Synthesis of Verbenindenes: A New Class of Chiral Indenyl Ligands Derived from Verbenone

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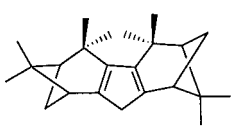
A new class of chiral indenes (verbenindenes), in which a verbenone moiety is annulated to an indene core, is prepared by a sequence of Shapiro lithiation and Nazarov cyclization reactions. Since the initial indenes are resistant to deprotonation, they are isomerized via [1,5]-sigmatropic shifts to obtain indenes that are readily deprotonated with *n*-butyllithium. Reaction of the indenide anions with chloro(1,5-cyclooctadiene)rhodium dimer produces verbenindenyl transition-metal complexes. Coordination of the indenyl ligand may occur with the *gem*-dimethyl bridge of the verbenone moiety syn or anti to the metal. Selectivity favors the less hindered anti complexes, and a crystal structure of a member of this series is presented.

Introduction

Transition-metal complexes containing chiral cyclopentadienyl or indenyl ligands are widely used in asymmetric catalysis and olefin polymerization reactions.[1] Most chiral indene ligands described in the literature are derived from bridged bis(indenes),[2] indenes containing a chiral substituent,[3] a conformationally restricted auxiliary,[2c,4] or bifunctional indenes that are desymmetrized with an additional donor ligand.[5] Another way of incorporating chirality in these ligands is through a fused bicyclic chiral auxiliary. This theme has been extensively developed with cyclopentadienyl ligands;[6] however, reports of chiral annulated indenes where attachment of a chiral bicyclic auxiliary to an indene moiety occurs are scarce.[2b,7] To our knowledge, none of these have been successfully coordinated to transition metals.

Previously, Paquette and co-workers prepared C_2-symmetric cyclopentadienes with bridged bicyclic subunits flanking both sides of the cyclopentadiene, **1** and **2**.[6a] Their objective was to prepare chiral, nonracemic



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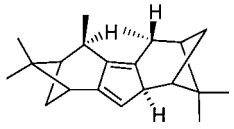

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transition-metal complexes for evaluation as catalysts for asymmetric reactions. The chiral bicyclic auxiliary was derived from (1*R*)-(+)-verbenone. However, these cyclopentadienes were found to be extremely difficult to deprotonate and the authors were unsuccessful in forming transition-metal complexes. Compound **1**, for example, was only deprotonated when refluxed in an excess of *n*-butyllithium in hexanes for 22−24 h. The resultant anion could be trapped with chlorotrimethylsilane but did not react with $CpTiCl_3$ or $CpZrCl_3$. Compound **2** was also found to be sterically constrained and resistant to deprotonation under vigorous conditions. Compound **2**, for example, was unreactive to *tert*-butyllithium/TMEDA in hexanes or sodium amide in ammonia. The authors concluded that these ligands

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(1) (a) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262. (b) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965.

(2) (a) Burk, M. J.; Colletti, S. L.; Halterman, R. L. *Organometallics* **1991**, *10*, 2998. (b) Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276. (c) Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954.

(3) Erker, G. *Pure Appl. Chem.* **1992**, *64*, 393.

(4) (a) Baker, R. W.; Hambley, T. W.; Turner, P.; Wallace, B. J. *Chem. Commun.* **1996**, *39*, 6573. (b) Baker, R. W.; Reed, J. N. H.; Wallace, B. J. *Tetrahedron Lett.* **1998**, *39*, 6573. (c) Baker, R. W.; Wallace, B. J. *Chem. Commun.* **1999**, 1405.

(5) (a) Kataoka, Y.; Saito, Y.; Nagata, K.; Kitamura, K.; Shibahara, A.; Tani, K. *Chem. Lett.* **1995**, 833. (b) Kataoka, Y.; Saito, Y.; Shibahara, A.; Tani, K. *Chem. Lett.* **1997**, 621. (c) Kataoka, Y.; Iwato, Y.; Yamagata, T.; Tani, K. *Organometallics* **1999**, *18*, 5423. (d) Lensink, C. *Tetrahedron: Asymmetry* **1995**, *6*, 2033.

(6) (a) Paquette, L. A.; Bzowej, E. I.; Kreuzholz, R. *Organometallics* **1996**, *15*, 4857. (b) Paquette, L. A.; Sivik, M. R.; Bzowej, E. I.; Stanton, K. J. *Organometallics* **1995**, *14*, 4865. (c) Halterman, R. L.; Tretyakov, A. *Tetrahedron* **1995**, *51*, 4371. (d) Garner, C. M.; Prince, M. E. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA; American Chemical Society: Washington, DC, 1994; Abstract ORGN 183. (e) Chen, Z.; Eriks, K.; Halterman, R. L. *Organometallics* **1991**, *10*, 3349. (f) Erker, G. *Pure Appl. Chem.* **1991**, *63*, 797. (g) Erker, G.; van der Zeijden, A. A. H. *Angew. Chem.* **1990**, *102*, 543. (h) Erker, G. *J. Organomet. Chem.* **1990**, *400*, 185. (i) Chen, Z.; Halterman, R. L. *Synlett* **1990**, *1*, 103. (j) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707. (k) Moriarty, K. J.; Rogers, R. D.; Paquette, L. A. *Organometallics* **1989**, *8*, 1512. (l) Colletti, S. L.; Halterman, R. L. *Tetrahedron Lett.* **1989**, *30*, 3513. (m) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883. (n) Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E. *J. Am. Chem. Soc.* **1987**, *109*, 8105. (o) McLaughlin, M. L.; McKinney, J.; Paquette, L. A. *Tetrahedron Lett.* **1986**, *27*, 5595. (p) Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1986**, *27*, 1461.

(7) Liu, C.; Sowa, J. R., Jr. *Tetrahedron Lett.* **1996**, *37*, 7241.

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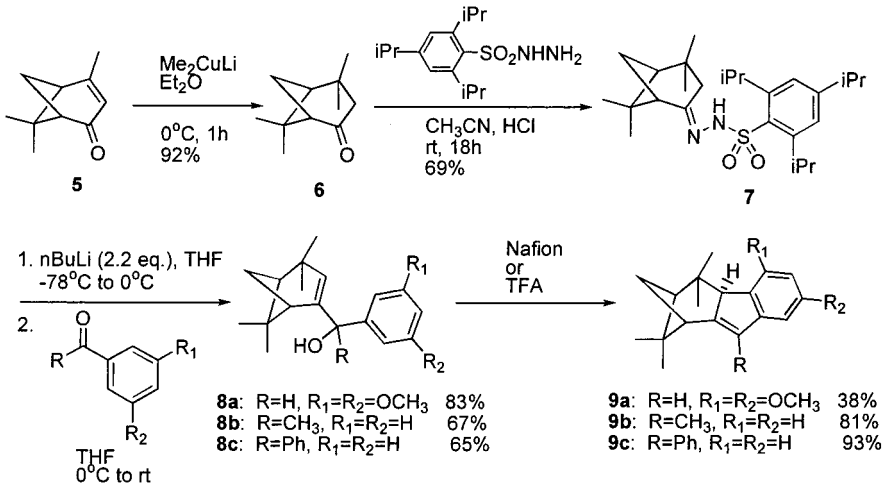
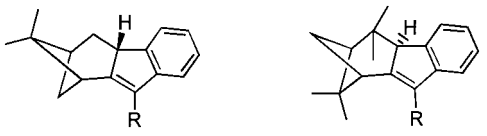
Scheme 1



were "overdesigned" because the bridging bicyclic framework was too sterically congested to allow deprotonation or complexation with a metal.

At the same time, we were interested in chiral annulated indenes having one bridged bicyclic subunit.[7] Although not C_2 symmetric, these should be less sterically congested than doubly annulated cyclopentadienes and may form useful transition-metal complexes. Two series of chiral annulated indenes derived from nopinone (nopinindene, **3**) and verbenone (verbenindene, **4**)



3 **4**

were prepared; however, we were also unsuccessful in deprotonating these derivatives and, thus, could not prepare transition-metal complexes. This paper presents our successful efforts in isomerizing the verbenindenes (**4**) to achieve structures that are readily deprotonated and coordinated to transition metals. These are the first chiral annulated indenes that have been coordinated to transition-metal complexes, and they set the stage for exploring their application in asymmetric catalysis.

Results and Discussion

The methodology for synthesis of the chiral annulated indenes was previously presented in a communication.[7] The readily available (1*S*)-(−)-verbenone (**5**) and its enantiomer[8] are the keys to the synthesis of the chiral ligand. Our synthetic approach begins with the construction of the chiral indene. This is accomplished by employing the Shapiro lithiation reaction,[9] which converts ketones to vinyllithium reagents, and the Nazarov cyclization,[10] as outlined in Scheme 1. For the Nazarov cyclization reaction to be successful, it is necessary to modify verbenone by conjugate addition with lithium dimethyl cuprate to ketone **6**.[6a] Ketone **6** is then treated with triisopropylbenzenesulfonyl hydrazide to prepare the trisyl hydrazone **7**, from which allylic alcohols **8a**−**c** are formed under Shapiro lithiation conditions.[9] Treatment of the allylic alcohols under Nazarov, acid-catalyzed electrocyclic conditions using either the strongly acidic resin Nafion NR50 or trifluoroacetic acid gives the chiral annulated indenes **9a**−**c**.[10]

There are two possible diastereomers of the fused indene products **9a**−**c**. In **9a**, a 9:1 ratio of diastereomers is observed by ^{1}H NMR; however, in **9b** and **9c**, only a single diastereomer is observed. Previously,[7] the stereochemistry of the hydrogen atom at the ring fusion of **9c** was assigned by NOE difference experiments as syn with respect to the *gem*-dimethyl bridge of the verbenone moiety. By analogy, the conformation of **9b** and the major isomer of **9a** are also assigned as syn. Molecular modeling shows that the hydrogen atom at ring fusion is sterically congested for the syn isomers. However, this is also the site of deprotonation that is required for transition-metal synthesis and our attempts at deprotonation were unsuccessful. This was not unexpected, especially given the extreme resistance to deprotonation of **2** observed by Paquette and coworkers.[6a]

We postulated that if we could isomerize the indenyl hydrogen from the sterically inaccessible ring-fused location to a more easily accessible location on the molecule, then deprotonation would be feasible. It is well-known that indenes undergo thermal rearrangements.[11] Experimental studies have shown that these transformations proceed via [1,5]-hydrogen shifts,[12] resulting in a repositioning of the hydrogen on indene.[13]

(8) Sivik, M. R.; Stanton, K. J.; Paquette, L. A. *Org. Synth.* **1993**, *72*, 57.

(9) (a) Shapiro, R. H. *Org. React.* **1976**, *23*, 405. (b) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147. (c) Chamberlin, A. R.; Bloom, S. H. *Org. React.* **1990**, *39*, 1. (d) Chamberlin, A. R.; Liotta, E. L.; Bond, F. T. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, p 77.

(10) (a) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6942. For reviews of the Nazarov reaction see: (b) Habermas, K. L.; Denmark, S. E.; Jones, T. K. In *Organic Reactions*; Paquette, L. A., et al., Eds.; Wiley: New York, 1994; Vol. 45, pp 1−158. (c) Denmark, S. E. In *Comprehensive Organic Synthesis*, Paquette, L. A., Ed.; Pergamon: New York, 1991; Vol. 5, pp 751−784.

(11) (a) Miller, B. *Advanced Organic Chemistry*: *Reactions and Mechanisms*; Prentice Hall: Upper Saddle River, NJ, 1998. (b) Jones, D. W.; Marmon, R. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, *6*, 681. (c) Freidrich, E. C.; Taggart, D. B. *J. Org. Chem.* **1975**, *40*, 720. (c) Gillespie, J. S., Jr.; Acharya, S. P.; Shamblee, D. A. *J. Org. Chem.* **1975**, *40*, 1838. (d) McCullough, J. J.; McClory, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 1962.

(12) For a recent theoretical treatment of [1,5]-H shifts see: Saettel, N. J.; Wiest, O. *J. Org. Chem.* **2000**, *65*, 2231.

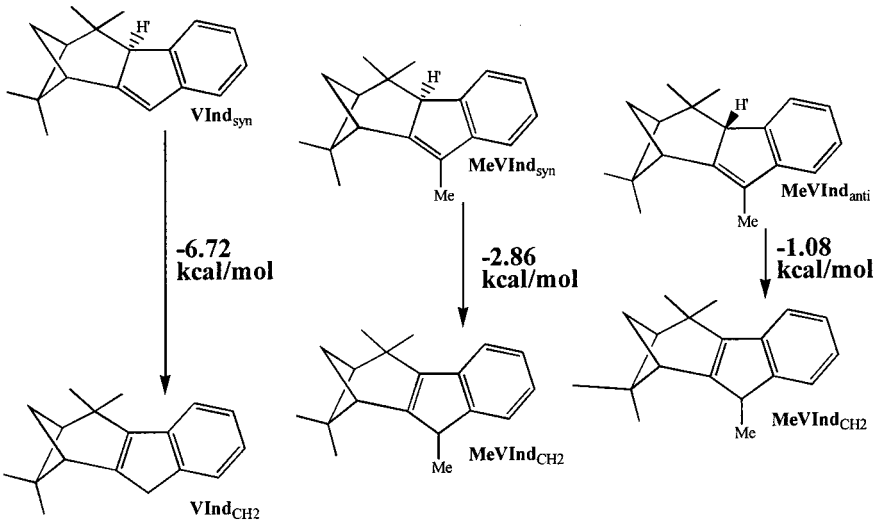
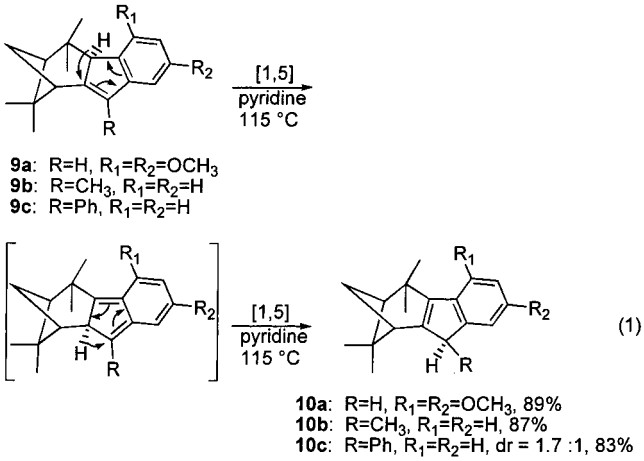


Figure 1. Structures and enthalpies of isomerization of verbenindene derivatives.

A similar isomerization on the chiral annulated indenes **9a**−**c** would reposition the hydrogen atom to a less hindered site. Indeed, this transformation was readily accomplished by refluxing the chiral indenes **9a**−**c** in pyridine (eq 1). The ^{1}H NMR spectrum shows that the



(1)

reaction is extremely clean and quantitative, and the desired verbenindenes **10a**−**c** are isolated in >80% yield.

This transformation appears to proceed through successive [1,5]-hydrogen shifts, as outlined in eq 1. Although only one isomer is possible for **10a**, two isomers are possible for **10b** and **10c**. We observed a single isomer for **10b**, which is likely the isomer in which the benzylic hydrogen is syn to the *gem*-dimethyl bridge of the verbenone moiety. However, for **10c**, a 1.7:1 mixture of diastereomers was observed by ^{1}H NMR. This was surprising, considering that [1,5]-hydrogen shifts occur suprafacially.[11] However, the doubly benzylic proton of **10c** imparts greater relative acidity, resulting in a possible acid/base reaction following the initial formation of **10c** through the sigmatropic process. Never theless, this simple one-pot reaction easily converts the series of verbenone-derived indenes which have sterically inaccessible protons to a series of verbenone-derived indenes with readily accessible protons.

We were interested in understanding the structural factors that drive the conversions of **9a**−**c** to **10a**−**c** (eq 1). Density functional (pBP/DN**) calculations were performed on the three possible isomers of the "unsubstituted" (**VInd**) and methyl-substituted (**MeVInd**) verbenindene derivatives, as illustrated in Figure 1. The calculations indicate that isomerization of the **VInd$_{syn}$** isomer to the **VInd$_{CH2}$** isomer is thermodynamically favorable by 6.72 kcal/mol. However, this isomerization increases the degree of substitution of the carbon−carbon double bond from tri- to tetrasubstituted. Thus, the isomerization of **MeVInd$_{syn}$** to **MeVInd$_{CH2}$**, which involves no change in the degree of substitution of the carbon−carbon double bond, was calculated. It is exothermic by only 2.86 kcal/mol.[14] This suggests that the increase in the degree of substitution of the carbon−carbon double bond is the major driving force for isomerization of the unsubstituted (**VInd**) isomers.

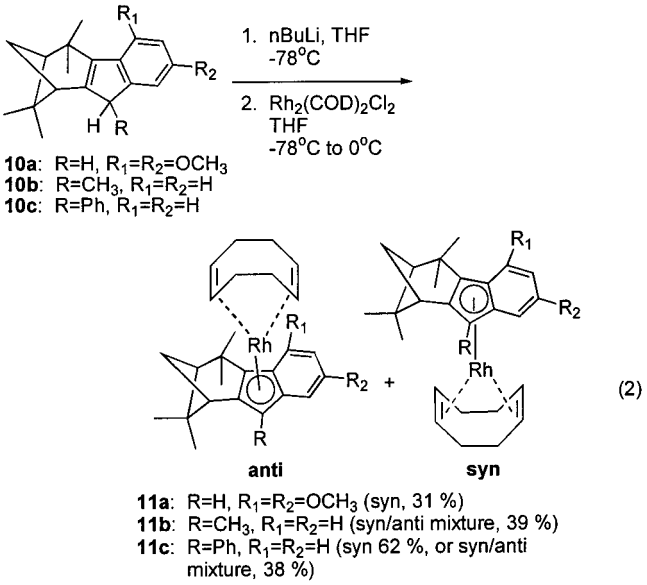
The **MeVInd$_{syn}$** to **MeVInd$_{CH2}$** transformation can only depend on the position of the hydrogen atom (H′) and the location of the carbon−carbon double bond. To gauge the relative importance of these structural factors, the **MeVInd$_{anti}$** to **MeVInd$_{CH2}$** transformation must be considered, as this has the same relative location of the carbon−carbon double bond (exocyclic with respect to the verbenone moiety) but differs in the position of the hydrogen atom (H′). The energy for this transformation is only −1.08 kcal/mol. Assuming this is the minimum energy required to change the location of the carbon−carbon double bond, this suggests that moving the hydrogen atom H′ out of its position syn to the *gem*-dimethyl bridge has a greater impact (−1.78 kcal/mol) on the isomerization reaction than does moving the double bond.

Remarkably, deprotonation of the isomerized indenes **10a**−**c** occurs smoothly on addition of *n*-BuLi at −78

(13) Roth, W. R. *Tetrahedron Lett.* **1964**, 1009.

(14) The calculations also indicate that the syn isomers are less thermodynamically stable than the anti isomers. This contrasts with the results of the Nazarov cyclization reaction (Scheme 1), which gives the syn isomer as the major product. It appears that the formation of the syn isomer is kinetically controlled, as the transition state leading to this isomer is less hindered than that of the anti isomer.[7]

°C. Moreover, adding chloro(1,5-cyclooctadiene)rhodium-(I) dimer and warming to 0 °C enables the complexation of the chiral indene moiety to the rhodium metal to give verbenindenyl transition-metal complexes **11a**−**c** (eq 2).



(2)

However, there are differences in the ways the three ligands coordinate to the metal. The indenide anion of **10a** selectively forms one diastereomer of **11a**; this is the anti diastereomer (vide infra).

The reaction of **10b** with rhodium(I) under similar conditions gives an inseparable mixture of diastereomers (1.6:1 ratio), which likely results from complexation of the metal to both the syn and anti faces of the chiral indenide. This product mixture has only been partially characterized due to instability. Attempts to selectively prepare a single diastereomer by allowing the mixture of the anion of **10b** and the rhodium dimer to slowly warm from −78 to 0 °C over 90 min resulted in the same mixture of diastereomers. Reaction of **10b** was attempted with bis(1,5-cyclooctadiene)rhodium(I) trifluoromethylsulfonate under similar conditions, but no reaction occurred.

When the anion of **10c** is reacted with the rhodium-(I) dimer by rapidly warming the reaction mixture from −78 to 0 °C, a 1.3:1 mixture of diastereomers is observed by ^{1}H NMR. Fortunately, a single diastereomer of **11c** is obtained by slowly warming the anion of **10c** and the rhodium(I) dimer to from −78 to 0 °C over 90 min. Thus, single isomers of complexes **11a** and **11c** are selectively obtained by the appropriate choice of reaction conditions.

X-Ray Crystal Structure Analysis of 11a. Because the verbenindenyl ligand is diastereotopic, we were interested in obtaining a crystal structure of one of the rhodium complexes in order to determine its preferred coordination. In addition, a crystal structure would give a measure of the slip-fold distortion parameters of the indenyl ligand.[15] X-ray diffraction quality crystals of complex **11a** were grown from anhydrous hexane at 4 °C in a Schlenk flask.[16] The molecular structure of **11a** is illustrated in Figure 2.

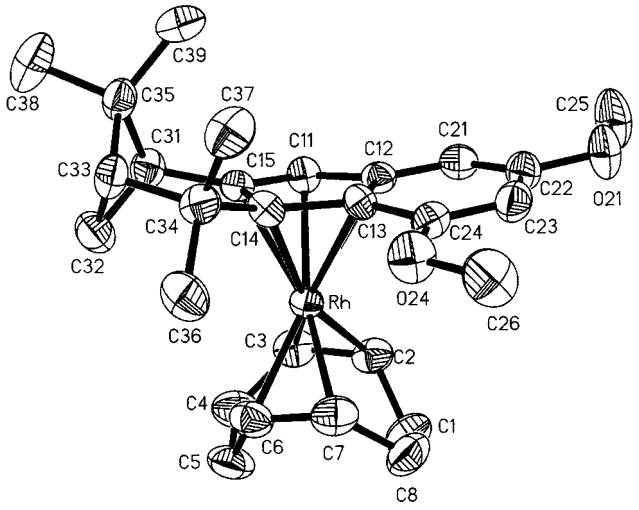


Figure 2. Atomic displacement plot of **11a**. Selected bond distances (Å): Rh−C11, 2.218(6); Rh−C12, 2.380(6); Rh−C13, 2.350(6); Rh−C14, 2.262(6); Rh−C15, 2.256(6); C11−C12, 1.460(9); C12−C13, 1.411(9); C13−C14, 1.475-(9); C14−C15, 1.418(8); C15−C11, 1.425(9). Rh−η^5-C_5-(centroid) = 1.941 Å, ΔMC = 0.120 Å, fold angle (Ω) = 6.0°.

Variations in the Rh−η^5-C_5 bond distances show that the indenyl ligand is slightly distorted toward an η^3−η^2 binding mode typical of indenyl ligands.[17] The degree of distortion of the indenyl ligand from planarity is given in terms of ΔMC and fold angle (Ω).[18] Thus, for **11a** ΔMC is 0.120 Å (ΔMC), indicating that the benzo moiety is more weakly coordinated than the allylic moiety. However, comparison with bis(ethylene)indenylrhodium, IndRh(C_2H_4)$_2$ (ΔMC = 0.152 Å),[19] indicates that there is less distortion from planarity in the ligand of **11a**. That the fold angle (Ω) of **11a** is 6.0° further indicates that the indenyl ligand is distorted toward an η^3−η^2 binding mode, although the degree of distortion is less than that of the unsubstituted indenyl ligand in IndRh(C_2H_4)$_2$, which has a fold angle of 7.4°.

The crystal structure shows that complexation of the rhodium to the chiral indenyl ligand occurs on the face of the ligand which is anti to the *gem*-dimethyl bridge of the verbenone moiety. Therefore, the bridge *gem*-dimethyl group of the indenide seems to provide enough steric hindrance to allow the facial selectivity necessary to form a single diastereomer of **11a**. Because the verbenone moiety has a distinct ^{1}H NMR spectrum, this result allows general assignment of the stereochemical coordination of the indenyl ligand by ^{1}H NMR.

Comparison of the ^{1}H NMR data of **11a** and **11c** indicates they are oriented with the same facial selectivity (Figure 3). The endo bridge hydrogen atom H_a, which is syn to the rhodium, appears as a doublet at δ 2.60 for **11a** and appears at a similar position for **11c** (δ 2.37 d).[20] These have become substantially deshielded from their positions in the free ligand (e.g., δ 1.50 d in **11a**). The exo bridgehead hydrogen atom H_s appears at

(15) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929.
(16) Tidwell, T. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 331.
(17) (a) Veiros, L. F. *Organometallics* **2000**, *19*, 3127. (b) Calhorda, M. J.; Veiros, L. F. *Coord. Chem. Rev.* **1999**, *185*−*186*, 37.
(18) ΔMC is defined as the average bond distance between the metal and the carbons of the benzo moiety minus that between the metal and the allylic moiety. The fold angle is defined as the angle between the planes of the ligand formed by the η^3 moiety (C11, C15, C14) and the η^2 moiety (C11, C12, C13, C15).[15]
(19) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

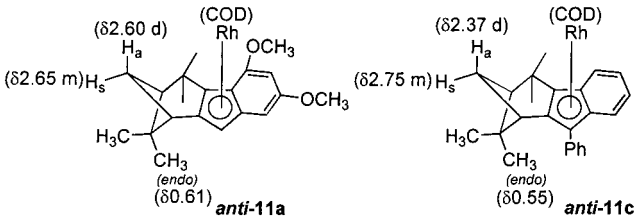


Figure 3. Comparison of stereochemistry of coordination of the indenyl ligands on **11a** and **11c** by ^{1}H NMR spectroscopy. Selected chemical shifts are given in parentheses.

slightly lower field for **11a** (δ 2.65 dt) and **11c** (δ 2.75 dt). In **11a**, the endo bridgehead methyl group lies above the plane of the indenyl ligand; thus, it is strongly shielded (δ 0.61) compared to the resonances of the three other methyl groups at δ 1.29, 1.31, and 1.38 (these resonances have not been assigned). A similar pattern is seen in **11c**, where the endo methyl group has a shift of δ 0.55 while the three other methyl groups appear further downfield (δ 1.36, 1.42, and 1.43). Since **11a** and **11c** exhibit similar patterns in the ^{1}H NMR, they have similar structures.

In the ^{1}H NMR spectrum of **11c**, in which a mixture of diastereomers was obtained, an additional set of resonances (see Experimental Section) is obtained that are dramatically different from those of the anti complex.[21] Although we were unable to isolate this complex, these resonances are more typical of syn coordination, as shown in eq 2.[6k] Integration indicates that the formation of the anti complex is slightly favored over that of the syn complex by a ratio of 1.3:1. For **11b**, however, parameters exist such that complexation of the transition metal to both faces of the indenyl ligand occurs. The reason for the lack of diastereoselectivity for the reaction with ligand **10b** is under investigation.

Conclusion

We have prepared a novel series of chiral annulated indenes derived from verbenone, which we term verbenindenes. Furthermore, we show that the verbenindenes are readily deprotonated and are successfully complexed to rhodium(I). These are the first transition-metal complexes containing indenyl ligands that are fused to a bicyclic chiral auxiliary. The key transformation for developing these ligands is a proposed sigmatropic rearrangement, which allows a sterically inaccessible hydrogen to be isomerized to a more easily accessed location in the chiral annulated indene. The complexation reaction is diastereoselective for two of the three chiral annulated indenes that were prepared. An X-ray crystallographic analysis shows that the rhodium is complexed to the sterically less hindered face which is anti to the *gem*-dimethyl bridge of the verbenone moiety. Given the efficient route developed, as well as the ability to incorporate substitution, the verbenindenes have potential to be used as metallocene ligands for applications in asymmetric synthesis. Their utility in this area is currently under investigation and will be reported in due course.

Experimental Section

All reagents and solvents were used as purchased from Aldrich without purification. The (1*S*)-(−)-verbenone that was purchased from Aldrich was of 94% chemical purity, and an optical purity of 54% was determined by polarimetry. Intermediate **6** ((1*S*,5*S*)-(−)-4,4,6,6-tetramethylbicyclo[3.1.1]heptan-2-one) was prepared using a previously reported method.[6a] The syntheses of intermediates **7**, **8a**−**c**, and **9a**−**c** are given in the Supporting Information. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were recorded at 300 and 75 MHz, respectively, on a Bruker AC-300 spectrometer using tetramethylsilane as an internal standard. All mass spectra were obtained by chemical ionization on a Hewlett-Packard Series 1100 MSD LC/MS. Melting points were determined on a Thomas-Hoover Mel-temp apparatus and are uncorrected. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. Theoretical calculations were performed on an IBM 390E laptop computer with a Pentium II processor or on a Dell Dimension L866r PC with a Pentium III processor using PC Spartan Pro, version 1.0.3 (Wavefunction, Inc., Irvine, CA).

Preparation of [1*S*-(1α,3α,4a*β*)]-5,7-Dimethoxy-1,2,3,4-tetrahydro-2,2,4,4-tetramethyl-1,3-methano-1*H*-fluorene (10a). A solution of **9a** (2.05 g, 6.87 mmol) in anhydrous pyridine (25 mL) was refluxed under a nitrogen atmosphere for 2 h. The reaction mixture was cooled, diluted with ethyl acetate (250 mL), washed with 1 N HCl (2 × 100 mL), water (2 × 100 mL), dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by flash chromatography (silica gel, 4% ethyl acetate/hexane) to give **10a** (1.82 g, 89%) as a white solid: mp 100−103 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.67 (s, 1H), 6.45 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.24 (dd, J = 23.0, 44.1 Hz, 2H), 2.50−2.38 (m, 2H), 1.88 (t, J = 5.9 Hz, 1H), 1.50 (d, J = 8.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.8, 152.6, 147.1, 147.0, 138.3, 126.7, 101.9, 96.9, 56.7, 55.5, 54.7, 43.7, 43.65, 40.2, 38.5, 32.3, 28.6, 27.6, 25.0, 24.9; MS (CI): MH^+ m/z 299, calcd 298.43. Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50: H, 8.78. Found: C, 80.56; H, 8.84.

Preparation of [1*S*-(1α,3α,4a*β*)]-2,2,4,4,9-Pentamethyl-1,2,3,4-tetrahydro-1,3-methano-1*H*-fluorene (10b). A solution of **9b** (0.63 g, 2.50 mmol) in anhydrous pyridine (10 mL) was refluxed under a nitrogen atmosphere for 6 h. The reaction mixture was cooled, diluted with ethyl acetate (200 mL), washed with 1 N HCl (2 × 100 mL) and water (3 × 100 mL), dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by flash chromatography (silica gel, 1% EtOAc/hexane) to give **10b** (0.55 g, 87%) as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 3.16 (q, J = 7.5 Hz, 1H), 2.55−2.45 (m, 2H), 1.89 (t, J = 5.8 Hz, 1H), 1.48 (d, J = 8.9 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 3H), 1.25 (d, J = 7.5 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.98, 150.31, 143.52, 138.03, 126.48, 123.34, 123.09, 119.79, 56.64, 45.26, 43.91, 42.70, 38.50, 36.63, 28.90, 28.73, 25.39, 24.95, 15.06; MS (CI): MH^+ m/z 253, calcd 252.40. Anal. Calcd for $C_{19}H_{24}$: C, 90.42: H, 9.58. Found: C, 90.32; H, 9.46.

Preparation of [1*S*-(1α,3α,4a*β*)]-9-Phenyl-2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-1,3-methano-1*H*-fluorene (10c). A solution of **9c** (2.27 g, 7.23 mmol) in anhydrous pyridine (125 mL) was refluxed under a nitrogen atmosphere for 18 h. The reaction mixture was cooled, diluted with ethyl acetate (400 mL), washed with 1 N HCl (2 × 250 mL) and

(20) The designations H_a (anti) and H_s (syn) indicate the stereochemistry of the methano bridge hydrogens with respect to the *gem*-dimethyl bridge. These assignments are based on general assignments made for bicyclo[3.1.1]heptane derivatives, where H_a is generally upfield from H_s. In addition, H_a generally appears as a doublet, whereas H_s is a multiplet that is coupled to H_a and the two bridgehead protons. See: Badjah-Hadj-Ahmed, A. Y.; Meklati, B. Y.; Waton, H.; Pham, Q. T. *Magn. Reson. Chem.* **1992**, *30*, 807.

(21) Paquette et al. have also shown distinctive differences in the ^{1}H NMR spectra of syn and anti coordination modes of verbenone-derived cyclopentadienide complexes.[6k]

water (3 × 250 mL), dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by flash chromatography (silica gel, 1% ethyl acetate/hexane) to give **10c** (1.89 g, 83%) as a colorless oil. The material was isolated as a 1.6:1 mixture of diastereomers: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42−6.95 (m, 18H), 4.40 (s, 1H), 4.29 (s, 1H), 2.58−2.41 (m, 2H), 2.33−2.25 (m,2H), 1.94−1.80 (m, 2H), 1.60−1.50 (m, 2H), 1.48 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.24 (s, 3H), 0.95 (s, 3H), 0.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.3, 149.7, 149.3, 144.3, 140.2, 139.8, 139.2, 138.9, 130.4, 129.2, 129.0, 128.7, 128.6, 127.0, 126.9, 126.8, 124.7, 124.3, 123.9, 119.9, 119.8, 57.5, 56.8, 56.4, 56.3, 43.9, 43.3, 42.8, 42.6, 38.8, 38.7, 32.8, 32.4, 31.3, 29.1, 28.9, 28.1, 28.0, 25.8, 25.4, 24.8, 24.7; MS (CI) M+H *m*/*z* 315, calcd 314.47. Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.40; H, 8.41.

Preparation of [(1,2,5,6-η)-1,5-Cyclooctadiene]-*anti*-[(4a,4b,8a,9,9a-η)-[1*S*-(1α,3α,4aβ)]-5,7-dimethoxy-1,2,3,4-tetrahydro-2,2,4,4-tetramethyl-1,3-methano-1*H*-fluorenyl]-rhodium (11a). A solution of the indene **10a** (0.51 g, 1.69 mmol) in anhydrous THF (10 mL) was cooled to −78 °C under a nitrogen atmosphere. A solution of *n*-BuLi in hexanes (1.6 M, 1.2 mL, 1.86 mmol) was added dropwise by syringe. After 15 min, chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.42 g, 0.85 mmol) was added in one portion. The reaction mixture was warmed slowly to 0 °C over approximately 90 min. The solvent was then removed in vacuo and replaced with anhydrous hexane (10 mL). The reaction solution was filtered, concentrated, and purified by flash chromatography (neutral alumina, 10% ethyl acetate/hexane). An orange-red eluate was isolated to give 0.27 g (31%) of **11a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.14 (d, J = 2 Hz, 1H), 6.10 (d, J = 2 Hz, 1H), 4.69 (s, 1H), 3.90−3.80 (m, 10H), 2.65 (dt, J = 9.0 Hz, J = 5.5 Hz, 1 H), 2.54 (t, J = 5.4 Hz, 1H), 2.29 (d, J = 9.1 Hz, 1H), 1.92−1.72 (m, 5H), 1.50 (m, 1H), 1.38 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 0.61 (s, 3H); MS (CI) M+H *m*/*z* 509, calcd 508.49.

Preparation of [(1,2,5,6-η)-1,5-Cyclooctadiene][(4a,4b,-8a,9,9a-η)-[1*S*-(1α,3α,4aβ)]-2,2,4,4,9-pentamethyl-1,2,3,4-tetrahydro-1,3-methano-1*H*-fluorenyl]rhodium (11b, Syn and Anti Diastereomeric Mixture). This mixture of compounds was prepared as an inseparable mixture of diastereomers using the same procedure as for **11a**, except with the use of indene **10a** in 39% yield as an unstable orange oil. ^{1}H NMR showed a 1.6:1 mixture of diastereomers by integration of the COD olefin resonances of the anti complex (δ 3.32 m, 3.80 m) and syn complex (δ 3.24 br m, 3.67 br m). Further interpretation of the NMR was complicated by decomposition of the sample. MS (CI): M+H *m*/*z* 462.1, calcd 462.2.

Preparation of [(1,2,5,6-η)-1,5-Cyclooctadiene]-*syn*-[(4a,4b,8a,9,9a-η)-[1*S*-(1α,3α,4aβ)]-9-phenyl-2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-1,3-methano-1*H*-fluorenyl]-rhodium (11c). This compound was prepared using the same procedure as **11a**, except with the use of **10c** in 62% yield as air-stable, red crystals: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49 (d, J = 8.1 Hz, 1H), 7.39 (m, 3H), 7.25 (m, 3H), 7.08−6.96 (m, 2H), 3.77 (m, 2H), 3.32 (m, 2H), 2.92 (t, J = 5.4 Hz, 1H), 2.75 (dt, J = 9.3 Hz, J = 6.0 Hz, 1H), 2.37 (d, J = 9.4 Hz, 1H), 1.96−1.71 (m, 7H), 1.60−1.50 (m, 2H), 1.43 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 0.55 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.1, 129.7, 128.7, 126.3, 123.8, 123.7, 122.2, 121.0, 120.3, 119.8, 108.4, 108.3, 107.9, 107.9, 98.9, 90.6, 90.5, 73.6, 73.4, 70.1, 69.9, 57.7, 44.7, 41.8, 38.6, 34.4, 32.5, 30.7, 30.3, 28.7, 28.0, 25.8; MS (CI) M+H *m*/*z* 525, calcd 524.56. Anal. Calcd for $C_{32}H_{37}Rh$: C, 73.27; H, 7.11. Found: C, 73.10; H, 7.11.

Preparation of [(1,2,5,6-η)-1,5-Cyclooctadiene][(4a,4b,-8a,9,9a-η)-[1*S*-(1α,3α,4aβ)]-9-phenyl-2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-1,3-methano-1*H*-fluorenyl]rhodium (11c, Syn and Anti Mixture of Diastereomers). These were prepared as an inseparable mixture of diastereomers using the same procedure as for **11a**, except with the use of indene **10c**, and the reaction mixture was warmed rapidly from −78 to 0 °C after addition of the rhodium dimer by placing the reaction mixture in an ice bath. The product mixture was obtained in 38% yield as air-stable, red crystals. Because the ^{1}H NMR spectrum of the anti complex is known (see above), these resonances were separated out, leaving the following resonances associated with the syn complex: ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 9.6 Hz, 1H, H_a), 1.29 (s, 3H), 1.47 (s, 3H), 1.65 (s, 3H), 1.7−2.0 (br m, mixture of syn and anti resonances), 2.29 (s, 3H), 2.43 (m, 1H), 2.90 (br s, 2H), 2.68 (m, 1H), 3.57 (br s, 2H), 6.8−7.0 (m, mixture of syn and anti resonances), 7.2−7.4 (m, mixture of syn and anti resonances), 7.80 (d, J = 8.4 Hz, 1H). Integration of the COD olefinic protons (anti, δ 3.32, 3.77; syn, δ 2.90, 3.57) gave an anti:syn ratio of 1.3:1. Anal. Calcd for $C_{32}H_{37}Rh$: C, 73.27; H, 7.11. Found: C, 73.37; H, 7.11.

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Supporting Information Available: Text giving synthesis and characterization data for intermediates **7**, **8a**−**c**, and **9a**−**c** and tables giving calculated energies of verbenindene derivatives in Figure 1 and complete X-ray crystallographic data for **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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