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Synthesis and Structure of a C_2-Symmetric, Doubly Bridged *ansa*-Titanocene Complex

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A chiral, doubly bridged *ansa*-titanocene complex with C_2 symmetry has been synthesized in four steps from bicyclo[3.3.1]nonane-2,6-dione. The design of the complex precludes the formation of *meso* or C_1 diastereomers or conformers.

There continues to be a great deal of interest in the synthesis of chiral group 4 *ansa*-metallocene complexes.[1] The interest stems originally from their application as precatalysts for the isotactic polymerization of propylene,[2] but their potential as reagents for organic synthesis has become increasingly recognized.[1,3−5] The complexes that have seen the greatest amount of study for both purposes are derivatives of compounds **1** and **2** (Figure 1),[6] which were first synthesized by Brintzinger.[6a,c] Work in our laboratories has established that certain derivatives of enantiopure **1-Ti** and **1-Zr** may be used for the catalytic asymmetric hydrogenation of imines[3a] and for the synthesis of enantiopure allylic amines,[3b] respectively, while Collins has used other derivatives to effect the enantioselective allylation of aldehydes[4a] and asymmetric Diels−Alder reactions,[4b] respectively. Complex **1-Zr** has also seen use in the enantioselective hydrogenation and oligomerization of olefins under Ziegler−Natta polymerization conditions.[5]

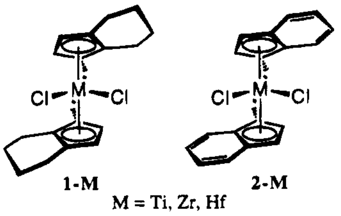

Figure 1.

Despite these successes, a number of drawbacks have until now limited the further application of complexes **1** to asymmetric synthesis. The procedures for the synthesis of **1**, while very short and inexpensive, are difficult to scale up, and the complexation steps can be capricious.[6] Also, the synthesis of analogs of **1** with systematically varying electronic and steric properties has yet to be accomplished.[7] The compounds are usually synthesized in racemic form as a mixture of *rac* and *meso* diastereomers, and the *rac* diastereomer must be separated and resolved.[6] The resolution is accomplished kinetically using 1,1′-bi-2-naphthol, but, in the case of **1-Ti**, unreacted, enantioenriched starting material racemizes upon chromatography,[4b] while, in the case of **1-Zr**, it is lost completely.[3b] Last, the stereolability[6a,b] of **1-Ti** gives cause to worry about the possibility of racemization of the metal complex in the course of reactions catalyzed by it.[3a,8]

Various research groups have designed and synthesized complexes that retain the rigid C_2 symmetry and highly stereodifferentiated reactive sites of **1** and **2** and that also offer solutions to some of these problems. One approach to the resolution problems has been to replace the ethylene backbone of **1** and **2** with a stereogenic spacer while retaining the bis(1-indenyl) framework. Complexes **3-6** represent this approach (Figure 2).[9] Unfortunately, complexes **3**, **4**, and **5a** lack C_2 symmetry in the solid state and/or in solution on the NMR time scale, probably because of the long bridges,[10] while complex **5b** is obtained as the C_1 (i.e., pseudo-*meso*) diastereomer, and complex **6** is obtained as a mixture of diastereomers. A stereogenic bridge is also retained in ligands **7**, with the indenyl groups replaced with the more synthetically flexible 3-methylcyclopentadienyl groups, but unfortunately complexation of the ligands proceeds in a nondiastereoselective fashion.[11] In an important new development, groups led by Halterman

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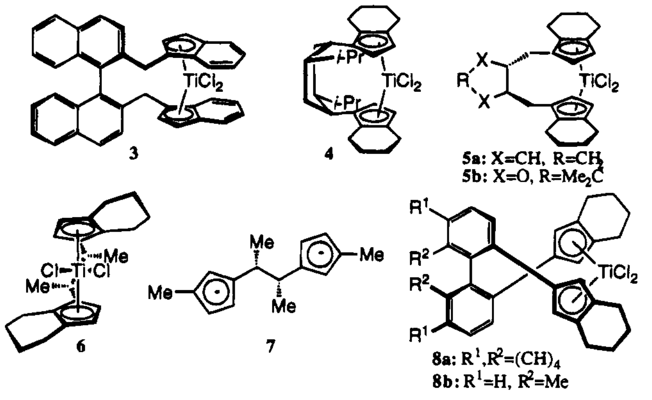


Figure 2.

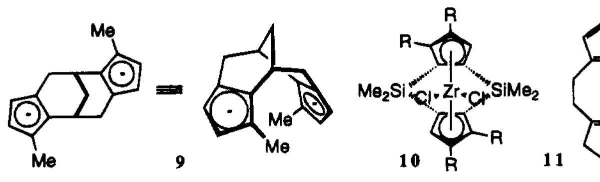
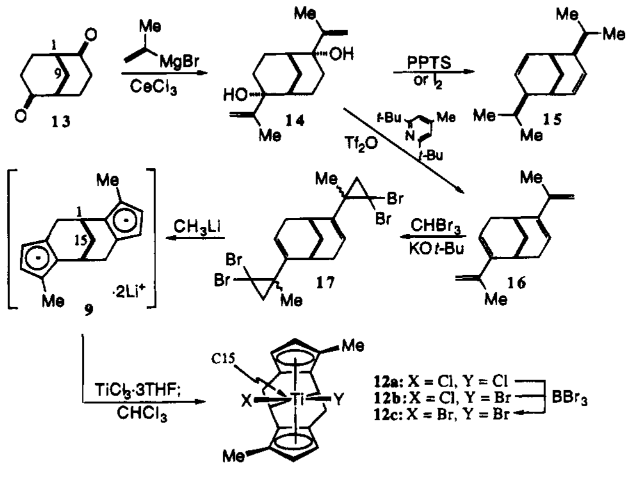


Figure 3.

and Bosnich have independently synthesized the enantiopure, C_2-symmetric complex **8a**, in which the ligand consists of a stereogenic bridge linking two 2-indenyl groups, which have chemically equivalent faces, so that only one diastereomer is formed upon complexation.[12a,b] Bosnich has also synthesized the related complex **8b**, and similar biphenyl-bridged complexes have been synthesized independently by both Bosnich and Brintzinger.[12b,c] With respect to the synthetic flexibility problem, Brintzinger has synthesized a series of analogous complexes in several systems and tested them for their polymerization activity, but these are usually obtained as *rac-meso* mixtures which would have to be separated and resolved to be of use in organic synthesis.[13]

We considered that the possible problem associated with the stereolability of enantiopure **1-Ti** and its derivatives might be solved if we were to design a chiral complex with a ligand in which the two cyclopentadienyl groups were doubly bridged. We were certain that the double bridge would cause the metalation of the ligand to proceed diastereoselectively, solving another common problem in the synthesis of *ansa*-metallocene complexes. In our new ligand, we wanted to preserve the C_2 symmetry and the 1,2,3-substitution pattern on the cyclopentadienyl rings that had proven so successful in complexes **1**; at the same time, we desired that this ligand be chiral, not prochiral, and that it could be resolved *before* complexation to the metal was accomplished. It seemed that the doubly bridged C_2 ligand **9** (Figure 3) would suit our purposes. After the work described herein was completed, other groups disclosed studies in which doubly bridged ligands also figured: Brintzinger recently published the synthesis of complexes **10**, which feature two dimethyl silylene bridges,[14] and McLaughlin described the synthesis of the D_{2h} ligand, **11**, whose resemblance to **9** is clear (Figure 3).[15]

Scheme 1



Our synthesis of the racemic titanium complex, **12**, of ligand **9** is shown in Scheme 1. The synthesis began with the known chiral compound 2,6-bicyclo[3.3.1]nonanedione, **13**.[16] Annulation of the cyclopentadienyl groups onto the bicyclo[3.3.1]nonane skeleton was accomplished using the Skattebøl strategy developed by Paquette[17] and recently utilized by Nantz.[11] Addition of 2 equiv of isopropenylmagnesium bromide to **13** (as the racemate) proceeded in the presence[18] of $CeCl_3$ to give diol **14** as a single diastereomer in 82% yield after recrystallization. Acid-catalyzed dehydration of **14** with various catalysts caused double bond migration to occur after loss of H_2O to give the undesired tetraene **15**, but 2 equiv of trifluoromethanesulfonic anhydride and 4 equiv of 2,6-di-*tert*-butyl-4-methylpyridine gave the desired tetraene **16** as an unstable oil in 65% yield. Dibromocarbene addition to **16** proceeded uneventfully to give the unstable tetrabromide **17** in 86% yield as a mixture of diastereomers. Finally, a double Skattebøl rearrangement[19] was effected by addition of **17** to an excess of methyllithium; the reaction mixture, which presumably contained **9**, was then immediately treated with $TiCl_3{\cdot}3THF$ followed by $CHCl_3$, to give a 1:3:2 (by ^1H NMR) mixture of complexes **12a–c**, which differed only in the halides, in 18% yield. Halide metathesis using BBr_3 gave pure **12c** in 82% yield after recrystallization from toluene. To our disappointment, treatment of the crude solution of **9** with $ZrCl_4{\cdot}2THF$ or $HfCl_4{\cdot}2THF$ failed to give any identifiable products.

Complex **12c** crystallized in space group $I\bar{4}2d$ as discrete molecules which pleasingly possessed crystallographically imposed C_2 symmetry, with the Ti atom and C15 lying on the axis. Two perspectives on the complex are shown in Figure 4. As can be seen, the

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(12) (a) Halterman, R. L.; Ramsey, T. M. *Organometallics* **1993**, *12*, 2879. (b) Ellis, W. W.; Hollis, T. K.; Odenkirk, W.; Whelan, J.; Ostrander, R.; Rheingold, A. L.; Bosnich, B. *Organometallics* **1993**, *12*, 4391. (c) Huttenloch, M. E.; Diebold, J.; Rief, U.; Brintzinger, H. H.; Gilbert, A. M.; Katz, T. J. *Organometallics* **1992**, *11*, 3600.

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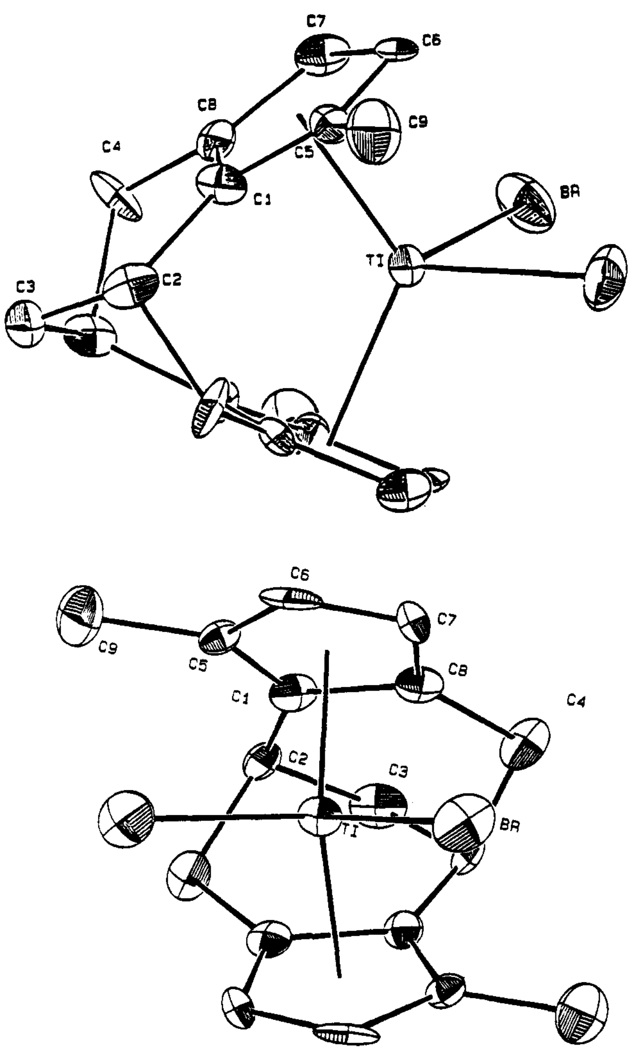

Figure 4. ORTEP views of **12c**. Selected bond distances (Å) and angles (deg) are as follows: Br—Ti, 2.506(3); Ti—C(1), 2.39(1); Ti—C(5), 2.45(1); Ti—C(6), 2.39(1); Ti—C(7), 2.36(2); Ti—C(8), 2.31(1); Br—Ti—Br, 95.4(1); C(1)—C(2)—C(3), 111(1); C(1)—C(2)—C(4), 108(1); C(2)—C(3)—C(2), 109(2).

substituent methyl groups clearly provide a strongly stereodifferentiated environment at the "front" of the complex. The Ti—C(cyclopentadienyl) distances in **12c** range from 2.31 to 2.45 Å, with a centroid—Ti distance of 2.06 Å; the comparable values in **1-Ti** range from 2.39 to 2.52 Å, with a centroid—Ti distance of 2.10 Å,[6b] and those in one of the *rac* complexes of **7** vary from 2.35 to 2.47 Å, with an average centroid—Ti distance of 2.09 Å.[11] Ligand **9** is thus seen to be more compact than **7** or the ligand found in **1**, which may explain why attempts to metalate it with Zr and Hf were unsuccessful. However, the centroid—metal—centroid angle of 124.2° in **12c** is only slightly smaller than the value of 128.5° in **1-Ti** and the average value of 128° in the complexes of ligand **7**,[6b,11] and the Ti—centroid—C-(cyclopentadienyl) angles in **12c** vary less than 5° from the perpendicular, so it seems that **12c** is a relatively unstrained species, despite its rigid polycyclic nature. The low yield of complexes **12** is perhaps due to a low yield of **9** in the Skattebøl rearrangement.[19]

The synthesis of **12** is quite short and flexible; analogs containing substituents other than methyl groups could conceivably be made by adding different Grignard reagents to **13**.[20] With respect to the synthesis of enantiopure **12**, it should be noted that enantiopure **13** has been obtained by kinetic resolution with baker's yeast,[21a] by resolution of the corresponding diol using camphanic acid chloride,[21b] and, most efficiently, by lipase-catalyzed enantioselective hydrolysis of the diacetate of the diol;[21c] the synthesis of enantiopure **12** is therefore a real possibility. Other cage diketones might also serve as suitable precursors for rigid, stereochemically defined C_2 complexes. We are continuing our efforts to design new chiral group 4 complexes that might serve as useful reagents for organic synthesis and as precatalysts for olefin polymerization.

Experimental Section

General Procedures. Solvents and common reagents were obtained commercially and used as received or purified as follows: THF, ether, hexane, benzene, and toluene were distilled from Na/benzophenone under argon or nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. 2,6-bicyclo[3.3.1]nonanedione (**13**)[16] and $TiCl_3(THF)_3$[22] were prepared using previously described procedures. Nuclear magnetic resonance spectra were recorded on a Bruker AC-250, Varian XL-300, or Varian Unity-300 spectrometer. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ.

(1*RS*,2*SR*,5*RS*,6*SR*)-2,6-Diisopropenyl-2,6-dihydroxybicyclo[3.3.1]nonane (14). A 1.98 g amount (13.0 mmol) of bicyclo[3.3.1]nonane-2,6-dione was added into a suspension of 9.86 g (40.0 mmol) of anhydrous $CeCl_3$ in THF (30 mL). The resulting solution was stirred at room temperature overnight prior to the addition of the Grignard reagent (*vide infra*). Then, a 100 mL three-necked flask, which was fitted with an addition funnel and a condenser, was carefully evacuated and dried under vacuum. The apparatus was cooled and refilled with argon and was then charged with 0.96 g (40.0 mmol) of Mg and 20 mL of THF. The THF suspension was brought to reflux and then was treated dropwise with a solution of 2-bromopropene (3.0 mL, 33.8 mmol) in THF (5 mL). After the addition of 2-bromopropene, the solution was allowed to reflux for an additional 1 h and was then cooled to room temperature. After the cooling of both diketone/THF and Grignard/THF solutions to 0 °C, the Grignard reagent was added to the diketone/THF solution via cannula. The resulting solution was allowed to stir at 0 °C under an argon atmosphere for 1 h and was then quenched with 10% acetic acid in H_2O. The solution was further diluted with Et_2O, EtOAc, and H_2O and was placed in a separatory funnel. The organic layer was separated from the aqueous layer and was washed sequentially with H_2O and saturated aqueous Na_2CO_3. The resulting organic solution was dried over $MgSO_4$ and then evaporated to provide a white solid. This material was then recrystallized from toluene/hexane to provide 2.52 g (82%) of **14** as an off-white solid. Mp = 113–116 °C. IR (KBr): 3365, 3089, 2931, 1748, 1639, 1450, 1374, 1335, 1287, 1196, 1182, 1125, 1065, 1042, 1027, 997, 961, 943, 897 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.03 (broad s, 2H), 4.96 (broad s, 2H), 1.87–2.13

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[20] It is possible that the yields of the dibromocarbene addition and Skattebøl rearrangement would be adversely affected by larger substituents.[19b,20a] However, other strategies for the annulation of a cyclopentadienyl group onto a polycyclic ketone have been developed.[1,20b,c] (a) Sutton, S. C.; Nantz, M. H. ACS Organic Division Abstract No. 274 for the 206th National Meeting of the American Chemical Society in Chicago, IL, August 22–27, 1992. (b) Paquette, L. A.; Sivik, M. R. *Organometallics* **1992**, *11*, 3503. (c) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707.

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(m, 8H), 1.73 (s, 6H), 1.32–1.96 (m, 6H). ^{13}C{H}NMR (300 MHz, C_6D_6): δ 149.2, 112.1, 75.7, 33.8, 33.3, 28.0, 23.5, 18.9. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.70; H, 10.13. HRMS: calc for $C_{15}H_{24}O_2$ *m/e* 236.1776; found, *m/e* 236.1769.

2,6-Diisopropenylbicyclo[3.3.1]nona-2,6-diene (16). A 250 mL, 3-necked flask, equipped with a condenser, was charged with 2.20 g (9.3 mmol) of (1*RS*,2*SR*,5*RS*,6*SR*)-2,6-diisopropenyl-2,6-dihydroxybicyclo[3.3.1]nonane and 8.61 g (41.9 mmol) of 2,6-di-*tert*-butyl-4-methylpyridine. The apparatus was evacuated, refilled with argon, and then charged with 100 mL of CH_2Cl_2. After cooling of the CH_2Cl_2 solution to 0 °C, 3.5 mL (20.8 mmol) of trifluoromethanesulfonic anhydride was added to the solution, dropwise, via syringe. The resulting solution was allowed to warm to room temperature (a white precipitate formed during warming) and then brought to reflux. After 50 min, the solution was cooled to room temperature. Volatiles were removed under vacuum to provide a white precipitate. The precipitate was treated with 400 mL of hexane and filtered through a fritted funnel. The organic filtrate was then placed in a separatory funnel, diluted with ether (100 mL), washed once with 200 mL of H_2O and three times with 120 mL portions of 1 N HCl, and then washed with 300 mL of saturated Na_2CO_3/H_2O solution. The resulting organic solution was concentrated in vacuo to provide a viscous brown liquid. Flash chromatography of this material (pentane eluent) provided 1.32 g (65%) of **16** as a viscous colorless liquid. Compound **16** is thermally unstable and decomposes (via polymerization) within several days at room temperature. Therefore, it must be stored as a dilute pentane solution at −20 °C to prevent polymerization. IR (film): 3089, 3040, 2967, 2923, 2867, 2825, 2664, 1630, 1604, 1452, 1429, 1370, 1308, 1278, 1200, 1183, 1103, 1092, 1059, 985, 936, 879, 829, 818 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76 (m, 2H), 5.03 (broad s, 2H), 4.90 (broad s, 2H), 2.87 (m, 2H), 2.44 (m, 2H), 2.17 (m, 2H), 1.87 (d, *J* = 1.0 Hz, 6H) 1.75 (t, *J* = 3.1Hz, 2H). ^{13}C{H}-NMR (300 MHz, $CDCl_3$): δ 142.1, 139.8, 123.2, 109.7, 32.3, 29.4, 27.0, 21.0. HRMS: calcd for $C_{15}H_{20}$, *m/e* 200.1565; found, *m/e* 200.1570.

2,6-Bis(2,2-dibromo-1-methylcyclopropanyl)bicyclo-[3.3.1]nona-2,6-diene (17). A 3.81 g amount (34.0 mmol) of potassium *tert*-butoxide was suspended in 80 mL of pentane under an argon atmosphere. The suspension was then charged sequentially with 12 mL of *tert*-butyl alcohol and 1.20 g (6.0 mmol) of 2,6-diisopropenylbicyclo[3.3.1]nona-2,6-diene in pentane (20 mL). The resulting solution was cooled to 0 °C, and then 2.41 mL (27.6 mmol) of $CHBr_3$ was added to the solution, dropwise, via syringe. After the addition was complete, the reaction mixture was warmed to room temperature and stirred at room temperature for 4 h. The resulting solution was then quenched with saturated aqueous NH_4Cl and diluted with ether and H_2O. The resulting solution was placed in a separatory funnel. The organic layer was separated from the aqueous layer. The aqueous layer was extracted twice with 120 mL portions of ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated to provide a dark brown oil. Flash chromatography of the material (pentane eluent) provided 2.81 g (86%) of **17** as a viscous colorless gum. ^{1}H NMR (300 MHz, $CDCl_3$) of the material indicates the presence of three diastereomers which show downfield proton resonances at δ 5.68 (m, 2H) and 5.49 (m, 2H) as well as a pair of resonances at 5.60 (m, 1H) and 5.45 (m, 1H). Compound **17** is thermally unstable and decomposes within several days at room temperature. Therefore, the material must be stored at −20 °C to prevent decomposition. The diastereomeric mixture of **17** was used directly without further purification.

Doubly Bridged *ansa*-Titanocene Complexes (12a–c). A 250 mL 3-necked flask equipped with a condenser was carefully evacuated, flame dried, refilled with argon, cooled, and then charged with 2.9 mL of a solution of methyllithium (1.4 M in ether, 4.1 mmol). The solution was further diluted with 20 mL of ether and was cooled to 0 °C. Then, the solution was charged with a solution of 0.54 g (1.0 mmol) of 2,6-bis-(2,2-dibromo-1-methylcyclopropanyl)bicyclo[3.3.1]nona-2,6-diene in ether (50 mL). After the addition of the **17** was complete, the reaction mixture was allowed to warm to room temperature. The resulting solution was then heated to reflux (a white suspension slowly formed). After 1 h, the solution was cooled to room temperature, and 0.406 g of $TiCl_3(THF)_3$ in 40 mL of THF was added to the solution via cannula (the addition of $TiCl_3(THF)_3$ caused an immediate color change of the solution from colorless to green-black). After the solution was stirred for 2 h, the volatiles were removed in vacuo to provide a dark precipitate. The precipitate was exposed to the air, treated with 50 mL of $CHCl_3$, and stirred at room temperature for 6–10 h to afford an orange suspension. The resulting suspension was filtered through a fritted funnel, providing a red filtrate. Volatiles were removed under vacuum to give a dark red precipitate. The precipitate was then washed with hexane and dissolved in a minimum amount of hot toluene. The resulting toluene solution was cooled to −20 °C overnight, providing dark red crystals of titanocene dihalide complexes. Crystalline material was isolated by decanting the supernatant and drying under vacuum to give 52 mg of crystalline material. The supernatant was further concentrated and was again cooled to −20 °C overnight, affording 19 mg of crystalline titanocene complexes. The total amount of titanocene dihalides isolated was 71 mg (18%). ^{1}H NMR (300 MHz, $CDCl_3$) of the resulting crystalline material indicated three titanocene dihalide complexes were generated in the reaction including the following: 15% of the titanocene dichloride (**12a**) which displays Cp *H* resonances at δ 6.54 (d, *J* = 3.2 Hz, 2H) and 6.09 (d, *J* = 3.2 Hz, 2H); 51% of a bromotitanocene chloride (**12b**) which has the Cp *H* resonances at δ 6.82 (d, *J* = 3.3 Hz, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 6.31 (d, *J* = 3.3 Hz, 1H), and 6.11 (d, *J* = 3.3 Hz, 1H); 34% of a titanocene dibromide (**12c**) which shows Cp *H* resonances at δ 6.88 (d, *J* = 3.9 Hz, 2H) and 6.33 (d, *J* = 3.9 Hz, 2H).

(η^5,η^5-[(1*RS*,2*RS*,8*RS*,9*RS*)-3,10-Dimethyltetracyclo-[6.6.1.0^{2,6}.0^{9,13}]pentadeca-3,5,10,12-tetraene-2,9-diyl])titanium Dibromide (12c). A 71 mg amount (0.18 mmol) of the doubly bridged *ansa*-titanocene dihalides (**12a–c**) was weighed into a 100 mL Schlenk tube. The apparatus was evacuated, refilled with argon, and then charged with CH_2Cl_2 (20 mL). After cooling of the solution to −78 °C, 0.2 mL of BBr_3 (1.0 M in CH_2Cl_2, 0.20 mmol) was added to the solution, dropwise, via syringe. The resulting solution was allowed to warm to room temperature and was stirred at room temperature for 1 h. The volatiles were then removed under vacuum to provide a dark brown precipitate. The precipitate was dissolved in 30 mL of toluene, and the mixture was filtered through a fritted funnel. The resulting dark red filtrate was concentrated in vacuo, providing a dark red solid. This material was dissolved in a minimum amount of hot toluene, and the solution was cooled to −20 °C overnight to give dark red crystals of the titanocene dibromide. The crystalline material was isolated by decanting the supernatant and was dried under vacuum to afford 49 mg of **12c**. The supernatant was further concentrated and was again cooled to −20 °C overnight, providing 14 mg of additional **12c**. The total amount of **12c** isolated was 63 mg (82%). Mp (dec) = 334–336 °C. IR (KBr): 3099, 2947, 1655, 1484, 1447, 1375, 1343, 1317, 1282, 1136, 1054, 897, 826 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (d, *J* = 3.9 Hz, 2H), 6.33 (d, *J* = 3.9 Hz, 2H), 3.39 (broad s, 2H), 2.76–2.93 (m, 4H), 2.34 (broad s, 2H), 2.25 (s, 6H). ^{13}C{H} NMR (300 MHz, $CDCl_3$): δ 134.81, 133.64, 133.45, 125.08, 119.56, 38.84, 33.61, 30.62, 16.24. Anal. Calcd for $C_{17}H_{18}Br_2Ti$: C, 47.49; H, 4.22, Found: C, 47.78; H, 4.15.

Crystallographic Parameters. **12c**: $C_{17}H_{18}TiBr_2$, MW = 430.04, crystal dimensions (mm) 0.130 × 0.180 × 0.400, crystal system tetragonal, space group $I\bar{4}2d$; lattice parameters a =

20.142(4) Å, $c = 7.463(2)$ Å; $V = 3028(1)$ Å^3, Z value = 8, μ(Mo Kα) = 57.76 cm^{-1}, no. of unique reflections = 1222, $R = 0.038$, $R_w = 0.039$.

X-ray Crystal Structure Analysis for (η^5,η^5-[(1*RS*,2*RS*,8*RS*,9*RS*)-3,10-Dimethyltetracyclo[6.6.1.0^{2,6}.0^{9,13}]pentadeca-3,5,10,12-tetraene-2,9-diyl])titanium Dibromide (12c). Data were measured on a Rigaku AFC6R diffratometer. Mo Kα (λ = 0.710 69 Å) graphite-monochromated radiation and a 12 kW rotating anode generator were used. The unit cell dimensions were obtained by a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $11.50 < 2\theta < 15.74°$. The data were collected at a temperature of 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.30° with a take off angle of 6.0°. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 310.0 mm. Of the 2252 reflections which were collected, 1222 were unique ($R_{\text{int}} = 0.145$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability.

The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.16688×10^{-6}). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 398 observed reflections with unweighted and weighted agreement factors of

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.038$$

$$R_w = [(\sum w(|F_o| - |F_c|)^2 / \sum w F_o^{\,2})]^{1/2} = 0.039$$

The standard deviation of an observation of unit weight was 1.16. The weighting scheme was based on counting the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corp.

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Supplementary Material Available: Text describing X-ray experimental procedures and tables listing crystallographic data, final positional parameters, thermal parameters, bond distances and angles, and torsion angles for **12c** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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