# Synthesis, Structure, and Properties of Chiral Titanium and Zirconium Complexes Bearing Biaryl Strapped Substituted Cyclopentadienyl Ligands

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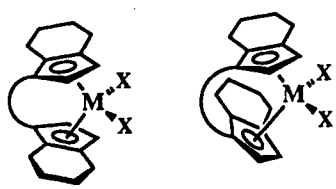
*Received June 23, 1993*®

The synthesis and characterization of 2,2′-bis(2-tetrahydroindenyl)biaryl metallocenes of titanium and zirconium which alleviate many of the stereochemical problems associated with previous ligand systems are described. Such systems give only a single chiral isomer of the complex, the biaryl link determines the chirality of the complex, and the tetrahydroindenyl ligands project their $C_2$ chirality directly to the site of reaction. The reaction of the di-Grignard of *o*-bis(chloromethyl)benzene with the 2,2′-dimethyl esters of biphenyl, 6,6′-dimethylbiphenyl, and binaphthyl gave the corresponding bis(carbinols) in good yields. Acid catalyzed dehydrations of these diols gave the bis(2-indene) compounds in high yield. Both the racemic and the homochiral forms of the bis(2-indene) of the 6,6′-dimethylbiphenyl compound were prepared. Reaction of the dilithio anions of these indene compounds with $TiCl_3$ and $ZrCl_4$ gave the corresponding bis(indenyl) complexes which are sensitive to protic media and decomposed, in some cases rapidly, to the indene ligands. The protic sensitivity has been studied. The *in situ* prepared bis(2-indenyl) complexes are readily reduced with $H_2$ and Adam's catalyst to the tetrahydroindenyl complexes. The Ti(IV) and Zr(IV) tetrahydroindenyl complexes are stable in protic media. The yields of the complexes are generally good. X-ray diffraction structures for a bis(tetrahydroindenyl)·0.5(hexane) and a bis(indenyl)metal complex (Ti(IV)) have been determined and confirm the expected structures.

Chiral complexes of titanium(IV) and zirconium(IV) incorporating two appropriately substituted cyclopentadienyl (Cp) ligands are finding increasing application in enantioselective synthesis[1] and stereoselective polymerization.[2] The most effective stereoselective species are those of the type 1 where the two tetrahydroindenyl,




1 rac 1 meso

indenyl or otherwise substituted cyclopentadienyl groups are linked by a bridge at the 1,1′-positions.[3] The strap linking the Cp rings can consist of one carbon or silicon atom or it can embody two or more carbon atoms. The Cp-centroid–metal–Cp-centroid angle for titanium(IV) and zirconium(IV) bis(Cp) complexes typically fall in the range 128–136° so that the most strain-free strap is the one consisting of two aliphatic carbon atoms. With these two-carbon strap systems, however, both racemic (1 rac) and meso (1 meso) isomers are almost always formed. Consequently, tedious separation procedures or photochemical interconversions are usually required to obtain the pure isomers. One approach that has been used in order to attempt to circumvent the isomer separation problem was to substitute the Cp rings with judiciously positioned bulky groups in order to force the system to adopt the desired racemic form. Such an approach has proved marginally successful,[3d-f] but even if it were, it would be restrictive because the substitution pattern which gave the desired racemic isomer in preponderance may not be the one that is most effective in stereoselection.

When the strap is increased to three or more carbon atoms, generally the racemic isomer predominates at least for the bis(indenyl) and -(tetrahydroindenyl) systems. Although this solves one problem, it gives rise to a second.

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® Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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(3) (a) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. (b) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (c) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21. (d) Collins, S.; Hong, Y.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2349. (e) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695. (f) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359. (g) Röll, W.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *322*, 65. (h) Rieger, B. *J. Organomet. Chem.* **1992**, *428*, C33. (i) Rieger, B.; Steimann, M.; Fawzi, R. *Chem. Ber.* **1992**, *125*, 2373.

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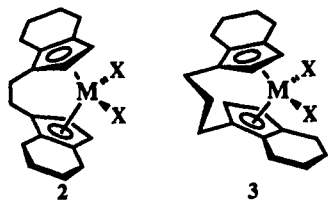
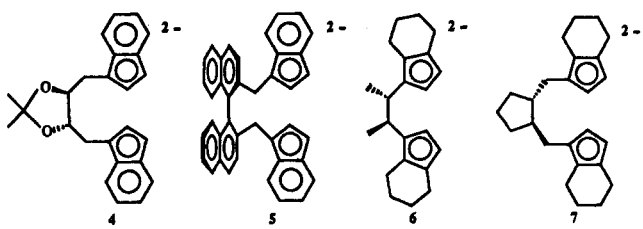
The inherent tilt angle of the Cp rings accommodates the larger span of the strap by rotating the Cp rings.[4] Consequently, substituents on the two Cp rings are driven to adopt an unsymmetrical disposition with respect to the X–M–X bisector. The result is that the complexes are no longer $C_2$ symmetric. Examples of a $C_2$ symmetric two-carbon strap and a $C_1$ unsymmetric three-carbon strap system are shown in **2**[3a,b,c] and **3**.[3g] Such $C_1$ structures




2 3

make the two coordination positions bearing the X groups sterically inequivalent so that stereoselective reactions involving these sites will be controlled by different steric environments, leading to ambiguity in defining the origins of the stereoselection. This ambiguity remains even if the sites become equivalent on an NMR time scale, as is observed in some cases.[3g,5,6]

Adding to the difficulties associated with the use of these complexes for enantioselective reactions is the necessity of resolving the racemic isomer. Because resolution is unpredictable and time consuming and requires large quantities of material, a number of attempts were made to circumvent these problems by introducing chiral centers in the strap. The idea behind this design was the expectation that the chirality of the strap would induce a single diastereomer of the complex and thus avoid the resolution step. Four examples of such ligands are shown: **4**,[7] **5**,[8] **6**,[9] **7**.[5] Each of these ligands proved to have

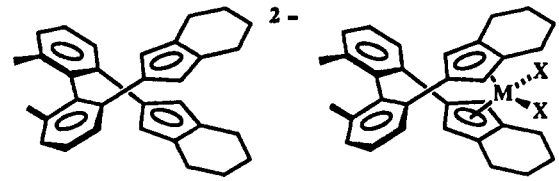



4 5 6 7

its own difficulties. Ligand **4** possesses an acid sensitive acetonide group and only "meso" isomers were isolated of the titanium(IV) and zirconium(IV) complexes. Whereas both **5** and **7** gave only a single diastereomer of the racemic form, the complexes were not $C_2$ symmetric. Ligand **6** does give $C_2$ symmetric complexes but the titanium(IV) dichloro complexes consist of formed, giving two diastereomers of the racemic form and substantial amounts of the "meso" isomer. Laborious methods were required to obtain a single pure chiral diastereomer. The corresponding zirconium(IV) complex of **6** was formed almost exclusively as the "meso" isomer.

It is clear from this brief and selective survey that progress in this area requires the design and ready accessibility of conceptually different classes of ligands which embody the following characteristics. First, the ligand should produce only a single chiral isomer of the complex. Second, it should possess $C_2$ symmetric chirality when bound to the metal. Third, the ligand itself should be chiral and should project its chirality about the reaction centers. Fourth, the synthetic procedures should be simple and efficient.

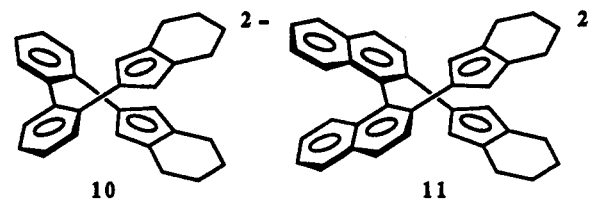
It occurred to us, as it had to others,[10,11] that one possible solution which addressed these demands was to prepare complexes of the ligand class exemplified by biphenacene **8**, the complexes of which would have the structure **9**.




**8** (S)-Biphenacene **9** [M((S)-Biphenacene)$Cl_2$]

Such complexes are chiral about the metal center by virtue of the imposed chirality of the biphenyl unit so that the 2-substituted tetrahydroindenyl groups project about the potential reaction centers in a twisted $C_2$ symmetric array. Further, by appropriate substitution, the ligand can be made to extend its chirality to any required distance.

This paper describes efficient synthetic methods for preparation of (*R,S*)- and (*S*)-biphenacene, norbiphenacene **10**, and their titanium(IV) and zirconium(IV) complexes. Also included are the syntheses of the anal-




**10** Norbiphenacene **11** Binapacene

ogous ligand (*R,S*)-binapacene **11** and its titanium(IV) complex. For the synthesis of the ligands we sought methods which would give high yields and which would preserve the configurational integrity of homochiral precursors.

**1. Synthesis of the Biphenacene Precursor.** The precursor to biphenacene was prepared by the methods outlined in Scheme I. The steps **12** → **13** and **14** → **15** followed literature procedures[12] with slight modification. The material **12** is commercially available, all of the steps to (*R,S*)-**16** proceed in high yields, the procedures are technically simple, and large quantities of material can be conveniently employed. We were unable to obtain resolution of (*R,S*)-**16** with (+)-brucine by explicitly following the published procedure.[12] The procedure given in the Experimental Section is reproducible and gives both the *R* and *S* isomers in high yield without extensive fractional

(4) Smith, J. A.; Seyerl, J. v.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175.
(5) Hollis, T. K.; Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 2812.
(6) Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276.
(7) Bandy, J. A.; Green, M. L. H.; Gardiner, I. M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1991**, 2207.
(8) Burk, M. J.; Colleti, S. L.; Halterman, R. L. *Organometallics* **1991**, *10*, 2998.
(9) Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 1869.
(10) Huttenloch, M. E.; Diebold, J.; Rief, U.; Brintzinger, H. H.; Gilbert, A. M.; Katz, T. J. *Organometallics* **1992**, *11*, 3600.
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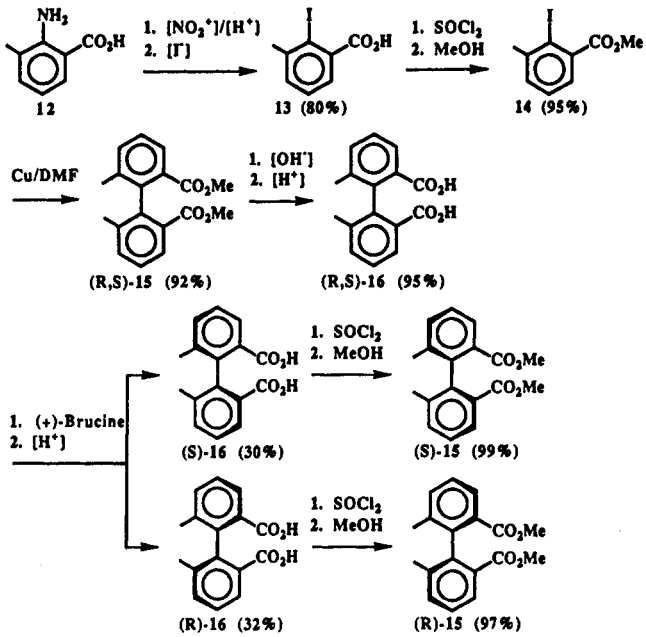
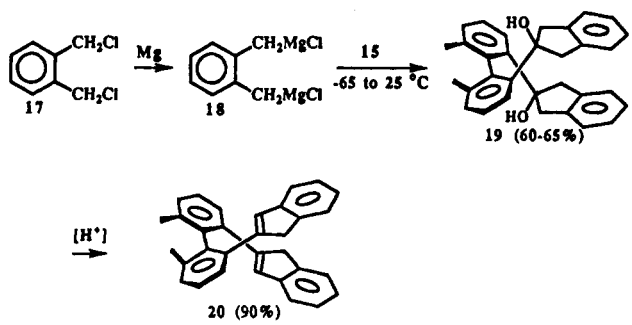
(12) Kanoh, S.; Muramoto, H.; Kobayashi, N.; Motoi, M.; Suda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3659.

**Scheme I**

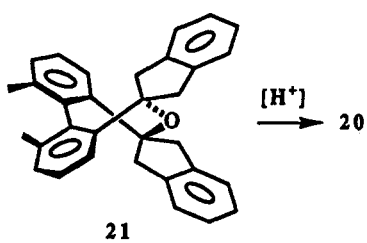



crystallization. Comparing the literature optical rotations and the published chiral column chromatography data,[12] we estimate that both *R* and *S* isomers are >99.8% enantiomerically pure.

The crucial step in the synthesis is the formation of the di-Grignard **18**. Following the procedure of Lappert[13] explicitly gave high yields of **18**. Addition of (*R,S*)-**15** to the Grignard solution produced the crystalline diol **19** in



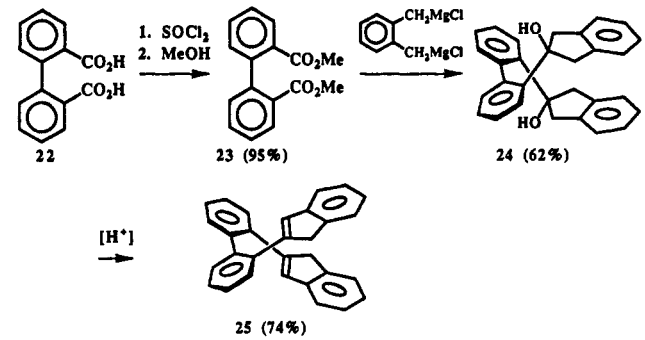

excellent yield when it is recognized that the di-Grignard solution contains other reactive Grignard species.[14] Dehydration of **19** proceeds by two paths, one directly to the product **20** and the other via the cyclic ether **21**. The




proportion of each path depends on the acid used, on its concentration, and on the solvent medium. We have not found conditions where the formation of the ether **21** is avoided. The biphenacene precursor (*R,S*)-**20** is a robust crystalline compound. Although the optically active forms of the diol **19** are crystalline, the optically active forms of the dehydrated product (*R*)- or (*S*)-**20** are low melting solids which are difficult to crystallize.

**2. Synthesis of the Norbiphenacene Precursor.** Since biphenyldicarboxylic acid **22** is cheap and commercially available and since homochiral complexes are not required for isotatic polymerization of propylene we considered it useful to report the synthesis of the norbiphenacene precursor **25**. The method is outlined in Scheme II. The procedure in Scheme II follows that

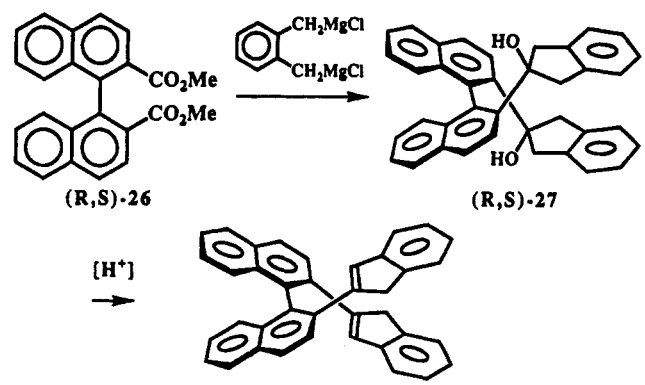
**Scheme II**




described for biphenacene except that the dehydration step **24** → **25** proved difficult. In benzene and chlorinated solvents *p*-toluenesulfonic acid generates a small amount of **25** (~10%) and the cyclic ether which is unreactive to catalytic quantities of this acid. Using equivalent amounts of trifluoroacetic acid also generates the ether which then reacts to give unidentified (black) decomposition products. Tosylation or mesylation of **24** also gave the ether as the major product. Eventually, we found that by using 1 equiv of *p*-toluenesulfonic acid in THF/cyclohexane (1:4) the diol **24** was dehydrated to **25** in good yield after the solvent was removed on a rotatory evaporator at 50 °C. Several evaporations of the solvent mixture were required to complete the reaction. The resistance of the cyclic ether of **24** to dehydration compared to the ready dehydration of **21** probably reflects the greater steric strain present in the dimethylated ether.

**3. Synthesis of the Binapacene Precursor.** The binapacene precursor **28** was prepared from the diester **26** by methods (Scheme III) similar to those described for

**Scheme III**



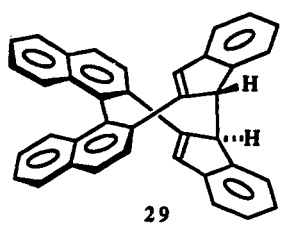

the biphenacene precursor. The racemic ester, (*R,S*)-**26**, was prepared with slight modifications of literature procedures.[15-18] The diol, (*R,S*)-**27**, is very insoluble in all

(13) Lappert, M. F.; Martin, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1959.
(14) Harvey, S.; Junk, P. C.; Raston, C. L.; Salem, G. *J. Org. Chem.* **1988**, *53*, 3134.
(15) Bergmann, E. D.; Szmuszkovicz, J. *J. Am. Chem. Soc.* **1951**, *73*, 5153.

common solvents except for THF, and the bulk of the material was not purified. It was converted cleanly to the more soluble bis(indene), (*R,S*)-**28**, in good overall yield from (*R,S*)-**26**. The production of (*R,S*)-**26** proceeds via both the direct and cyclic ether pathways.

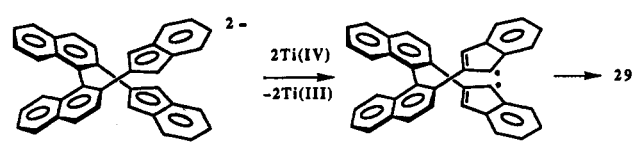
Compared to the synthesis of the (*R,S*)-biphenacene diester precursor, (*R,S*)-**15**, which requires three simple steps, the preparation of the binaphthyl diester, (*R,S*)-**26**, requires five cumbersome and lengthy steps when large scale preparations are involved. Because of this and because, at least superficially, binapacene and biphenacene appear to be structurally equivalent, we did not proceed with the resolution of the binaphthyl system. Moreover, as we note presently, its titanium and zirconium complexes were more difficult to prepare than those of the biphenacene ligands.

**4. Synthesis of [Ti((*R,S*)-binapacene)$Cl_2$].** Attempts to prepare [M((*R,S*)-binapacene)$Cl_2$] complexes by conventional methods gave a number of unexpected results. Reaction of the dilithio salt of (*R,S*)-**28** with 1 equiv of [$TiCl_4$·2THF] in THF solution leads to a dark, almost black, solution. After refluxing this solution for 15 h, the solution was cooled and HCl gas was bubbled through the solution. Within a few seconds the solution became almost colorless. Upon removal of the solvent there remained blue [$TiCl_3$·3THF] as a solid and the organic residue consisted of a 1:1 mixture of the binapacene precursor, (*R,S*)-**28**, and the cyclic compound **29**. The $^1H$ NMR of **29** indicates that a single symmetric diastereomer is produced. Molecular models indicate that the twisted binaphthyl fragment strongly favors the production of the shown isomer.




**29**

The presence of titanium(III) suggests that the dianion **30** is capable of reducing titanium(IV) and initiating the radical coupling **30** → **31** → **29**. Given the stoichiometry, namely 1:2 for **30**:Ti(III), after the radical coupling occurs,




**30** **31**

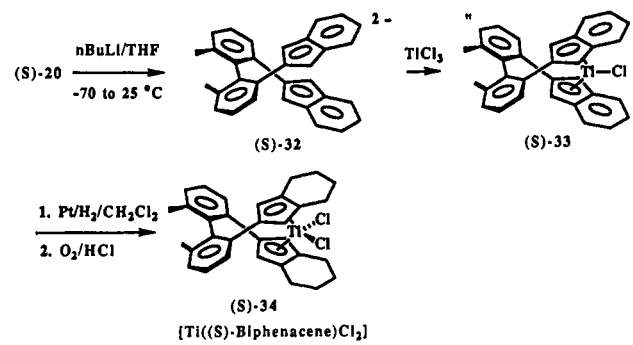
the resulting Ti(III) could react with the remaining dianion **30**. As we show presently, it does, but the putative product [$Ti^{III}$(**30**)Cl] is decomposed by acid to give the starting bis(indene) ligand **28**. This was confirmed by allowing the dianion **30** to react with [$TiCl_3$·3THF] which gave a dark colored solution, but upon addition of aqueous 6 N HCl the solution is slowly decolorized and from it is isolated the starting bis(indene) compound **28** in nearly quantitative yields. No **29** was detected. Thus unlike the aliphatic strapped bis(indenyl) complexes of Ti(III) which are stable to strong HCl, the binaphthyl strapped complexes are decomposed by acid to give the ligand precursor. Reaction of the lithium bis(indenyl) species **30** with [$ZrCl_4$·2THF] in refluxing THF led to the formation of a clear yellow solution, suggesting that the expected complex [Zr(**30**)$Cl_2$] was formed. Upon removal of the solvent under vacuum, the residue was extracted with $CH_2Cl_2$. The extract contained only the ligand precursor **28**. If, as we suspect, the bis(indenyl)zirconium complex formed, the water present in the solvent appeared sufficient to decompose the complex.

Crystal structures[10] of these biaryl strapped complexes indicate that little or no steric strain is engendered by the biaryl strap. We therefore assume that the presence of the two contiguous aromatic systems associated with the Cp groups led to facile protonation of these bis(indenyl) complexes. If this is so and the bis(indenyl) complexes are indeed formed, then we supposed that the tetrahydroindenyl analogues would be more stable. This proved to be the case.

Thus the dianion **30** was allowed to react with 1 equiv of [$TiCl_3$·3THF] in THF solution and the solvent was removed in vacuo. The residue was taken up in dry $CH_2Cl_2$ and was then hydrogenated under ambient conditions using Adam's catalyst. After oxidation in the presence of dilute HCl, the light brown complex, [Ti((*R,S*)-binapacene)$Cl_2$], was isolated as feathery needles in low yield (~5%). This complex is stable to mild acid. We note that under the mild reduction conditions no hydrogenation of the naphthalene groups was observed.

**5. Synthesis of Biphenacene and Norbiphenacene Complexes.** Because of the synthetic difficulties associated with the preparation of the binapacene complexes we chose to concentrate on the titanium(IV) and zirconium(IV) complexes of biphenacene and norbiphenacene.

**Scheme IV**



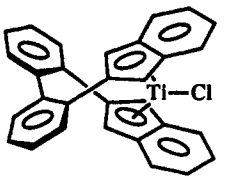

The bis(indenyl) precursor complexes of these metals are also acid sensitive but less so than the binaphthyl analogues. The procedure adopted for the preparation of these complexes is exemplified by the sequence in Scheme IV. The bis(indenyl) dianion in THF solution was allowed to react with [$TiCl_3$·3THF] at 25 °C for 4 h, the solvent was removed, and the residue was taken up in dry $CH_2Cl_2$ and was hydrogenated with Adam's catalyst at ambient pressure and temperature for 24 h. After filtration the complex was air oxidized in the presence of 0.5 N aqueous HCl. A similar procedure was adopted for the preparations of the [Ti(norbiphenacene)$Cl_2$] complexes. The corresponding zirconium(IV) complexes were prepared similarly from [$ZrCl_4$·2THF].

These procedures gave purple crystals of [Ti(norbiphenacene)$Cl_2$] and [Ti((*S*)-biphenacene)$Cl_2$] in about

(16) Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J. Org. Chem.* **1986**, *51*, 3762.
(17) Colleti, S. L.; Halterman, R. L. *Organometallics* **1991**, *10*, 3438.
(18) Weber, E.; Csöregh, I.; Stensland, B.; Czugler, M. *J. Am. Chem. Soc.* **1984**, *106*, 3297.

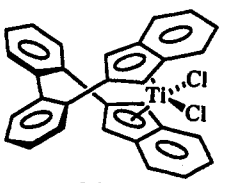
45% yield. The analogous yellow compounds of zirconium were obtained in about 25% yield as crystals. All of these compounds are robust, are air stable as crystals, are not acid sensitive, and can be manipulated in the same way as other analogous metallocenes. The optically active complexes are more soluble than the racemic forms. Under the conditions described in the Experimental Section all of these complexes can be obtained in yields comparable to or better than those described for other strapped metallocenes, and the methods are no more complex.

**6. Stability of Bis(2-indenyl) Complexes.** Our synthetic work suggested that the bis(2-indenyl) complexes bearing biaryl straps were unstable in protic media. In order to obtain a more quantitative assessment of the stability of these complexes, we have isolated and characterized the Ti(IV) bis(2-indenyl) complex with the biphenyl strap. When the dilithium salt of **25** was allowed to react with [$TiCl_3$·3THF] in THF solution at 25 °C, a dark-orange precipitate of what is believed to be the species **35** is formed. This very oxygen sensitive compound was



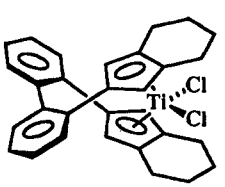

**35**

dissolved in $CH_2Cl_2$/THF in the presence of oxygen. Upon removal of the $CH_2Cl_2$, dark-brown crystals of the Ti(IV) compound, **36**, formed in low yield.




**36**

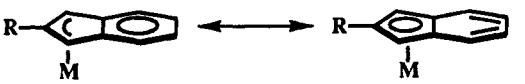
This compound, **36**, is indefinitely stable in $CH_2Cl_2$ solutions, but it is not stable in the presence of protic solvents or acids. The destruction of the complex was followed by $^1H$ NMR in $CD_2Cl_2$ solutions. Thus a 0.009 M solution of **36** in $CD_2Cl_2$ in the presence of MeOH (0.09 M) at 25 °C slowly decomposes over 70 h, regenerating quantitatively the bis(indene) ligand, **25**. Similarly, a $CD_2Cl_2$ solution of **36** in the presence of 1 M aqueous HCl leads to the formation of the ligand, **25**, in about 70 h. On the other hand, addition of 10 equiv of $CF_3CO_2H$ to a 0.016 M solution of **36** in $CD_2Cl_2$ leads to the successive substitution of the chloro ligands by trifluoroacetate, and after 1 week at room temperature only 25% of the ligand is displaced from the complex. This behavior of **36** is in sharp contrast to its tetrahydro-2-indenyl analogue, **37**,




**37**

which is indefinitely stable under these, and even more severe, conditions. The fact that **36** is more stable to $CF_3CO_2H$ than it is to MeOH indicates that the strength of the acid is not the sole factor governing the stability of the bis(2-indenyl) complexes and that the conjugate base plays a role in the decomposition mechanism.

Presumably, the instability of the biaryl strapped bis(2-indenyl) complexes is related to the existence of **38** ($\eta^3$ ring slipped[19]) and **39** ($\eta^5$) resonance forms. When R is an appropriately oriented aryl group, we expect that conjugation will stabilize the $\eta^3$-form. The dependence of the rate of decomposition of **36** on the conjugate base suggests that coordination of the conjugate base to Ti(IV) is required to generate the $\eta^3$-form which is then protonated. If this is so, then the structure of **36** need not reflect a tendency to ring slippage.[19a]




**38** **39**

**7. Crystal Structures.** Crystal structures of (racemic)[Ti((*R*,*S*)-biphenacene)$Cl_2$]·0.5(hexane) and of the bis(2-indenyl) complex, **36**, were determined. The homochiral complexes of biphenacene did not give suitable crystals for X-ray diffraction. Crystallographic data for the two structures are collected in Table I, and selected

**Table I. Crystal Data for the Biphenacene (*R*,*S*)-34 and Indenyl 36 Complexes**

| | | |
|---|---|---|
| | (a) Crystal Parameters | |
| formula | $C_{32}H_{32}Cl_2Ti$·0.5$C_6H_{14}$ ((*R*,*S*)-**34**) | $C_{30}H_{20}Cl_2Ti$ (**36**) |
| fw | 578.4 | |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| *a*, Å | 11.111(3) | 10.843(4) |
| *b*, Å | 18.804(6) | 13.939(5) |
| *c*, Å | 14.937(4) | 15.209(5) |
| $\beta$, deg | 110.08(2) | 102.18(3) |
| *V*, Å$^3$ | 2931.1(13) | 2247.0(12) |
| *Z* | 4 | 4 |
| *D*(calc), g cm$^{-3}$ | 1.311 | 1.476 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 4.97 | 6.36 |
| temp, K | 296 | 230 |
| cryst size, mm | 0.20 × 0.32 × 0.56 | 0.02 × 0.26 × 0.26 |
| cryst color | deep red | black |
| | (b) Data Collection | |
| diffractometer | Siemens P4 | |
| monochromator | oriented graphite | |
| radiation | Mo K$\alpha$ | |
| wavelength, Å | 0.710 73 | |
| 2$\theta$ limits, deg | 4 < 2$\theta$ < 45 | 4 < 2$\theta$ < 45 |
| std reflns | 3 std/197 rflns | |
| decay, % | ~2 | ~2 |
| octants collcd | ±11,+20,+16 | +11,+15,+16 |
| no. of rflns collcd | 3988 | 3040 |
| no. of independt rflns | 3818 | 2925 |
| no. of independt rflns, $F_o \geq 3\sigma(F_o)$ | 2550, $F_o \geq 5\sigma(F_o)$ | 1501, $F_o \geq 4\sigma(F_o)$ |
| *T*(max)/*T*(min) | N/A | 1.41 |
| | (c) Refinement | |
| $R(F)$,[a] % | 5.43 | 7.18 |
| $R_w(F)$,[b] % | 7.64 | 7.99 |
| GOF | 1.30 | 1.36 |
| $\Delta/\sigma$(max) | 0.013 | 0.001 |
| $\Delta(\rho)$, e Å$^{-3}$ | 1.33 | 1.37 |
| $N_o/N_v$ | 8.1 | 5.0 |

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w^{-1} = \sigma^2F_o + gF_o^2$.

(19) (a) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (b) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (c) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929.

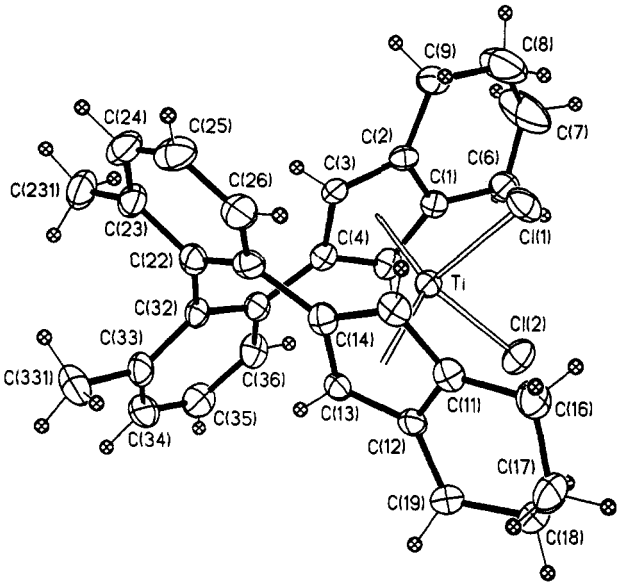



**Figure 1.** Molecular structure of [Ti((*R*,*S*)-biphenacene)-$Cl_2$], (*R*,*S*)-**34**, drawn with 35% probability ellipsoids.

**Table II. Selected Bond Distances and Angles for the Biphenacene (*R*,*S*)-34**

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| Ti–Cl(1) | 2.337(2) | Ti–Cl(2) | 2.346(2) |
| Ti–C(1) | 2.476(6) | Ti–C(2) | 2.506(6) |
| Ti–C(3) | 2.384(7) | Ti–C(4) | 2.391(7) |
| Ti–C(5) | 2.390(6) | Ti–C(11) | 2.477(6) |
| Ti–C(12) | 2.497(6) | Ti–C(13) | 2.382(6) |
| Ti–C(14) | 2.381(5) | Ti–C(15) | 2.386(5) |
| C(22)–C(32) | 1.489(9) | | |
| | Bond Angles (deg) | | |
| Cl(1)–Ti–Cl(2) | 94.1(1) | C(13)–C(14)–C(15) | 106.2(5) |
| C(2)–C(1)–C(5) | 108.3(5) | C(11)–C(15)–C(14) | 109.7(6) |
| C(1)–C(2)–C(3) | 108.2(5) | C(21)–C(22)–C(23) | 119.6(6) |
| C(2)–C(3)–C(4) | 108.4(5) | C(21)–C(22)–C(32) | 122.5(5) |
| C(3)–C(4)–C(5) | 106.0(5) | C(23)–C(22)–C(32) | 117.9(6) |
| C(1)–C(5)–C(4) | 108.8(5) | C(31)–C(32)–C(33) | 119.3(5) |
| C(12)–C(11)–C(15) | 108.1(6) | C(22)–C(32)–C(31) | 120.9(6) |
| C(11)–C(12)–C(13) | 107.5(5) | C(22)–C(32)–C(33) | 119.8(5) |
| C(12)–C(13)–C(14) | 108.3(6) | | |

**Table III. Selected Bond Distances and Angles for the Indenyl 36**

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| Ti–Cl(1) | 2.355(4) | Ti–Cl(2) | 2.318(4) |
| Ti–C(1) | 2.362(11) | Ti–C(2) | 2.407(12) |
| Ti–C(3) | 2.395(12) | Ti–C(4) | 2.544(10) |
| Ti–C(9) | 2.489(12) | Ti–C(11) | 2.409(13) |
| Ti–C(12) | 2.418(13) | Ti–C(13) | 2.347(12) |
| Ti–C(14) | 2.464(11) | Ti–C(19) | 2.526(11) |
| C(26)–C(27) | 1.484(14) | | |
| | Bond Angles (deg) | | |
| Cl(1)–Ti–Cl(2) | 93.7(1) | C(13)–C(14)–C(19) | 106.7(10) |
| C(2)–C(1)–C(9) | 107.0(9) | C(11)–C(19)–C(14) | 108.4(10) |
| C(1)–C(2)–C(3) | 108.3(10) | C(21)–C(26)–C(25) | 118.2(10) |
| C(2)–C(3)–C(4) | 107.4(10) | C(21)–C(26)–C(27) | 116.8(10) |
| C(3)–C(4)–C(9) | 109.1(9) | C(25)–C(26)–C(27) | 124.7(10) |
| C(1)–C(9)–C(4) | 107.2(10) | C(28)–C(27)–C(32) | 118.4(10) |
| C(12)–C(11)–C(19) | 107.8(10) | C(26)–C(27)–C(28) | 116.5(10) |
| C(11)–C(12)–C(13) | 106.7(11) | C(26)–C(27)–C(32) | 124.9(10) |
| C(12)–C(13)–C(14) | 109.7(10) | | |

bond lengths and angles for the two structures are given in Tables II and III. The structure of [Ti((*R*,*S*)-biphenacene)$Cl_2$]·0.5(hexane) is shown in Figure 1, and that of **36** is shown in Figure 2. In addition we provide a superposition of the two structures in Figure 3. Aside

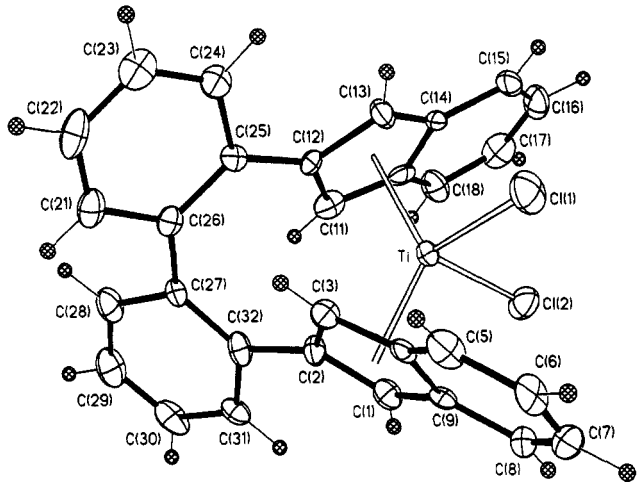



**Figure 2.** Molecular structure of the titanium(IV) dichloro complex, **36**, drawn with 35% probability ellipsoids.

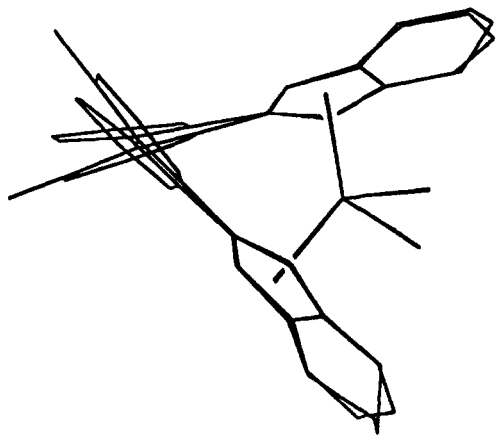


**Figure 3.** Superimposed structures of [Ti((*R*,*S*)-biphenacene)$Cl_2$], (*R*,*S*)-**34**, and the titanium(IV) dichloro complex, **36**. This computer generated superimposition was made by fitting the titanium, the two chloride atoms, and the two centroids of each molecule.

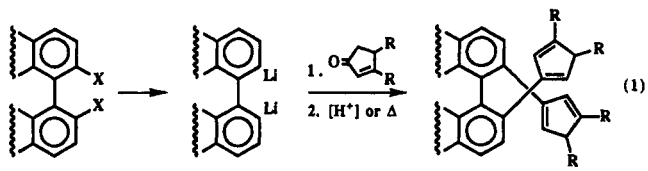
from the dihedral twist of the biphenyl straps the gross structural features of the two molecules are very similar (Figure 3).

The carbon–carbon bond lengths of the Cp rings of the two structures are similar and fall within the range found for Cp rings bonded to Ti(IV).[3] The Cp-centroid–Ti–Cp-centroid angle for [Ti((*R*,*S*)-biphenacene)$Cl_2$] is 133.7° whereas for **36** this same angle is 131.6° both of which fall within the normal range for these types of complexes. The larger angle for the former undoubtedly reflects the greater dihedral twist of the substituted biphenyl strap in [Ti-((*R*,*S*)-biphenacene)$Cl_2$] which is 69° whereas this twist is only 55° in the biphenyl strap of **36**. The methyl groups of the biphenacene strap are within VDW contact; the two methyl carbon atoms are separated by 3.45 Å and cause the expansion of the dihedral angle. The Ti–Cl and Ti–Cp-centroid distances and the Cl–Ti–Cl angles are very similar for the two structures. Thus the crystal structures of the two molecules provide no structural differences which might suggest that **36** should be unstable in protic media. The ground state structure, however, need not necessarily reflect the tendency to ring slippage of the indenyl groups. We note that in these structures the phenyl and Cp groups have small dihedral twist angles ranging from 20 to 24°, indicating that substantial overlap

between $\pi$-orbitals of the phenyl and Cp systems is possible, as is required for our ring slippage hypothesis.

## Discussion

The synthetic methods described here for the preparation of the biaryl strapped bis(2-tetrahydroindenyl) ligand precursors are efficient and have a number of distinct advantages over previously reported methods.[10,11] These other methods generally employed the dilithio salt of the biaryl strap to react with an $\alpha,\beta$-unsaturated cyclic ketone (eq 1). The problems with this method are, first,



(1)

that the reaction of the dilithio reagent with the $\alpha,\beta$-unsaturated cyclic ketone is a poor yield process because of ready enolization of the ketone and because both 1,2 and 1,4 addition can occur. Second, after the bis(cyclopentadiene) product is formed, intramolecular Diels–Alder addition leads to a product which requires high temperature cracking and simultaneous capture of the Cp ligands by a strong base to form the dianion. Third, if homochiral biaryl straps are required, the formation of the biaryl dihalides from the resolved diamines and the derived dilithio salts pose questions of configurational stability. The synthetic approach for obtaining the tetrahydroindenyl complexes described here obviates these problems.

Unlike the conventional strapped metallocenes where the indenyl or tetrahydroindenyl ligands are attached at the 1-position, the present systems allow for $C_2$ projection of chirality over the remaining coordination positions. This $C_2$ chiral array should provide an ideal chiral environment for certain types of enantioselective transformations, particularly those where the center of reaction is distant from the metal. Diels–Alder additions are such a case. We have reported[20] that bis(pentamethylcyclopentadienyl)titanium(IV) diaquo complexes are effective Diels–Alder catalysts. We have prepared the complex [Ti((*S*)-biphenacene)$(H_2O)_2$]$(CF_3SO_3)_2$ which at 2 mol % catalyst loadings in $CH_2Cl_2$ solutions rapidly catalyzes the Diels–Alder reaction between methacrolein and cyclopentadiene at −78 °C to give a 98:2 exo:endo ratio of the products. The enantiomeric excess was found to be 80% for the exo isomer. We shall report on the enantioselective catalysis by these types of complexes shortly.

## Experimental Section

The following solvents were distilled under nitrogen immediately before use: tetrahydrofuran from potassium, methylene chloride from $CaH_2$, hexane from $CaH_2$, and diethyl ether from $LiAlH_4$. The magnesium metal used in the Grignard reaction was 50-mesh powder (99+% Aldrich) stored and dispensed under argon in a glovebox. (+)-Brucine was obtained from Eastman Laboratory Chemicals. The adducts $TiCl_4$·2THF, $TiCl_3$·3THF, and $ZrCl_4$·2THF were prepared by established procedures.[21] Manipulations of air- or moisture-sensitive metal compounds were carried out under an argon atmosphere using Schlenk techniques.

**I. Ligand Precursor Preparations. 1A. (*R,S*)-6,6′-Dimethylbiphenyl-2,2′-dicarboxylic Acid ((*R,S*)-16). Methyl 2-Iodo-3-methylbenzoate (14).** Compound 13 (33.19 g, 126 mmol), prepared by the method of Suda,[12] was suspended in toluene (70 mL), and $SOCl_2$ (30 mL, 411 mmol) was then added. The mixture was brought to reflux over 45 min and then refluxed for 2 h, becoming a clear brown solution. $SOCl_2$ and toluene were then removed under high vacuum, giving an amber oil. To this residue was added MeOH (80 mL), and a vigorous exothermic reaction ensued. After stirring for 15 min, the reaction was refluxed for 1 h and then stirred 20 h at room temperature. The solvent was removed under vacuum, giving a dark amber fluid which was dissolved in $Et_2O$ (300 mL) and stirred with $NaHCO_3$ (3 g). To this mixture was added $H_2O$ (150 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ (1 × 100 mL), diluted aqueous $Na_2S_2O_3$ (1 × 100 mL), $H_2O$ (1 × 100 mL), and brine (1 × 100 mL) and dried ($MgSO_4$). After filtration the solvent was removed, giving a light amber oil (36.0 g) which was distilled to give **14** (33.27 g, 95%), a light yellow oil: $bp_{0.5}$ 109–112 °C (lit.[12] $bp_5$ 130–140 °C).

**(*R,S*)-6,6′-Dimethylbiphenyl-2,2′-dicarboxylic Acid ((*R,S*)-16).** To a solution of NaOH (9.05 g, 226 mmol) in $H_2O$ (50 mL) was added (*R,S*)-**15** (13.53 g, 45 mmol), prepared by the method of Suda,[12] in *p*-dioxane (25 mL). The mixture was refluxed for 17 h, giving a homogeneous solution. The *p*-dioxane was then removed under vacuum, and concentrated HCl (19 mL) was slowly added while rapidly stirring. A thick white precipitate formed and was filtered and was washed with $H_2O$ (100 mL). The solid was then suspended in EtOH (100 mL) and heated when most of the solid dissolved. Concentrated HCl (1 mL) was then added to coagulate the insoluble material which was then removed by filtration. Water (270 mL) was slowly added to the hot filtrate, and upon cooling, fine white crystals formed. More $H_2O$ (50 mL) was added, and the mixture was refrigerated (5 °C) for 18 h. The white crystals were filtered, washed with cold 30% aqueous EtOH (1 × 50 mL), and air dried, giving (*R,S*)-**16** (11.71 g, 95%): mp 241–243 °C (lit.[12] mp 240–241 °C).

**1B. (*R*)- and (*S*)-6,6′-Dimethylbiphenyl-2,2′-dicarboxylic Acid ((*R*)-16, (*S*)-16).** (+)-Brucine (15.76 g, 40 mmol) was dissolved in hot EtOH (60 mL) and filtered through Celite to remove traces of an insoluble material, and to the filtrate (total volume 70 mL EtOH) was added (*R,S*)-**16** (10.80 g, 40 mmol). The mixture was heated to dissolve the solids and acetone (30 mL) was then added. The cloudy solution was briefly heated until it cleared and was then allowed to cool to room temperature. After 24 h the crystals were filtered, washed with cold EtOH/acetone (7/3, 1 × 100 mL) and the white crystals (11.91 g) [$[\alpha]_D^{RT}$ = +35.58° (10 cm, *c* = 1.0 g/100 mL, MeOH)] were recrystallized from hot EtOH (300 mL) by slow cooling to room temperature. After 24 h the crystals were filtered out and washed with cold EtOH (1 × 50 mL), giving long white needles of the brucine salt of (*R*)-**16** (9.53 g, 36% based on the racemic mixture) [$[\alpha]_D^{RT}$ = +38.15° (10 cm, *c* = 1.0 g/100 mL, MeOH) (lit.[12] $[\alpha]_D^{25}$ = +38.1 (*c* = 1.0, MeOH))]. The mother liquor from the first crystallization was concentrated under vacuum to a yellow paste which was dissolved in hot EtOH (25 mL). The resulting solution was allowed to stand at room temperature for 24 h and then was refrigerated (5 °C) for 48 h. The crystals were then filtered, washed with cold EtOH (1 × 50 mL) and pentane (1 × 50 mL), and air dried. The white-yellow solid (14.58 g) was dissolved in hot MeOH (70 mL). Hot acetone (30 mL) was then added and the solution was allowed to cool slowly to room temperature. After 18 h the dense mass of crystals was filtered out and washed with cold EtOH (1 × 30 mL), giving long white needles of the brucine salt of (*S*)-**16** (8.47 g, 32% based on the racemic mixture) [$[\alpha]_D^{RT}$ = −41.95° (10 cm, *c* = 1.0 g/100 mL, MeOH) (lit.[12] $[\alpha]_D^{25}$ = −39.2° (*c* = 1.0, MeOH))]. The brucine salt of (*S*)-**16** (8.12 g, 12 mmol) was suspended in ethyl acetate (25 mL), and the mixture was rapidly stirred while 1 N HCl (25 mL) was added. After 1

(20) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464.
(21) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

h all the solid had dissolved and more ethyl acetate (50 mL) was added. The layers were separated, the aqueous phase was extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were washed with 1 N HCl (3 × 30 mL) and brine (2 × 30 mL), and dried ($Na_2SO_4$). After filtration the solvent was removed under vacuum. The white solid residue (3.56 g) was dissolved in a minimum volume of hot $CH_2Cl_2$, and benzene/cyclohexane (1/3, 16 mL) was then added. Most of the $CH_2Cl_2$ was boiled off, and upon cooling, crystals formed. After several hours at room temperature pentane (8 mL) was added and the mixture was refrigerated (5 °C) overnight. The white crystals were filtered out and washed with cyclohexane/pentane (1/20, 1 × 25 mL) and pentane (1 × 10 mL) to give (*S*)-**16** (3.08 g, 93%) [$[\alpha]_D^{RT}$ = +21.78° (10 cm, *c* = 1.0 g/100 mL, MeOH) (lit.[12] $[\alpha]_D^{25}$ = +22.1° (*c* = 1.0, MeOH))]. The brucine salt of (*R*)-**16** (9.43 g, 14 mmol) was similarly converted back to the diacid but was filtered through Celite after the initial reaction with 1 N HCl to remove an insoluble white solid. The compound was obtained as white crystals of (*R*)-**16** (3.46 g, 90%): $[\alpha]_D^{RT}$ = −21.52° (10 cm, *c* = 1.0 g/100 mL, MeOH) (lit.[12] $[\alpha]_D^{25}$ = −21.3° (*c* = 1.0, MeOH)).

**1C. (*R*)- and (*S*)-Dimethyl 6,6′-Dimethylbiphenyl-2,2′-dicarboxylate ((*R*)-15, (*S*)-15). (*S*)-Dimethyl 6,6′-Dimethylbiphenyl-2,2′-dicarboxylate ((*S*)-15).** Thionyl chloride (40 mL, 560 mmol) was added to a stirred suspension of (*S*)-6,6′-dimethylbiphenyl-2,2′-dicarboxylic acid ((*S*)-**16**) (14.71 g, 54.4 mmol, $[\alpha]_D^{RT}$ = +21.8° (10 cm, *c* = 1.0 g/100 mL, MeOH)) in toluene (40 mL) under nitrogen. The mixture was gradually heated to reflux whereupon the acid dissolved. After refluxing for 3 h, the solvents were removed under reduced pressure, and then MeOH (70 mL) was added to the residue, a light yellow-green oil, under nitrogen. The solution was refluxed for 2 h, after the slightly exothermic initial reaction had subsided, and then the solvent was removed under reduced pressure. The residue, a viscous yellow-green oil, was treated with $Et_2O$ (350 mL) and saturated aqueous $NaHCO_3$ (100 mL), and the mixture was vigorously stirred (15 min). The organic phase was washed with saturated aqueous $NaHCO_3$ (1 × 100 mL) and brine (2 × 100 mL) and dried ($Na_2SO_4$). After filtration the solvent was removed and the residual oil was freed of $Et_2O$ under high vacuum (0.5 mm) and crystallized upon cooling, yielding (*S*)-dimethyl 6,6′-dimethylbiphenyl-2,2′-dicarboxylate ((*S*)-**15**), a light yellow solid (16.09 g, 99.1%): mp 44–45 °C; $[\alpha]_D^{RT}$ = +56.4° (10 cm, *c* = 2.0 g/100 mL, benzene) (lit.[12] $[\alpha]_D^{25}$ = +55.8° (*c* = 2.0, benzene)).

**(*R*)-Dimethyl 6,6′-Dimethylbiphenyl-2,2′-dicarboxylate ((*R*)-15).** The procedure described previously for (*S*)-6,6′-dimethylbiphenyl-2,2′-dicarboxylic acid ((*S*)-**16**) was repeated on (*R*)-6,6′-dimethylbiphenyl-2,2′-dicarboxylic acid (13.75 g, 50.9 mmol, $[\alpha]_D^{RT}$ = −21.5° (10 cm, *c* = 1.0 g/100 mL, MeOH)), yielding (*R*)-dimethyl 6,6′-dimethylbiphenyl-2,2′-dicarboxylate ((*R*)-**15**), a light yellow solid (14.85 g, 97.5%): mp 43.5–45 °C; $[\alpha]_D^{RT}$ = −56.2° (10 cm, *c* = 2.0 g/100 mL, benzene) (lit.[12] $[\alpha]_D^{25}$ = −55.3° (*c* = 2.0, benzene)).

**1D. (*R,S*)- and (*S*)-2,2′-Bis(2-1*H*-indenyl)-6,6′-dimethylbiphenyl ((*R,S*)-20 and (*S*)-20). (*R,S*)-2,2′-Bis(2,3-dihydro-2-hydroxy-1*H*-inden-2-yl)-6,6′-dimethyl-1,1′-biphenyl ((*R,S*)-19).** The di-Grignard reagent **18** was prepared by the method of Lappert[13] as follows. To a suspension of Mg (3.062 g, 125 mmol) in dry THF (10 mL) under argon was added 1,2-dibromoethane (0.2 mL) and the mixture was heated briefly to initiate a vigorous reaction. After 15 min THF was removed under vacuum and fresh THF (30 mL) was added. Freshly distilled α,α′-dichloro-*o*-xylene (5.49 g, 31 mmol) was dissolved in THF (390 mL) and slowly added to the stirred Mg suspension over 4 h. The reaction was stirred an additional 12 h, cooled to −78 °C, and a solution of (*R,S*)-**15** (3.10 g, 10 mmol) in dry THF (50 mL) was added over 1 h. The gray mixture was then allowed to warm to room temperature, becoming a green solution. After 2 h at room temperature $H_2O$ (45 mL) was slowly added, the mixture was filtered, and THF was removed under vacuum. To the residue was added $CH_2Cl_2$ (50 mL) and aqueous 1 N $NH_4Cl$ (100 mL), and the layers were then separated. $CH_2Cl_2$ was washed with $H_2O$ (2 × 100 mL), dried ($MgSO_4$) and filtered, and the solvent was removed under vacuum to give a yellow oil (6.07 g). The oil was chromatographed on basic alumina (50 g, Brockman I) and eluted with hexane/$CH_2Cl_2$ (1/1), $CH_2Cl_2$, $CH_2Cl_2$/ethyl acetate (10/1), and finally $CH_2Cl_2$/ethyl acetate (5/1). Removal of solvent under vacuum gave a white solid (3.10 g) which was dissolved in hot $CH_2Cl_2$ (10 mL), diluted with hexane (50 mL) and the $CH_2Cl_2$ was then boiled off. Upon cooling, crystals formed and the mixture was refrigerated (5 °C) for several hours. The crystals were filtered cold and washed with cold hexane (15 mL), giving (*R,S*)-**19** (2.41 g, 52%) as white-yellow crystals: mp 169–171 °C. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 2 H), 7.26–7.21 (m, 4 H), 7.17–7.03 (m, 6 H), 3.65 (d, *J* = 6.1 Hz, 2 H), 3.42 (d, *J* = 6.2 Hz, 2 H), 3.37 (s, 2 H), 3.03 (d, *J* = 6.4 Hz, 2 H), 2.55 (d, *J* = 6.3 Hz, 2 H), 1.94 (s, 6 H). Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77. Found: C, 86.00; H, 6.69.

**(*R,S*)-2,2′-Bis(2-1*H*-indenyl)-6,6′-dimethyl-1,1′-biphenyl ((*R,S*)-20).** To a solution of the diol (*R,S*)-**19** (1.001 g, 2.242 mmol) in $CH_2Cl_2$ (6 mL) was added pTsOH·$H_2O$ (0.211 g, 1.11 mmol). The mixture was stirred rapidly for 28 h. The reaction mixture was then washed with aqueous $NaHCO_3$ (0.23 g, 10 mL) and $H_2O$ (2 × 15 mL) and dried ($MgSO_4$). The solvent was removed on a rotary evaporator, and upon dissolution of the resultant oil in pentane and subsequent concentration a pale yellow solid (0.94 g) was obtained. The product was purified by chromatography over silica gel (20 g) with hexane/$CH_2Cl_2$ (4/1) as the eluant. The concentrated eluate was crystallized by dissolution in hexane/$CH_2Cl_2$ (3/1, 40 mL) followed by gentle warming on a steam bath to remove the $CH_2Cl_2$. Colorless plates (0.807 g) were collected and washed with pentane. A second crop (0.063 g) was obtained similarly from the filtrate for a total yield of 0.870 g (94%) of (*R,S*)-**20**: mp 194–196 °C. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.8 Hz, 2 H), 7.35–7.26 (m, 4 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 7.17–7.04 (m, 6 H), 6.33 (s, 2 H), 3.36 (br s, 4 H). Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.58; H, 6.31.

**(*S*)-2,2′-Bis(2,3-dihydro-2-hydroxy-1*H*-inden-2-yl)-6,6′-dimethyl-1,1′-biphenyl ((*S*)-19).** A THF solution (580 mL) of the di-Grignard was prepared from 7.45 g (42.6 mmol) of α,α′-dichloro-*o*-xylene and 4.14 g (170 mmol) of Mg. To this solution at −78 °C was added (*S*)-dimethyl 6,6′-dimethylbiphenyl-2,2′-dicarboxylate (3.972 g, 13.31 mmol) in THF (75 mL). After complete addition of the diester (*S*)-**15** to the di-Grignard, the reaction mixture was allowed to slowly warm to room temperature and was then stirred a further 2 h before quenching. After a similar workup to that described before, a light yellow solid (8.10 g) was obtained. This was dissolved in $CH_2Cl_2$/cyclohexane (1/2, 45 mL) and was gently warmed on a steam bath to remove $CH_2Cl_2$. Fluffy white crystals (3.672 g) of (*S*)-**19** were collected and were washed with pentane. A further 0.431 g of product was obtained by chromatography of the filtrate over basic alumina (Brockman I, 60 g) with a solvent mixture ranging from hexane/$CH_2Cl_2$ (5/1) to $CH_2Cl_2$/ethyl acetate (10/1) and a subsequent crystallization as described above. The total yield of (*S*)-**19** was 4.104 g (69%): $[\alpha]_D^{RT}$ = +126.1° (10 cm, *c* = 0.1 g/10 mL, benzene); mp 95–97 °C. Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77. Found: C, 86.10; H, 6.67.

**(*S*)-2,2′-Bis(2-1*H*-indenyl)-6,6′-dimethyl-1,1′-biphenyl ((*S*)-20).** The procedure outlined for the preparation of (*R,S*)-**20** was followed with 4.060 g (9.091 mmol) of the diol (*S*)-**19** and 0.866 g (4.55 mmol) of pTsOH·$H_2O$ in 9 mL of $CH_2Cl_2$ with the following changes. The reaction mixture was stirred rapidly for 40 h prior to workup, as described previously. A light orange oil (3.63 g) was obtained which was chromatographed over silica gel (60 g) with hexane/$CH_2Cl_2$ (4/1) as the eluant. The product was isolated as a clear oil, which was identified as pure by $^1H$ NMR and TLC. It was difficult to crystallize and thus was placed under vacuum until a white foam of constant weight (3.22 g, 86%) was obtained. This material was used directly in subsequent reactions.

**2A. Dimethyl Biphenyl-2,2′-dicarboxylate (23).** Thionyl chloride (165 mL) was added to a stirred mixture of diphenic acid (**22**) (50.0 g, 206 mmol) in toluene (165 mL) under nitrogen. The mixture was gradually heated to reflux whereupon the acid dissolved. After refluxing for 3 h the solvents were removed from the brown slightly turbid mixture under reduced pressure, and then MeOH (350 mL) was added to the residue, a light brown solid, under nitrogen. The mixture was refluxed for 1 h, yielding a light yellow-green solution, and then the solvent was removed under reduced pressure and the residue vigorously stirred with $Et_2O$ (250 mL) and saturated aqueous $NaHCO_3$ (150 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ (2 × 200 mL), $H_2O$ (1 × 200 mL), and brine (2 × 100 mL) and dried ($MgSO_4$). After filtration the solvent was removed and the residue, an off-white solid, recrystallized from MeOH, yielding dimethyl biphenyl-2,2′-dicarboxylate (**23**) a white crystalline solid, 48.3 g (87%): mp 73–74 °C (lit.[12] mp 73–74 °C).

**2B. 2,2′-Bis(2-1*H*-indenyl)biphenyl (25).(*R,S*)-2,2′-Bis(2,3-dihydro-2-hydroxy-1*H*-inden-2-yl)-1,1′-biphenyl ((*R,S*)-24).** The di-Grignard of $\alpha,\alpha'$-dichloro-*o*-xylene was prepared from 8.58 g (49.0 mmol) of the dichloride and 4.81 g (198 mmol) of Mg in a solution of 640 mL of THF following the literature procedure.[13] The mixture was cooled to −65 °C and stirred rapidly. A solution of dimethyl biphenyl-2,2′-dicarboxylate (**23**) (4.59 g, 17.0 mmol) in THF (75 mL) was added dropwise over 40 min. A thick white precipitate formed during the addition. The mixture was warmed to 0 °C over 1 h, during which time the precipitate dissolved, giving a green solution. Water (100 mL) was added, the mixture was filtered, and the solvent was removed on a rotary evaporator, giving a yellow oil. This was dissolved in cyclohexane (50 mL), and the solution was concentrated to a yellow solid. After dissolution in $CH_2Cl_2$ (200 mL), the solution was washed with $NH_4Cl$ (2.0 g, 100 mL) and $H_2O$ (2 × 100 mL) and dried ($MgSO_4$). After concentration to a yellow foam (8.6 g), the material was dissolved in warm $CH_2Cl_2$ (50 mL). Hexane (125 mL) was added, and the $CH_2Cl_2$ was removed by gentle heating on a stream bath. After storage at 5 °C for 16 h, fluffy white crystals (4.44 g, 62%) of (*R,S*)-2,2′-bis(2,3-dihydro-2-hydroxy-1*H*-inden-2-yl)-1,1′-biphenyl ((*R,S*)-**24**) were collected and washed with pentane: mp 195–197 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, $J$ = 7.9 Hz, 1.3 Hz, 2 H), 7.43–7.29 (m, 4 H), 7.24–7.03 (m, 10 H), 3.71 (d, $J$ = 16.1 Hz, 2 H), 3.48 (br s, 2 H), 3.34 (d, $J$ = 16.0 Hz, 2 H), 3.17 (d, $J$ = 16.4 Hz, 2 H), 2.74 (d, $J$ = 16.3 Hz, 2 H). Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.16; H, 6.05.

**(*R,S*)-2,2′-Bis(2-1*H*-indenyl)-1,1′-biphenyl (25).** To a solution of diol (*R,S*)-**24** (1.00 g, 2.39 mmol) in THF (40 mL) was added pTsOH·$H_2O$ (0.44 g, 2.33 mmol). Cyclohexane (160 mL) was added to the resultant solution. This was concentrated to a light pink solid on a rotary evaporator at an external bath temperature of 50 °C over 5 min. This procedure of dissolution in THF/$C_6H_{12}$ with subsequent concentration was repeated three more times, with the only change being that a slightly larger quantity of cyclohexane (200 mL) was used during the final step. The resulting black solid was dissolved in $CH_2Cl_2$ (100 mL) and was washed with aqueous $NaHCO_3$ (1.0 g, 100 mL). The aqueous layer was extracted with $CH_2Cl_2$ (2 × 20 mL), and the combined organic layers were dried ($MgSO_4$). Upon removal of the solvent, a white solid (0.74 g) was obtained. This was dissolved in hot $CHCl_3$ (20 mL). Hexane (20 mL) was added. Upon cooling, white needles formed. More hexane (100 mL) was added, and the material was stored at 5 °C for 14 h. White needles (0.573 g) were collected and washed with pentane. A second crop (0.103 g) was obtained from the residue, giving a total yield of 0.676 g (74%) of **25**: mp 211–213 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, $J$ = 7.2 Hz, 2 H), 7.42–7.24 (m, 8 H), 7.21–7.06 (m, 6 H), 6.28 (s, 2 H), 3.28 (d, $J$ = 23.7 Hz, 2 H), 3.10 (d, $J$ = 22.8 Hz, 2 H). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.02; H, 5.49.

**3. (*R,S*)-2,2′-Bis(2-1*H*-indenyl)-1,1′-binaphthalene ((*R,S*)-28).** A solution of (*R,S*)-dimethyl binaphthyl-2,2′-dicarboxylate ((*R,S*)-**26**) (2.67 g, 7.2 mmol) in dry THF (50 mL) was added dropwise over ~1 h to a stirred solution of the di-Grignard reagent (**18**) (prepared by the method of Lappert[13] from magnesium powder (2.01 g, 82.7 mmol) and $\alpha,\alpha'$-dichloro-*o*-xylene (3.60 g, 20.6 mmol) in dry THF (275 mL)) cooled under argon in a −70 °C bath. The reaction mixture which contained a light brown precipitate was allowed to come to room temperature over 2 h, during which time the precipitate dissolved and the solution acquired a brown-red color. After 1 h at room temperature the mixture was filtered under argon and $H_2O$ (5 mL) added to the filtrate. The filtrate was concentrated under reduced pressure and the last trace of solvent (THF and $H_2O$) removed by azeotroping with benzene (2 × 50 mL). The yellow-green solid residue was triturated with $Et_2O$ (100 mL) and filtered out, and the precipitate was washed with $Et_2O$ (3 × 25 mL). The precipitate was then triturated with $H_2O$ (100 mL) and filtered out and the precipitate washed with $H_2O$ (3 × 25 mL), MeOH (2 × 25 mL), and $Et_2O$ (2 × 25 mL) and air dried, yielding an off-white powdery solid (3.3 g). [An analytical sample of (*R,S*)-2,2′-bis(2,3-dihydro-2-hydroxy-1*H*-inden-2-yl)-1,1′-binaphthalene ((*R,S*)-**27**) was obtained from the solid, which contained inorganic salts, by crystallization from acid-free 1,2-dichloroethane/cyclohexane: mp 272–276 °C dec. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.04 (br d, $J$ = 8.8 Hz, 2 H), 7.91 (br d, $J$ = 7.9 Hz, 2 H), 7.86 (d, $J$ = 8.8 Hz, 2 H), 7.46–7.40 (m, 2 H), 7.30–7.01 (m, 10 H), 6.87 (br d, $J$ = 7.3 Hz, 2 H), 3.71 (d, $J$ = 16.1 Hz, 2 H), 3.55 (d, $J$ = 16.1 Hz, 2 H), 3.50 (br s, 2 H), 2.81 (d, $J$ = 16.5 Hz, 2 H), 2.35 (d, $J$ = 16.5 Hz, 2 H). Anal. Calcd for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83. Found: C, 87.46; H, 5.81.] The solid was vigorously stirred with $CH_2Cl_2$ (75 mL), trifluoroacetic acid (3 mL) was added, and the green mixture was stirred overnight. The mixture was filtered, and the filtrate was washed with $H_2O$ (3 × 100 mL) and dried ($Na_2SO_4$). After filtration the solvent was removed and the residue was chromatographed on silica gel (40 g, eluting with hexane/$CH_2Cl_2$; 4/1) to give a white solid (~1.6 g) which was crystallized from $CH_2Cl_2$/hexane ($CH_2Cl_2$ boiled off), yielding (*R,S*)-2,2′-bis(2-1*H*-indenyl)-1,1′-binaphthalene ((*R,S*)-**28**), a white crystalline solid (1.45 g, 41.8%): mp 194–196 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, $J$ = 8.7 Hz, 2 H), 7.91 (br d, $J$ = 8.1 Hz, 2 H), 7.86 (d, $J$ = 8.7 Hz, 2 H), 7.44–7.39 (m, 2 H), 7.30–6.99 (m, 12 H), 6.52 (s, 2 H), 3.19 (d, $J$ = 22.3 Hz, 2 H), 2.99 (d, $J$ = 22.3 Hz, 2 H). Anal. Calcd for $C_{38}H_{26}$: C, 94.57; H, 5.43. Found: C, 94.35; H, 5.18.

**II. Metal Complex Preparations.1. [M((*R,S*)-binapacene)$Cl_2$]. A. Reaction with $TiCl_4$.** A solution of (*R,S*)-2,2′-bis(2-1*H*-indenyl)-1,1′-binaphthalene ((*R,S*)-**28**) (1.45 g, 3.0 mmol) in dry THF (50 mL) under argon was cooled to −78 °C and *n*-butyllithium in hexane (1.6 M, 3.9 mL, 6.3 mmol) was added dropwise over 15 min. The resultant light red solution was stirred at −78 °C for 30 min during which time an orange precipitate appeared. The mixture was warmed to −30 °C and a yellow solution of $TiCl_4$·2THF (1.00 g, 3.0 mmol) in dry THF (50 mL) at ~−20 °C was rapidly cannulated into the dianion mixture. During the addition the precipitate dissolved and the solution became dark brown then black. After 15 min the reaction, which was now dark green with a white precipitate, was warmed to room temperature and then refluxed for 15 h. Anhydrous HCl gas was then bubbled through the room temperature reaction for 20 s. The initial dark green reaction mixture quickly turned a dark brown color and then became progressively lighter in color. The solvents were then removed under reduced pressure during which time a bright blue precipitate ($TiCl_3$·3THF) was noted. The solid residue was slurried with $CH_2Cl_2$ (25 mL) and aqueous 4 N HCl (70 mL) (aqueous phase acquired a purple color). The organic phase was filtered, washed with $H_2O$ (2 × 50 mL), saturated aqueous $NaHCO_3$ (1 × 50 mL), and $H_2O$ (1 × 50 mL) and dried ($Na_2SO_4$). After filtration the solvent was removed under reduced pressure and the residue (1.6 g; $^1$H NMR showed it contained a 1:1 mixture of (*R,S*)-2,2′-bis(2-1*H*-indenyl)-1,1′-binaphthalene ((*R,S*)-**28**) and (*R,S*)-**29**) was chromatographed on silica gel (60 g in hexane). Eluting with 20% $CH_2Cl_2$/hexane gave (*R,S*)-2,2′-bis(2-1*H*-indenyl)-1,1′-binaphthalene ((*R,S*)-**28**) (0.61 g) and, with 30% $CH_2Cl_2$/hexane, (*R,S*)-**29** (0.55 g) as an off-white powdery solid:

mp 278–281 °C dec. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, $J$ = 8.2 Hz, 2 H), 7.82 (d, $J$ = 7.3 Hz, 2 H), 7.73 (d, $J$ = 8.3 Hz, 2 H), 7.50–7.41 (m, 4 H), 7.35–7.14 (m, 8 H), 7.08 (d, $J$ = 7.1 Hz, 2 H), 6.19 (s, 2 H), 4.06 (s, 2 H).

**B. [Ti((*R,S*)-binapacene)$Cl_2$].** A solution of (*R,S*)-**28** (0.398 g, 0.825 mmol) in THF (15 mL) stirred under argon was cooled to −78 °C, and *n*-butyllithium in hexane (1.6 M, 1.2 mL, 2.3 mmol) was added dropwise. The solution became progressively light yellow, red, dark red, and finally yellow-brown. This solution was allowed to warm to −20 °C and then was cooled to −50 °C. A light blue solution of $TiCl_3$·3THF (0.310 g, 0.837 mmol) in a minimum of THF (19 mL) was added to the anion solution in aliquots over a 2-min period. The anion solution became darker. This solution was allowed to warm to room temperature (30 min) and then was refluxed for 2 h. After cooling to room temperature, the THF was removed under reduced pressure. The residue under argon was dissolved in dry $CH_2Cl_2$ (30 mL), and $PtO_2$ (0.0236 g, 0.104 mmol, 13 mol%) was added. This was stirred under 1 atm of $H_2$ for 24 h. This dark red solution was filtered into aqueous 0.5 N HCl (7 mL, 3.5 mmol) and was stirred in air for 18 h. The solution was washed with aqueous 0.5 N HCl and twice with $H_2O$. The organic layer was dried ($MgSO_4$), and the solvents were removed. The solid residue was then dissolved in boiling benzene (5 mL) and pentane (10 mL) was allowed to vapor diffuse into the solution, yielding 0.027 g (5%) of [Ti((*R,S*)-binapacene)-$Cl_2$] as very fine brown needles: $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 8.04 (m, 2 H), 7.95 (m, 2 H), 7.81 (d, $J$ = 8.73 Hz, 2 H), 7.47 (m, 2 H), 7.17 (m, 2 H), 6.96 (m, 2 H), 6.52 (d, $J$ = 2.23 Hz, 2 H), 4.29 (d, $J$ = 2.33 Hz, 2 H), 3.10 (m, 2 H), 2.63 (m, 4 H), 2.21 (m, 2 H), 2.00 (m, 2 H), 1.90 (m, 2 H), 1.51 (m, 4 H). Anal. Calcd for $C_{38}H_{32}Cl_2Ti$: C, 75.13; H, 5.31; Cl, 11.67. Found: C, 74.97; H, 5.21; Cl, 11.28.

**2. [M(norbiphenacene)$Cl_2$]. A. [Ti(norbiphenacene)-$Cl_2$].** A solution of **25** (0.750 g, 1.96 mmol) in dry, degassed THF (35 mL) under argon was cooled to −70 °C and then was treated dropwise by syringe with a solution of *n*-butyllithium in hexane (1.6 M, 2.6 mL, 4.2 mmol) over 10 min. The clear solution turned orange upon the addition of the first few drops of nBuLi, and then turned green when the addition was complete. The solution was stirred at −70 °C for 30 min, during which time a green precipitate formed. Upon warming to −25 °C, the precipitate dissolved. The solution was cooled to −40 °C and a solution of $TiCl_3$·3THF (0.872 g, 2.35 mmol) in THF (55 mL) that had been cooled to 0 °C was added via cannula over 2 min. The reaction mixture immediately turned dark reddish-brown. The cooling bath was removed, and the solution was allowed to warm to room temperature. After 15 min of warming, a fine red precipitate formed. The mixture was stirred at room temperature for 16 h. The solvent was then removed in vacuo, giving a brown oily residue. This was dissolved in dry $CH_2Cl_2$ (50 mL), $PtO_2$ (0.053 g, 0.23 mmol) was added, and the suspension was stirred rapidly at room temperature under $H_2$ for 24 h. During this time, 180 mL of $H_2$ was consumed. The system was flushed with $N_2$, and the dark red mixture was filtered through Celite under $N_2$. After the addition of aqueous 0.5 N HCl (8 mL), the mixture was rapidly stirred under a slow current of air for 20 h. After filtration through Celite, the solution was washed with aqueous 0.5 N HCl (1 × 50 mL) and $H_2O$ (2 × 50 mL) and dried ($MgSO_4$). The solvent was removed, giving a dark red oil. After dissolution of the oil in cyclohexane, the solvent was once more removed, giving a dark reddish-brown granular solid (0.96 g). This material was dissolved in a minimal amount of warm $CH_2Cl_2$. After the addition of hexane (30 mL), the $CH_2Cl_2$ was removed by gentle heating on a steam bath. The solution was allowed to cool to room temperature, whereupon crystallization began, and then was stored at −25 °C for 15 h. Purple crystals (0.361 g) were collected and washed with pentane. The filtrate was concentrated to a red oily residue and dissolved in cyclohexane (20 mL). After crystals formed, pentane (5 mL) was added to the mixture and it was stored at 5 °C for 2 h. Red crystals (0.040 g) were collected and washed with cyclohexane and then pentane. The resulting filtrate was also concentrated and the residue was slurried with cyclohexane (15 mL). A light red powder (0.067 g) was collected and washed with pentane. The three batches were combined and crystallized from hexane (20 mL) as described above. Large purple blocks (0.368 g) of product were obtained. A second crop (0.036 g) was obtained from hexane (10 mL), for a total yield of [Ti(norbiphenacene)$Cl_2$] of 0.404 g, 40%. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.48–7.43 (m, 4 H), 7.40–7.34 (m, 4 H), 6.34 (d, $J$ = 2.6 Hz, 2 H), 4.88 (d, $J$ = 2.6 Hz, 2 H), 3.26–3.16 (m, 2 H), 2.78–2.64 (m, 4 H), 2.38–2.28 (m, 2 H), 2.15–1.95 (m, 4 H), 1.64–1.51 (m, 4 H). Anal. Calcd for $C_{30}H_{28}Cl_2Ti$: C, 71.02; H, 5.56. Found: C, 71.24; H, 5.44.

**B. [Zr(norbiphenacene)$Cl_2$].** To a solution of **25** (1.00 g, 2.61 mmol) in THF (48 mL) under argon was added *n*-butyllithium in hexane (1.6 M, 3.6 mL, 5.8 mmol), as described previously. The dianion produced was cooled to −40 °C, and a solution of $ZrCl_4$·2THF (1.34 g, 3.41 mmol) in THF (29 mL) was added via cannula over 2 min. The resultant dark yellow solution was warmed to room temperature and then was heated to reflux for 4 h. The solvent was removed in vacuo and replaced with dry $CH_2Cl_2$ (55 mL) producing a cloudy green solution with a white precipitate. This was stirred rapidly with $PtO_2$ (0.068 g, 0.30 mmol) under $H_2$ for 14 h, and 230 mL of $H_2$ was consumed. After the system was purged with $N_2$, the mixture was filtered through Celite and then was washed with aqueous 0.5 N HCl (50 mL) and $H_2O$ (2 × 50 mL) and dried ($MgSO_4$). The solution obtained was concentrated to a yellow oil which was dissolved in hexane and concentrated to a yellow foam (0.88 g). The material was purified by chromatography over silanized silica gel (13 g) with benzene as the eluant. The product was crystallized by dissolving it in a minimal amount of $CH_2Cl_2$, adding cyclohexane (25 mL), and removing the $CH_2Cl_2$ by gentle heating on a steam bath. Upon cooling to room temperature, crystallization began. Pentane (10 mL) was added, and the material was stored at −25 °C for 14 h. Yellow prisms (0.432 g, 30%) of [Zr(norbiphenacene)$Cl_2$] were collected and washed with pentane. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.52–7.49 (m, 2 H), 7.43–7.37 (m, 4 H), 7.29–7.26 (m, 2 H), 6.39 (d, $J$ = 2.7 Hz, 2 H), 4.79 (d, $J$ = 2.7 Hz, 2 H), 3.04–2.95 (m, 2 H), 2.74–2.54 (m, 4 H), 2.39–2.30 (m, 2 H), 2.06–1.85 (m, 4 H), 1.66–1.48 (m, 4 H). Anal. Calcd for $C_{30}H_{28}Cl_2Zr$: C, 65.43; H, 5.13. Found: C, 65.70; H, 5.05.

**3. [M(biphenacene)$Cl_2$]. A. [Ti((*R,S*)-biphenacene)$Cl_2$] ((*R,S*)-34).** The procedure outlined for the preparation of [Ti-(norbiphenacene)$Cl_2$], was followed using (*R,S*)-**20** (0.598 g, 1.46 mmol), *n*-butyllithium in hexane (1.6 M, 2.0 mL, 3.2 mmol), and $TiCl_3$·3THF (0.752 g, 2.03 mmol) with the following changes. (*R,S*)-**20** was dissolved in THF (12 mL) prior to the addition of nBuLi. The green solution of the dianion was stirred at −70 °C for 1 h, during which time it became darker in color but did not form a precipitate. Upon warming to −45 °C, it was treated with $TiCl_3$·3THF in THF (45 mL). After warming to room temperature, the reaction mixture was stirred for 4 h with no formation of precipitate. The hydrogenation was performed in dry $CH_2Cl_2$ (35 mL) with $PtO_2$ (0.039 g, 0.17 mmol) over 20 h, during which time 140 mL of $H_2$ was consumed. Aerial oxidation was carried out over 18 h with aqueous 0.5 N HCl (0.9 mL). The workup consisted of washes with aqueous 0.5 N HCl (1 × 50 mL) and $H_2O$ (2 × 50 mL). Initial crystallization of the crude product (0.88 g) was from hexane (20 mL) as described for [Ti-(norbiphenacene)$Cl_2$] and afforded dark red needles (0.352 g) which were collected and washed with pentane. The filtrate was flash chromatographed over silica gel (10 g) with hexane/$CH_2Cl_2$ (3/1) as the eluant and gave a second crop of the product (0.044 g). The two batches were combined and crystallized once more to give purple prisms of [Ti((*R,S*)-biphenacene)$Cl_2$]·0.5$C_6H_{14}$ (0.385 g, 46%). The presence of 0.5 molecule of hexane in the crystal was confirmed by $^1$H NMR. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.43 (dd, $J$ = 7.4 Hz, 1.6 Hz, 2 H), 7.37–7.27 (m, 4 H), 6.34 (d, $J$ = 2.6 Hz, 2 H), 4.23 (d, $J$ = 2.6 Hz, 2 H), 3.26–3.11 (m, 2 H), 2.73–2.62 (m, 4 H), 2.35–2.24 (m, 2 H), 2.12–1.88 (m, 4 H), 2.05 (s, 6 H), 1.63–1.48 (m, 4 H). Anal. Calcd for $C_{32}H_{32}Cl_2$-Ti·0.5$C_6H_{14}$: C, 72.67; H, 6.80. Found: C, 72.70; H, 6.70.

**B. [Zr((*R,S*)-biphenacene)$Cl_2$].** The procedure outlined for the preparation of [Zr(norbiphenacene)$Cl_2$] was followed using (*R,S*)-**20** (0.651 g, 1.59 mmol), *n*-butyllithium in hexane (1.6 M, 2.3 mL, 3.7 mmol), and $ZrCl_4$·2THF (0.879 g, 2.23 mmol) with the following changes. (*R,S*)-**20** was dissolved in THF (11 mL) prior to the addition of nBuLi, and the preparation of the dianion followed the method described in the preparation of [Ti((*R,S*)-biphenacene)$Cl_2$]. $ZrCl_4$·2THF was dissolved in THF (19 mL) and cannulated into the dianion solution, and the mixture was stirred for 4 h at room temperature. The hydrogenation was performed in dry $CH_2Cl_2$ (45 mL) with $PtO_2$ (0.046 g, 0.20 mmol) over 14 h during which time 150 mL of $H_2$ was consumed. After filtration through Celite, the yellow solution was washed with aqueous 0.5 N HCl (1 × 50 mL) and $H_2O$ (3 × 50 mL) and dried ($MgSO_4$). After a second filtration through Celite, it was concentrated to a yellow oil. After dissolution in hexane it was then concentrated to a yellow foam (0.87 g). It was then chromatographed on silanized silica gel (10 g) with benzene as eluant. The yellow foam obtained was dissolved in hexane/cyclohexane/$CH_2Cl_2$ (3/2/1, 12 mL) and gently warmed on a steam bath to remove the $CH_2Cl_2$. After cooling to room temperature, pentane (10 mL) was added and the solution was stored at 5 °C for 15 h. The yellow needles (0.146 g, 16%) of [Zr((*R,S*)-biphenacene)$Cl_2$] were collected and washed with pentane. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.52–7.46 (m, 2 H), 7.36–7.28 (m, 4 H), 6.38 (d, *J* = 2.8 Hz, 2 H), 4.26 (*J* = 2.8 Hz, 2 H), 2.98 (dt, *J* = 16.4 Hz, 5.9 Hz, 2 H), 2.69–2.52 (m, 4 H), 2.31 (dt, *J* = 16.5 Hz, 5.9 Hz, 2 H), 2.03–1.82 (m, 4 H), 1.98 (s, 6 H), 1.64–1.44 (m, 4 H). Anal. Calcd for $C_{32}H_{32}Cl_2Zr$: C, 66.41; H, 5.57. Found: C, 66.22; H, 5.71.

**C. [Ti((*S*)-biphenacene)$Cl_2$] ((*S*)-34).** The procedure outlined for the preparation of [Ti((*R,S*)-biphenacene)$Cl_2$] was followed with (*S*)-**20** (0.988 g, 2.41 mmol), *n*-butyllithium in hexane (1.6 M, 3.4 mL, 5.4 mmol), and $TiCl_3$·3THF (1.07 g, 2.89 mmol), with the following changes. (*S*)-**20** was dissolved in THF (15 mL) prior to the addition of the nBuLi, and $TiCl_3$·3THF was dissolved in THF (65 mL). The hydrogenation was performed in dry $CH_2Cl_2$ (50 mL) with $PtO_2$ (0.055 g, 0.24 mmol) over 16 h, during which time 280 mL of $H_2$ was consumed. Aerial oxidation was carried out over 5 h with aqueous 0.5 N HCl (15 mL), and the workup consisted of washes with aqueous 0.5 N HCl (1 × 75 mL) and $H_2O$ (2 × 75 mL). Purple but slightly discolored crystals (0.601 g) were obtained by crystallization of the crude product from hexane (25 mL) as described for [Ti(norbiphenacene)$Cl_2$]. These were crystallized a second time from hexane (10 mL), affording purple crystals (0.495 g). The combined filtrates of the above crystallizations were flash chromatographed over silica gel (16 g) with hexane/$CH_2Cl_2$ (3/1) as the eluant, yielding 0.160 g of the product. The two batches of product were combined and crystallized from hexane (25 mL) yielding purple crystals of [Ti((*S*)-biphenacene)$Cl_2$]·0.4$C_6H_{14}$ (0.628 g, 46%). The 0.4 hexane of crystallization was confirmed by $^1$H NMR: $[\alpha]_{436}^{RT}$ = −3660° (10 cm, *c* = 4.0 mg/100 mL, $CHCl_3$). Anal. (crystallized from pentane) Calcd for $C_{32}H_{32}Cl_2Ti$·0.66$C_5H_{12}$: C, 72.73; H, 6.91. Found: C, 72.60; H, 6.92.

**D. [Zr((*S*)-biphenacene)$Cl_2$].** The procedure outlined for the preparation of [Zr((*R,S*)-biphenacene)$Cl_2$] was followed with (*S*)-**20** (1.41 g, 3.44 mmol), *n*-butyllithium in hexane (1.6 M, 4.9 mL, 7.8 mmol), and $ZrCl_4$·2THF (1.63 g, 4.13 mmol) with the following changes. (*S*)-**20** was dissolved in THF (17 mL) prior to the addition of nBuLi, and $ZrCl_4$·2THF was dissolved in THF (35 mL). The reaction mixture was refluxed for 4 h. The hydrogenation was performed in dry $CH_2Cl_2$ (70 mL) with $PtO_2$ (0.079 g, 0.35 mmol) over 17 h, during which time 320 mL of $H_2$ was consumed. The workup and chromatography over silanized silica gel (16 g) were as described for the racemic compound. The crude yellow solid obtained (0.7 g) was dissolved in $CH_2Cl_2$/pentane (1/1, 4 mL) and pentane was allowed to vapor diffuse into the solution. A yellow powdery solid (0.444 g) was collected and washed with pentane. After dissolution of the solid in a minimal amount of $CH_2Cl_2$, cyclohexane (20 mL) was added and the $CH_2Cl_2$ was removed by gentle heating on a steam bath. After cooling to room temperature, pentane (20 mL) was added, and the solution was then stored at −25 °C for 24 h. Yellow crystals (0.343 g) of the product were collected and were washed with pentane. A second crop (0.065 g) was obtained from the filtrate from a total yield of [Zr((*S*)-biphenacene)$Cl_2$] (0.408 g, 20%): $[\alpha]_{436}^{RT}$ = −555° (10 cm, *c* = 3.0 mg/50 mL, $CHCl_3$). Anal. (crystallized from pentane) Calcd for $C_{32}H_{32}Cl_2Zr$·0.75$C_5H_{12}$: C, 67.85; H, 6.53. Found: C, 67.98; H, 6.33. The 0.75 pentane of crystallization was confirmed by $^1$H NMR.

**4. [Ti(deshydronorbiphenacene)$Cl_2$] (36).** The procedure outlined for the preparation of [Ti(norbiphenacene)$Cl_2$] was followed with **25** (0.900 g, 2.35 mmol), *n*-butyllithium in hexane (1.6 M, 3.3 mL, 5.3 mmol), and $TiCl_3$·3THF (0.872 g, 2.35 mmol), with the following changes. Compound **25** was dissolved in THF (30 mL) prior to the addition of nBuLi, and $TiCl_3$·3THF was dissolved in THF (40 mL). The reaction mixture was stirred for 14 h at room temperature. It was then cooled to −70 °C, and the orange solid was collected on a fine porous glass frit under argon and was washed with cold THF (3 × 5 mL) and hexane (2 × 5 mL). After drying under vacuum, the crude solid (0.397 g) was obtained. A portion (0.295 g) of this solid was dissolved in $CH_2Cl_2$ (8 mL). Tetrahydrofuran (16 mL) was added, and the $CH_2Cl_2$ was removed under a fast current of argon with gentle heating. On exposure to air crystallization began, and the mixture was left at room temperature for 16 h. Black crystals of [Ti(deshydronorbiphenacene)$Cl_2$] (**36**) (0.0601 g) were collected and washed with THF (1 × 4 mL) and pentane (2 × 5 mL). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.78–7.74 (m, 4 H), 7.65–7.48 (m, 6 H), 7.37–7.32 (m, 2 H), 7.19–7.13 (m, 2 H), 7.06 (dd, *J* = 2.4 Hz, 0.4 Hz, 2 H), 7.01–6.98 (m, 2 H), 5.65 (dd, *J* = 2.4 Hz, 0.4 Hz, 2 H). Anal. Calcd for $C_{30}H_{20}Cl_2Ti$: C, 72.17; H, 4.04. Found: C, 71.93; H, 4.22.

**X-ray Structure Determinations.** Crystal structures of racemic [Ti((*R,S*)-biphenacene)$Cl_2$]·0.5$C_6H_{14}$, (*R,S*)-**34**, and the bis(2-indenyl) complex, **36**, have been determined. Crystallographic data are collected in Table I, and selected bond lengths and angles are collected in Tables II and III. Preliminary photographic characterization showed that both crystals possessed 2/*m* Laue symmetry. The systematic absences in the diffraction data uniquely established the space groups as $P2_1/n$ for both crystals. A solvent molecule, *n*-hexane, lies across a center of inversion in **34**. Bond lengths and thermal parameters in the hexane were constrained due to disorder of this solvent molecule. For **36**, an ellipsoidal semiempirical absorption correction was used. None was required for **34**.

Both structures were solved by direct methods and completed by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were treated as idealized, updated isotropic contributions except for the hexane molecule in **34** for which hydrogen atoms were ignored. Computations were made with the *SHELXTL PLUS* (4.27) program library (G. Sheldrick, Siemens, Madison, WI).

**Acknowledgment.** This work was supported by grants from the National Institutes of Health.

**Supplementary Material Available:** Tables of atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and H-atom coordinates and $B_{iso}$ (14 pages). Ordering information is given on any current masthead page.

OM930427X