivalent of trifluoromethanesulfonic acid to give 6 and subsequent addition of one equivalent of LiNH*t*Bu. Similarly, 8 and 5 can be synthesized by addition of the corresponding nucleophile to 6. As was observed

 $[(trop)_{2}Zr(Me)O/Bu] = 5$ $[(trop)_{2}Zr(Me)OSO_{2}CF_{3}] = 6$ $[(trop)_{2}Zr(Me)NH/Bu] = 7$ $[(trop)_{2}Zr(Me)NH-4-C_{8}H_{4}Me] = 8$

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for 3, placing 8 under vacuum for one hour led to decomposition to an uncharacterized white powder.

Preliminary experiments were carried out on the use of $[(trop)_2 Zr X_2]$ complexes as polymerization catalysts. Addition of a large excess of methylaluminoxane (MAO) to a solution of 2 in toluene under an ethylene atmosphere gave a purple solution that was active for the polymerization of this alkene. The measured polyethylene productivity of 17 kg mol⁻¹ h⁻¹, as determined by comparative studies, was roughly 14 times slower than ethylene polymerization by $[Cp_2 Zr Cl_2]/MAO$ under the same conditions.^[16] Further studies will be required to determine whether the trop ligands remain attached to the metal during polymerization, although the fact that [(trop)_2 Zr Me_2] retains these ligands on treatment with trifluoromethylsulfonic acid suggests that the trop—Zr bond is robust.

Straightforward synthetic routes can be devised for attaching substituents to the trop rings and for linking two trop ligands together to produce *ansa* analogues of the materials described here. Such studies are under way, as is the development of methods for attaching trop ligands to other metal centers.

Experimental Section

Synthesis and analytical data on complexes 1-SnMe₃, 2, 3, and 4 are given here. Data on complexes 5-8 will be provided elsewhere.

Safety note: Because of the high toxicity of tin compounds and the high neurological activity of tropidine derivatives, all work must be performed in a well-ventilated working area and skin contact prevented with protective clothing and gloves.

1-SnMe3: tert-Butyllithium (1.7 M in pentane, 52 mL, 88 mmol) was added dropwise over 15 min to tropine [9] (10.7 g, 88.9 mmol) in pentane (500 mL) at -100 °C. Deprotonation was allowed to proceed at $-80\,^\circ\mathrm{C}$ for 3 d. The resulting mixture was then cooled to -100 °C, and trimethyltin chloride (1 M in hexane, 104 mL, 104 mmol) was added over 15 min. The pale yellow solution immediately turned white with concomitant precipitation of white solid. The flask was warmed to room temperature over 1 h, and the mixture stirred for an additional 30 min. Water (100 mL) was carefully added, and the organic materials were extracted with pentane. The combined organic extracts were washed with brine and dried over sodium sulfate. The solvents were removed under water aspirator pressure, and the residue was distilled under vacuum (3 mtorr) at 50 °C to give 11.2 g (45%) of 1-SnMe₃. ¹H NMR (C_6D_6): $\delta = 5.52$ (m, 2 H, olefinic), 3.13 (m, 1 H, bridgehead), 3.04 (br s, 1 H, bridgehead), 2.42 (s, 4 H, NMe and CHSnMe₃), 2.07 (m, 2 H, CH₂), 1.81 (m, 1H, CH₂), 1.46 (m, 1H, CH₂), 0.06 (s, 9H, SnMe₃; further split by 8.7 and 7.7% of ¹¹⁹Sn and ¹¹⁷Sn, respectively; J = 25.5 Hz); ¹³C{¹H} NMR (C₆D₆): $\delta = 127.3$, 127.1 (olefinic), 60.1, 58.7 (bridgehead), 36.7 (C7 or C8), 34.8 (NMe), 33.1 (C7 or C8), 30.5 (CHSnMe₃), -10.1 (SnMe₃); HRMS: m/z calcd for $C_{11}H_{21}N_1Sn$: 287.0696; found: 287.0702.

2: A Schlenk flask was charged with a solution of $ZrCl_4 \cdot 2$ THF (758 mg, 2.01 mmol) in dichloromethane (25 mL). 1-SnMe₃ (1.16 g, 4.02 mmol) was added over 5 min with stirring. The solution immediately turned orange and was stirred for 4 d at room temperature. The reaction mixture was filtered, and the solid washed with dichloromethane. The volatile materials were removed in vacuo, and the residue was washed thoroughly with pentane and then extracted with toluene. The solvent was removed in vacuo to give 478 mg (59%) of an analytically pure, fine orange powder. ¹H NMR (CD₂Cl₂): $\delta = 5.72$ (dd, J = 7 Hz, 2H, central allylic), 4.31 (d, J = 7 Hz, 2H, terminal allylic), 4.29 (d, J = 7 Hz, 2H, terminal allylic), 3.73 (br s, 4H, bridgehead), 2.48 (s, 6H, NMe), 2.23 (s, 8H, CH₂); ¹H NMR (C₆D₆): $\delta = 5.38$ (dd, J = 7.3 Hz, 2H, central allylic), 4.26 (br s, 4H, terminal allylic), 3.54 (br s, 4H, bridgehead), 2.29 (s, 6H. NMe), 1.84 (s, 4H, CH₂), 1.68 (m, 4H, CH₂); ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 132.0$ (C3) 87.6 (C2 and C4), 67.0 (C1 and C5), 41.2 (NMe), 38.9 (CH₂); elemental analysis calcd for C₁₅₆H₂₄N₂Cl₂Zr₁: C 47.28, H 5.85, N 6.60; HRMS: m/z calcd: 404.0364; found: 404.0361.

3: Complex 2 (118 mg, 0.290 mmol) was dissolved in 10 mL of THF and cooled to -30 °C. Methyllithium (1.4 m in ether, 414 mL, 0.580 mmol) was added, and the reaction mixture stirred at room temperature for an additional 3.5 h. The solvent was evaporated under reduced pressure, and the residue extracted with pentane. The combined pentane extracts were filtered. The filtrate was recovered, and the volatile components were removed in vacuo to yield 94.6 mg (89%) of analytically pure, yellow solid. ¹H NMR (C₆D₆): $\delta = 4.86$ (dd, J = 7.4 Hz, 2H, central allylic), 3.87 (d, J = 7.3 Hz, 2H, terminal allylic), 3.86 (d, J = 7.4 Hz, 2H, central allylic), 3.31 (m, 4H, bridgehead), 2.12 (m, 4H, CH₂), 2.02 (s. 6H, NMe). 1.90 (m, 4H, CH₂), 0.22 (s. 6H, ZrMe₂); ¹H NMR (CD₂Cl₂): $\delta = 4.85$ (dd, J = 7.2 Hz, 2H, central allylic), 3.87 (d, J = 7.2 Hz, terminal allylic), 3.51 (br s, 4H, bridgehead), 2.30 (s. 6H, NMe). 2.23 (s. 8H, CH₂), -0.30 (s. 6H, ZrMe₂); ¹³C₁⁺H} NMR (C₆D₆): $\delta = 126.3$ (central allylic), 80.4 (terminal allylic), 66.8 (bridgehead), 40.4 (NMe), 39.9 (CH₂), 25.8 (ZrMe₂); ¹³C₁⁺H} NMR (CD₂Cl₂): $\delta = 149.7$ (central allylic),

103.9 (terminal allylic), 90.1 (bridgehead), 63.9 (NMe), 63.2 (CH₂), 47.6 (ZrMe₂); elemental analysis calcd for $C_{18}H_{30}N_2Zr_1$: C 59.12, H 8.27, N 7.66; found: C 59.43, H 8.38, N 7.60; LRMS (EI): *m/z* calcd: 364; found: 364.

4: Complex 2 (103 mg, 0.254 mmol) was dissolved in 10 mL THF and cooled to -30 °C. Benzylmagnesium chloride (1 M in ether, 481 mL, 0.481 mmol) was added, and the solution stirred at room temperature for 2 h. The solvents were removed in vacuo. Complex 4 was recovered by extraction of the residue with toluene. The volatile materials were removed to give 110 mg (88%) of an orange solid. Analytic cally pure crystals of 4 can be obtained by vapor diffusion of pentane into a toluene solution of this solid at -30 °C. ¹H NMR (C_6D_6): $\delta = 7.27$ (t, J = 7.7 Hz, 4H, Ar), 7.12 (t, J = 7.7 Hz, 4H, Ar), 6.90 (t, J = 7.2 Hz, 2H, Ar), 5.14 (dd, J = 7.4 Hz, 2H, central allylic), 3.80 (d, J = 7.3 Hz, 2H, terminal allylic), 3.78 (d, J = 7.3 Hz, 2H, terminal allylic), 1.72 (s, 8 H, CH₂); ¹³C{¹H} NMR (C_6D_6): $\delta = 155.8$ (C_{ipso}), 128.9 (central allylic), 128.0 (Ar), 125.7 (Ar), 119.4 (C_{para}), 83.8 (terminal analysis calcd for C₃₀H₃₈N₂Zr: C 69.58, H 7.40, N 5.41; found: C 69.56, H 7.60, N 5.21.

Polymerization of C_2H_4 by 2 and MAO: A Schlenk flask was charged with 2 (5.3 mg, 13 mmol) and 8 mL toluene and placed under 1 atm ethylene. MAO (Akzo, type 4; 3.4 mL, 13 mmol) was added over 1 min at room temperature. The yellow solution immediately turned dark orange, then blue and violet. The color vanished within 15–20 min. The solution was stirred under 1 atm ethylene for 45 min, and then the polymerization was stopped by careful addition of an acidified methanol solution (5% HCl). The mixture was filtered, and the polymer thoroughly dried in vacuo. Yield: 102 mg (17 kgmol⁻¹h⁻¹). Similar conditions were used for the control experiment with Cp₂ZrCl₂ (240 kgmol⁻¹h⁻¹).

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- [13] X-ray quality crystals of 2 were obtained by slow diffusion of pentane into a solution of the complex in toluene at -30 °C. The structure was solved by direct methods with a full matrix least-squares refinement. Details of the X-ray structures of 3 and 4 will be reported in a full paper. Crystal data for 2: C₁₆H₂₄C₁₂N₂Zr. Orange plate-like crystals (0.08 × 0.14 × 0.35 mm), monoclinic, space group P2₁/n (no. 14), a = 7.0931(2), b = 18.2744(2), c = 12.8139(3) Å; β = 85.777(1)°, V = 1652.53(5) Å³. Number of observed reflections [I > 3.00 σ(I)] 2193; 190 variables; R = 0.028, R_w = 0.035, R_{stt} = 0.042, GOF = 1.33. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100489. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code + (1223) 336-033; e-mail: deposit@chemerys.cam.ac.uk).
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High La^{III} Affinity of a Bis(spirobenzopyran) Azacrown Ether and Photoinduced Switching of its Ion Selectivity between Multivalent and Monovalent Metal Ions**

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The photochromicity of spirobenzopyran derivatives is due to photoisomerization between their electrically neutral spiropyran and zwitterionic merocyanine forms.^[1] The photochromism can often be used for controlling physical properties.^[2] We are interested in macrocyclic ligands that can switch their metal ion complexing ability and/or their ion selectivity photochemically, as well as their application in materials science and analytical chemistry. We therefore designed 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran derivatives with a crown ether moiety at the 8'-position, in which the phenolate oxygen atom of the merocyanine form plays an important role in metal ion complexation by forming a six-membered ring chelate with a nitrogen atom of the azacrown ether.^[3] The spirobenzopyran azacrown ethers can undergo photochemical switching upon complexing monovalent metal ions, and have been successfully applied in photoresponsive ion-conducting systems.[4]

Recently the crown ether derivative 1, which has two spirobenzopyran moieties, was designed for photocontrol of the complexation of divalent metal ions.^[5] In our studies, we found that, even in the dark, 1 binds multivalent metal ions much more strongly than its corresponding parent azacrown ether 2 (Scheme 1). Here we report the remarkably high affinity of 1 for La^{3+} and the photochemical switching of its ion selectivity between trivalent and monovalent metal ions.

Absorption spectra of solutions containing equimolar amounts of 1 and a metal ion in acetonitrile recorded in the dark showed a significant peak between 500 and 600 nm, which were assigned to the merocyanine form of the photochromic moiety; isomerization into this form was induced by complexation of the cation by the crown ether moiety. In general, the merocyanine absorption was much more intense for mulitivalent metal ions such as Ca^{2+} and La^{3+} than for monovalent ions such as Na^+ and K^+ . This suggests a higher affinity of 1 for multivalent metal ions than for monovalent ones. Clear evidence for this was given by ESI mass spectrometry. Figure 1 shows a mass spectrum of 1 and 2 in acetonitrile in the presence of the nitrates of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cd^{2+} , Pb^{2+} , La^{3+} , and Eu^{3+} . With 2, medium-intensity peaks were observed for the Na^+ and K^+ complexes and a very small peak was seen for the Ca^{2+}

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