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TETRAHEDRON

Pauson–Khand Approach to Chiral, Diastereomerically Pure Group 4 *ansa*-Metallocene Complexes.

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Abstract: The C_2-symmetric bis(1,6-enynes) *threo*-1,10-diphenyl-5,6-divinyl-1,9-decadiyne and *threo*-9,10-divinyl-5,13-octadecadiyne undergo the intramolecular Pauson–Khand reaction regio- and stereoselectively to give C_2-symmetric bis(enones) with two bicyclo[3.3.0]octyl moieties joined at the C6 position. Experiments aimed at converting the bis(enones) into chiral, diastereopure *ansa*-bridged group 4 metallocene complexes are described.

Keywords: Transition metals, metalation, Pauson–Khand reaction, elimination reactions, polycyclic aliphatic compounds.

INTRODUCTION

Research into chiral group 4 metallocene complexes continues unabated.[1] Much of the interest derives from the catalytic activities exhibited by these complexes in alkene polymerization, but new applications in synthetic organic chemistry are also being discovered.[2-6] The ethylene-bridged bis(tetrahydroindenyl)metal complexes, **1** (Scheme 1), first prepared by Brintzinger in the early 1980's,[7,8] display superb stereoselectivity in both alkene polymerization and small molecule synthesis, and they are still the standards by which newer metallocenes are judged. For a long time the available procedures for the synthesis of **1** were capricious,[9] and the resolution of **1** (for purposes of asymmetric synthesis) was low-yielding and difficult to scale up.[10] These problems have been at least partly circumvented by the development of new experimental procedures.[11,12] However, the synthesis of *analogs* of **1** featuring Cp's with different steric or electronic properties remains a difficult problem.[13] Such analogs would be useful mechanistic probes, and some might prove to be better catalysts or reagents.

The 1,2,3-substitution pattern of the Cp ring and the two-carbon bridge are the two main features of **1** from which its excellent stereochemical properties arise.[13,14] (The two-carbon bridge may be replaced with a one-silicon bridge without affecting the properties adversely.) Complex **2** shows these features in schematic form. In **2**, the R^1 groups provide stereochemical induction by projecting forward into the reactive "wedge" of the complex, while the R^2 groups provide conformational stability and ensure that the C_2 isomer forms preferentially over the C_s isomer in the course of the coordination of the ligand to the metal. Unfortunately,

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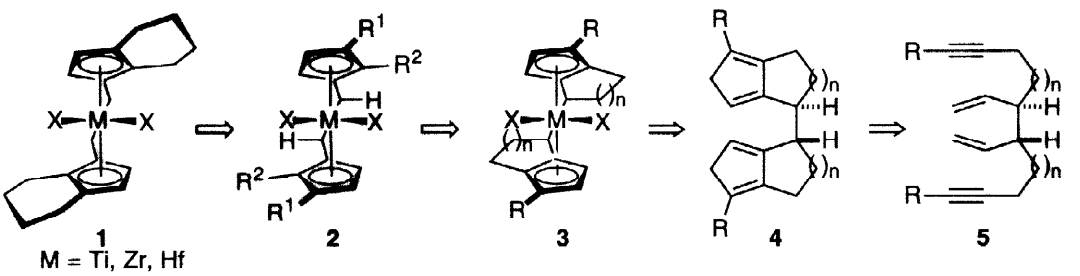
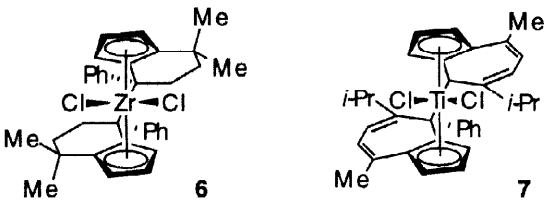


Scheme 1.

there are no good *general* synthetic routes to 1,2-bis(2,3-dialkylcyclopentadien-1-yl)ethanes. Some progress in this area has recently been reported by Halterman, who has used a double Pauson–Khand cyclization to prepare some ethylene-linked bicyclic cyclopentadienes.[15]

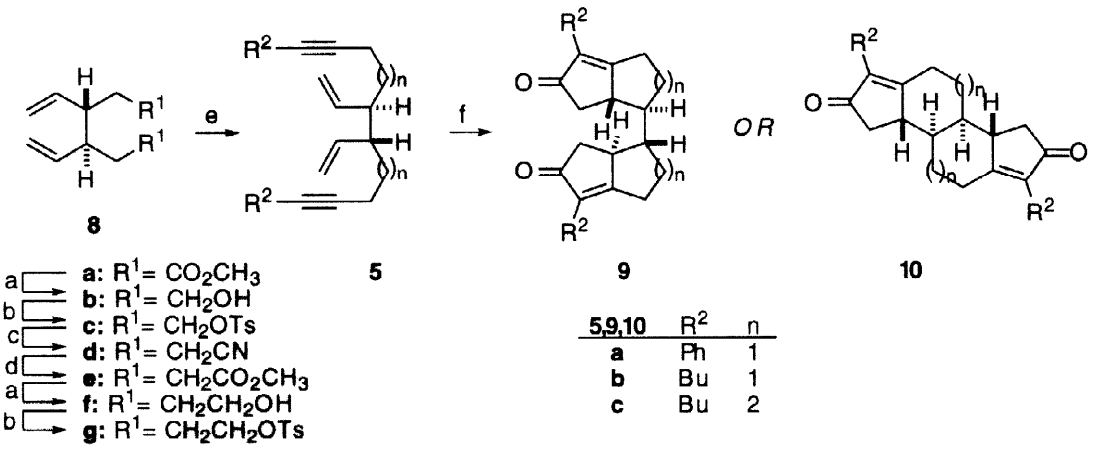
Models of **2** suggest that two C–H bonds on the two-carbon backbone are pointing in just the right direction to be joined up with the R^2 group, as in **3**. Complex **3** retains the 1,2,3-substitution pattern and the general shape of **1** and **2**, including the forward-pointing substituents. It also has a stereogenic backbone that precludes formation of a C_s isomer. In fact, if enantiopure **3** were required for asymmetric synthetic purposes, it could be prepared from enantiopure **4**, thus eliminating the need for resolution of a metallocene complex. Two complexes with structures like **3** have been reported. Erker prepared **6** by reductive coupling of a bicyclic fulvene with Ca, then transmetallation to Zr,[16] and Brintzinger prepared **7** by reductive coupling of guaiazulene with Mg, then transmetallation to $TiCl_3$.[17] Both **6** and **7** formed in racemic, diastereopure form, but neither **6** nor **7** has the forward-projecting groups of **3**, reducing their usefulness for stereoselective synthesis.



It seemed likely that the bicyclo[3.3.0]- or bicyclo[4.3.0]octane (n = 1 or 2, respectively) moieties in **4** could be prepared easily[15] by a Pauson–Khand (P–K) reaction[18] of diastereopure C_2-symmetric dienediynes **5**. Syntheses of **5** and investigations regarding their conversion to ligands **4** and metallocenes **3** are now reported. The synthesis of complex **3** (R = Ph, n = 1) was pursued with an eye toward Hammett studies of catalytic activity. Syntheses of **3** (R = Bu, n = 1, 2) were also investigated.

RESULTS AND DISCUSSION

Dimethyl *threo*-3,4-divinyladipate[19] (**8a**) was reduced to the diol (**8b**), and the ditosylate (**8c**) prepared therefrom was used to alkylate PhC≡CH and BuC≡CH to give dienediynes **5a** and **5b** (Scheme 2). Compound **8c** was also homologated to the dinitrile (**8d**) and thence to the diester (**8e**), the diol (**8f**), and the ditosylate (**8g**), which was used to alkylate BuC≡CH to give dienediyne **5c**. The alkylation of BuC≡CLi with **8c** or **8g** in THF proceeded only in the presence of DMPU, but the alkylation of PhC≡CLi with **8c** proceeded much more



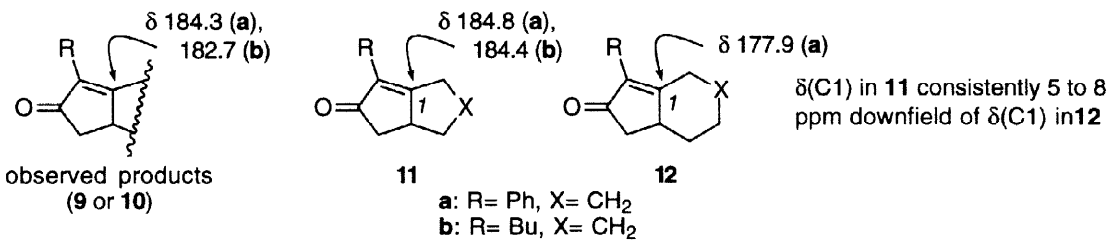
Scheme 2.[a]

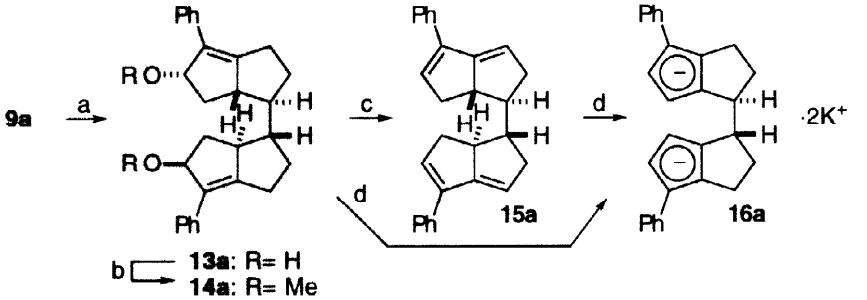
[a] (a) $LiAlH_4$, ether, 0 °C; Fieser work-up. (b) TsCl, pyr, 0 °C. (c) NaCN, EtOH, reflux. (d) 3 M aq. NaOH, reflux; CH_3OH, cat. H_2SO_4, reflux. (e) $R^2C{\equiv}CH$ / BuLi, THF, ±DMPU, 65-80 °C. (f) 2 $Co_2(CO)_8$, CH_2Cl_2, 0 °C; 12 NMO, 0 °C to rt.

smoothly in the *absence* of any polar aprotic solvent. In fact, the alkylation of PhC≡CH with **8c** in the presence of DMPU or DMSO gave **5a** in poorer yield and contaminated with significant quantities of by-products derived from alkylation followed by propargylic deprotonation. Alkylations of RC≡CLi may require that the C–Li bond dissociate to some extent before C–C bond formation can proceed. This dissociation must be considerably more difficult for the BuC≡C$^-$ ion (conjugate acid pK_a = 25) than it is for the less basic PhC≡C$^-$ ion (conjugate acid pK_a = 18.5). The DMPU may serve to promote the dissociation.

Compounds **5a** and **5b** underwent NMO-promoted P–K reactions[20] readily to give the corresponding C_2-symmetric bis(enones) in ca. 50% isolated yield. *Six* new C–C σ bonds were formed in each of these one-pot reactions.[21,22] In neither case was there *any* indication that a regio- or stereoisomer had formed.

Assigning the structures of the P–K products was not straightforward. In principle **5** could act either as a bis(1,6-enyne), giving **9**, or as a bis(1,7-enyne), giving **10**, and a spectroscopic experiment that would distinguish these two possibilities unambiguously could not be devised. An X-ray crystal structure would have solved the problem immediately, but crystals of either P–K product that were suitable for X-ray analysis could not be grown. Some assurance that the desired **9** had indeed been obtained in both cases was derived from the chemical shifts, 184.3 and 182.7 ppm, of the β-carbons of the enone moieties in the P–K products. These values were very close to the chemical shifts, 184.8 and 184.4 ppm, of the corresponding C's in **11a** and **11b**, "halves" of **9a** and **9b**,[23,24] while the corresponding C in **12a**, the "half" of **10a**, had a chemical shift of 177.9 ppm.[25] (Compound **12b**, the "half" of **10b**, was not a known compound.) Moreover, literature values





Scheme 3.[a]

[a] (a) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, 0 °C. (b) NaH, MeI, THF, 70-80 °C, 2 h. (c) NaH, MeI, THF, 80-90 °C, overnight. (d) *t*-BuOK, THF, 95 °C, 1.5 d.

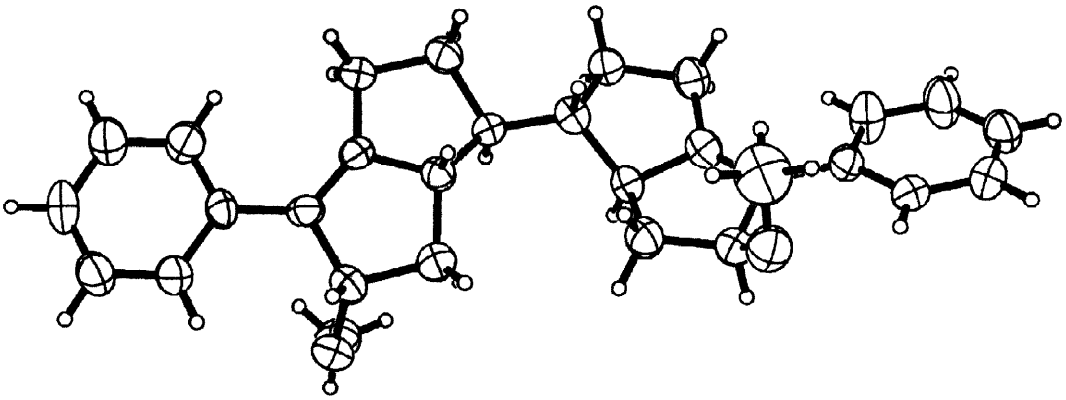
for chemical shifts of the β-carbons of the enone moieties of a series of 5-5 bicyclic enones **11** were consistently 5 to 8 ppm further downfield than they were in the 5-6 analogs, **12**.[23,26] This information suggested that if the P–K products were **10** and not **9**, then the β-carbons should have resonated upfield of 180 ppm, not downfield as was observed. The relative configurations of C5 and C6 in the bicyclo[3.3.0]octenone groups were assumed to be *trans*, in accord with literature precedent.[18] Definitive proof of the structures of the P–K products as **9a** and **9b** was eventually provided by the crystal structure of a later intermediate (vide infra).

To our knowledge, the cyclizations of **5a** to **9a** and **5b** to **9b** constitute the first examples of regioselectivity for 1,6-enyne over 1,7-enyne cyclization in the P–K reaction. Good stereoselectivities are usually observed in the P–K reactions of allylically substituted 1,6-enynes; the stereoselectivities are generally not quite as high as in the reactions of **5a** and **5b**, but rarely are the allylic substituents so large, either.[18]

By contrast to **5a** and **5b**, dienediyne **5c** gave only recovered starting material upon treatment with $Co_2(CO)_8$ under thermal conditions or in the presence of NMO. A Ti-mediated cyclocarbonylation[27] did provide some bis(enone) **9c** in poor (<25%) yield, but the product could not be brought to analytical purity. However, enough **9c** was obtained to show that the β-carbon of the enone moiety of **9c** resonated at 175.1 ppm in the ^{13}C NMR spectrum, 7.6 ppm upfield of **9b**, as expected. The failure of the P–K reaction of **5c** to proceed also provided further confirmation of the regioselectivity in the cyclizations of **5a** and **5b**.

The failure of **5c** to undergo the P–K reaction was puzzling in light of previous successful cyclizations of 1,7-enynes,[18] including a bis(1,7-enyne).[15] Previous 1,7-enynes lacked substituents in the allylic position. Because P–K reactions of allylically substituted enynes are highly stereoselective, the **5c**–$Co_2(CO)_6$ complex must have fewer conformations in which the P–K reaction can proceed than its less substituted congeners, and thus its P–K reaction must proceed more slowly than competing decomposition processes.

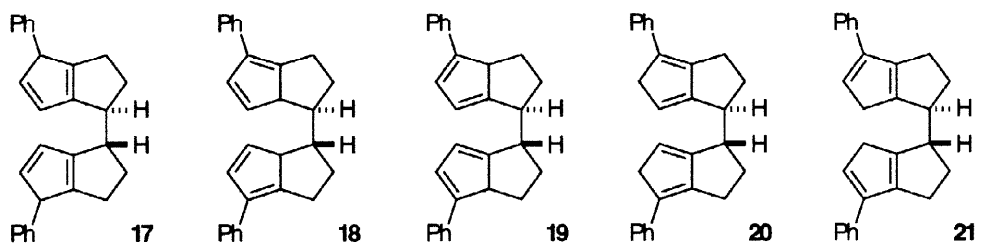
Enone **9a** was stereoselectively reduced to the diol **13a** using the Luche reagent (Scheme 3).[28] The reduction was assumed to take place from the convex faces of the bicyclic enones to give the more sterically hindered diol. Multiple attempts to eliminate H_2O from **13a** under either acidic or basic conditions gave only complex mixtures of unidentified products. However, diol **13a** could be methylated with NaH and MeI in hot THF to give the diether **14a**, which formed X-ray-quality crystals upon flash chromatographic purification.



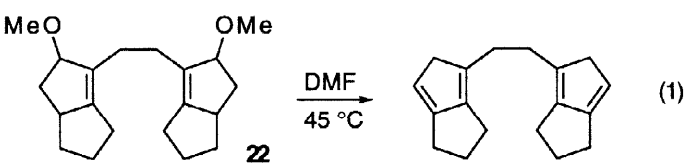
Thermal ellipsoid plot of **14a**

X-ray analysis confirmed the bicyclo[3.3.0]octane structure and the stereochemistry of the six stereocenters to be as predicted.

When the methylation of **13a** was allowed to proceed overnight, a somewhat sensitive nonpolar compound was unexpectedly obtained. The ^{1}H NMR spectrum of the product revealed C_2 symmetry, the presence of two *uncoupled* alkenyl H's, and the absence of any alkoxy H's, suggesting that elimination of MeOH had occurred to give tetraene **15a**, ironically the only tetraene elimination product *lacking* a cyclopentadiene group. Compounds **17-19** are other C_2 dienes that also have two alkenyl H's, but the alkenyl H's in these compounds would be expected to couple with $J \approx 3.0$ Hz, and besides **17-19** would be expected to convert easily to their more substituted isomers **20** and **21**.[16] It was not clear why the elimination proceeded so selectively to give only **15a**. Molecular mechanics and semiempirical calculations showed no substantial differences in energy between **15a** and **17-21**; in fact, **20** and **21** were calculated to be lower in energy than **15a**. The selective formation of **15a** may be explained by a kinetic preference for removal of the most acidic and least hindered H's in **14a**.



It should be noted that the elimination of MeOH from **14a** to give **16a** contrasts sharply with Halterman's report that thermal elimination of MeOH from bis(allylic ether) **22** in DMF gave a tetraene with the two double bonds in the *same* ring (eq. 1).[15] Perhaps the extra substituents in the "rear" rings of **14a** bias their conformations to favor the cross-ring eliminations.



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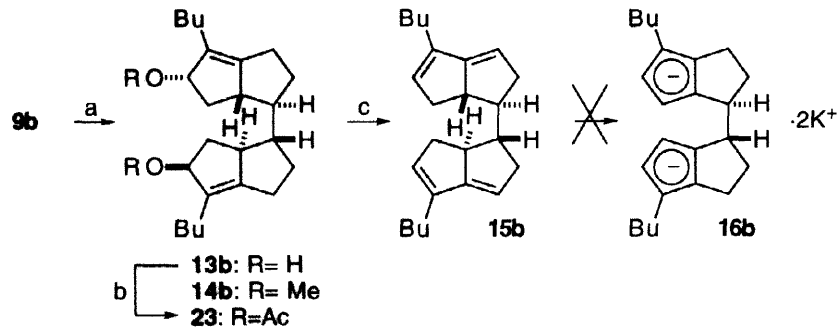


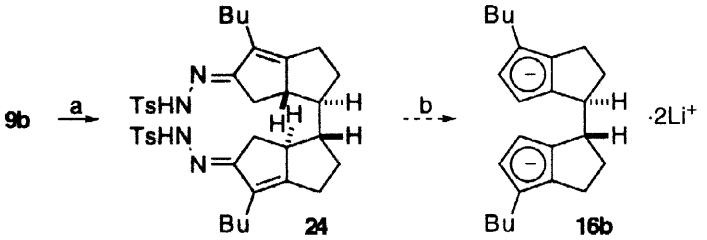
Scheme 4.[a]

[a] (a) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, 0 °C. (b) Ac_2O, Et_3N, cat. DMAP, CH_2Cl_2. (c) cat. $(Ph_3P)_4Pd$, THF, reflux.

Treatment of **15a** with *t*-BuOK in DMSO or THF gave bis(cyclopentadienide) dianion **16a**. In fact, it was soon found that **16a** could be prepared directly from **14a** by treatment with *t*-BuOK in THF. Dianion **16a** could be isolated as a dark red powder. The ^1H NMR spectrum of **16a** in DMSO clearly showed the two Cp H's as doublets (J = 3.3 Hz) at 5.72 and 5.25 ppm. The *ortho* H's on the Ph ring were shifted considerably upfield to 6.39 ppm, and the *para* H somewhat less so to 6.87 ppm, as might be expected from delocalization of the Cp's negative charge into the Ph ring. The ^1H NMR spectrum also showed that small amounts of THF, CH_3OK, and *t*-BuOK were present.

All attempts to add **16a** to $ZrCl_4$ or $TiCl_3$ have so far met with failure. When **16a** itself is mixed with $ZrCl_4 \cdot 2THF$ in THF, and the reaction mixture is evaporated, the ^1H NMR spectrum in C_6D_6 shows the presence of **20** or **21**. Similar results are obtained using donor-ligand-free $ZrCl_4$ in toluene[16] and $TiCl_3 \cdot 3THF$ in THF followed by $CHCl_3$ oxidation.[14] It is unclear whence the two extra H's are derived; a neutral radical derived from **16a** may abstract H· from the solvent. Such a phenylcyclopentadienyl radical would be expected to be quite low in energy. It might form directly by electron transfer from **16a** to the metal, or it might form via the metallocene by C–M bond homolysis. A number of other group 4 metallation methods have been examined, including protonation with AcOH followed by amine elimination with $Zr(NMe_2)_4$ in toluene,[11] silylation with Me_3SiCl followed by transmetallation with $ZrCl_4 \cdot 2THF$ in THF, and stannylation with Bu_3SnCl followed by transmetallation with $ZrCl_4$ in toluene.[29] In no case does the ^1H NMR spectrum of the crude reaction mixture show any sign of a metallocene complex. The reaction mixtures often turn green, supporting the notion that either metallation followed by Cp–Zr(IV) bond homolysis or direct electron transfer is occurring to give a phenylcyclopentadienyl radical and Zr(III). The preference of each bicyclo[3.3.0]octyl substituent to remain in a pseudocquatorial orientation and conformational restrictions about the bond linking the two bicyclic units may also contribute to the failure to achieve successful metallation, although others have achieved metallations with ligands just as constrained as ours.[13]

It was hypothesized that if the problems encountered in the transmetallation of **16a** were caused by the Ph group, they might not be encountered in the butyl series. Accordingly, **9b** was stereoselectively reduced to **13b** using the Luche reagent (Scheme 4).[28] Again, multiple attempts to eliminate H_2O from **13b** under either acidic or basic conditions gave only complex mixtures of unidentified products. Methylation of **13b** proceeded smoothly to give the diether **14b**, but all attempts to eliminate MeOH therefrom also failed. Finally, Pd-catalyzed elimination of AcOH from the diacetate **23** smoothly gave a tetraene, again as the single, undesired



Scheme 5.[a]

[a] (a) xs N_2H_4, EtOH, reflux; TsCl, Et_3N. (b) *n*-BuLi (Shapiro reaction).

regio- and stereoisomer **15b**. Thermal elimination of AcOH from **23** (ca. 250 °C) also gave **15b** as the only identifiable product, although the reaction was much less clean.

The kinetic factors that may promote the regioselective elimination of MeOH from **14a** to give only **15a** (and not **17-21**) are not germane to the regioselective elimination of AcOH from **14b** to give only **15b**. The fact that two mechanistically diverse methods for elimination of AcOH from **14b** give the *same* product suggests that there may be a *thermodynamic* preference for **15b** over its isomers. It must be noted, though, that calculations provide no evidence for such a preference, and the results contrast sharply with Halterman's (eq. 1).[15]

Alas, all attempts to convert **15b** to **16b** failed miserably. Evidently a Ph group was necessary for the isomerization of **15** to **16** to proceed.

A Shapiro reaction[30] route from **9b** to **16b** was also briefly investigated, as the Shapiro reaction was previously used to form cyclopentadienyl anions from cyclopentenones.[15,31] Compound **11b**, a model for **9b**, could be converted to its tosylhydrazone with a two-fold excess of $TsNHNH_2$, a catalytic amount of $TsOH{\cdot}H_2O$, and a large excess of anhydrous $MgSO_4$ in EtOH at room temperature. The same method failed completely to convert **9b** to its tosylhydrazone. (Halterman encountered similar difficulties in his work.)[15] However, when **9b** was combined with a large excess of N_2H_4 in EtOH at reflux, the solvent was evaporated, and the residue was treated with TsCl and Et_3N at 0 °C, the tosylhydrazone **24** could be isolated in 35% yield (Scheme 5). The purification of **24** had to be carried out rapidly, as it decomposed in solution at room temperature. Even though **24** could be obtained by this procedure, its instability and the low yield of tosylhydrazone formation made scale-up impractical, and this approach was also abandoned.

In conclusion, a Pauson–Khand route to novel tetracyclic, diastereopure, C_2-symmetric ligands for group 4 metallocene complexes **3** has been investigated. The P–K reaction was successfully used to prepare the linked bicyclo[3.3.0]octenone framework of the ligands. Unforeseen obstacles, however, prevented either the further transformation of the enones into cyclopentadienyl anions (in the case of *n*-butyl substitution) or the coordination of these anions to Ti or Zr (in the case of phenyl substitution). Improved technologies for executing the P–K reaction may make it possible to prepare linked bicyclo[4.3.0]octenones in better yields in the future. The derived bicyclo[4.3.0]octenols may not undergo elimination with the same undesired regioselectivity that ultimately thwarted the synthesis of **3**.

Acknowledgements. The author thanks Dr. Michael Lloyd for solving the X-ray structure of **14a** and the University of Kentucky for financial support of this work.

EXPERIMENTAL SECTION

General. Standard organic synthetic techniques and reagents were used. Starting materials were commercially available except where noted.

***threo*-3,4-Divinyl-1,6-hexanediol (8b).** Diester **8a** (4.32 g, 19.1 mmol)[19] was slowly added to a suspension of $LiAlH_4$ (1.84 g, 48.4 mmol) in dry ether (ca. 400 mL) cooled to 0 °C under an atmosphere of dry N_2. The suspension was then allowed to warm to room temperature. After 2 h, the solution was cooled to 0 °C again. Then water (1.85 mL), 15% aq. NaOH (1.85 mL), and water (5.55 mL) (Fieser work-up) were added sequentially. The mixture was allowed to warm to room temperature again. The suspension was filtered and evaporated, and the residue was dried in vacuo with heating to give 3.21 g **8b** (18.8 mmol, 99% yield) as a colorless, viscous oil. ^1H NMR (200 MHz, $CDCl_3$): δ 5.61 (m, 1H), 5.05 (m, 2H), 3.64 (m, 2H), 2.25 (m, 1H), 1.89 (s, 1H), 1.63 (m, 2H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 139.0, 116.7, 60.8, 44.6, 35.5. IR (neat): 3346 (vs), 3073, 2928, 1836 (w), 1638, 1422, 1048, 911 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.23; H, 10.53.

***threo*-3,4-Divinyl-1,6-hexanediyl di-*p*-toluenesulfonate (8c).** *p*-Toluenesulfonyl chloride (9.06 g, 47.5 mmol) was added to a solution of **8b** (3.20 g, 18.8 mmol) in pyridine (25 mL, 310 mmol) at 0 °C. After 3 h, the suspension was diluted with ether and water, and sufficient 3 N HCl was added to neutralize all the pyridine. The mixture was shaken, and the aqueous layer was extracted with more ether. The combined organic layers were dried over $MgSO_4$ and evaporated. The material was purified by flash chromatography (20%, then 24% EtOAc/ petroleum ether as eluant) and then dried in vacuo with heating to give 8.60 g **8c** (18.0 mmol, 96% yield) as an extremely viscous oil. On one occasion the oil set to a waxy solid, mp 74-76 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.78 (dd, 1.7 Hz, 8.3 Hz, 2H), 7.35 (d, 8.1 Hz, 2H), 5.36 (ddd, 10.1 Hz, 9.3 Hz, 17.0 Hz, 1H), 5.01 (dd, 1.9 Hz, 10.2 Hz, 1H), 4.85 (dd, 1.9 Hz, 17.0 Hz, 1H), 3.97 (m, 2H), 2.45 (s, 3H), 2.05 (m, 1H), 1.58 (m, 2H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 144.7, 136.5, 133.1, 129.8 (x2), 127.9 (x2), 118.4, 68.5, 43.9, 31.9, 21.6. IR (neat): 3072, 2979, 2922, 1639, 1598, 1463, 1422, 1363, 1307, 1292, 1177, 1097, 964, 910, 817, 763, 664 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_6S_2$: C, 60.22; H, 6.32. Found: C, 60.27; H, 6.35.

***threo*-4,5-Divinylsuberonitrile (8d).** A mixture of **8c** (10.03 g, 21.0 mmol) and NaCN (2.57 g, 52.4 mmol) in EtOH (100 mL) was allowed to reflux for 3.5 h. The solvent was evaporated, and the residue was dissolved in a mixture of ether and water and shaken. The organic layer was shaken with water, then brine, then dried over $MgSO_4$ and evaporated. The brown, viscous oil was purified by flash chromatography (18%, then 20% EtOAc in petroleum ether as eluant) and Kugelrohr distillation to give **8d** (3.10 g, 16.5 mmol, 79% yield) as a pale yellow oil. ^1H NMR (200 MHz, $CDCl_3$): δ 5.50 (m, 1H), 5.21 (m, 2H), 2.1-2.45 (m, 3H), 1.5-1.85 (m, 2H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 135.8, 119.3, 47.1, 28.3, 15.0, one peak obscured. IR (neat): 3076, 2934, 2881, 2245, 1638, 1425, 1000, 926 cm^{-1}. Anal. Calc. for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57. Found: C, 76.29; H, 8.58.

Dimethyl *threo*-4,5-divinylsuberate (8e). A suspension of **8d** (3.10 g, 16.5 mmol) in 3 N NaOH (80 mL) and EtOH (10 mL) was allowed to reflux overnight. The solution was then allowed to cool, and it was

extracted with ether. The aqueous layer was then acidified with 3 N HCl, and a thick white precipitate formed. Salt was added and allowed to dissolve, and the suspension was then filtered. The solid was rinsed with water to give the diacid as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.3 (broad, 1H), 5.52 (m, 1H), 5.08 (m, 2H), 2.32 (m, 2H), 2.06 (m, 1H), 1.45-1.85 (m, 2H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 180.2, 137.9, 117.6, 47.8, 31.9, 27.6. IR (KBr): 3057, 2931, 2726 (shoulder), 1698, 1428, 1325, 1263, 1207, 920 cm^{-1}. Anal. Calc. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.74; H, 8.34.

The diacid was redissolved in MeOH, 8 drops conc. H_2SO_4 were added, and the solution was allowed to reflux overnight. After cooling, the reaction was quenched with sat. aq. $NaHCO_3$. The organic solvent was evaporated, and the residue was dissolved in ether and water and shaken. The organic layer was shaken with brine. The combined aqueous layers were back-extracted with ether. The combined organic layers were dried over $MgSO_4$ and evaporated to give **5e** (3.81 g, 15.0 mmol, 91% yield over two steps) as a pale yellow liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.52 (m, 1H), 5.06 (m, 2H), 3.65 (s, 3H), 2.27 (m, 2H), 2.03 (m, 1H), 1.5-1.8 (m, 2H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 173.9, 138.0, 117.1, 51.2, 47.8, 31.8, 27.6. IR (neat): 3074, 2951, 1738, 1436, 1251, 1194, 1171, 997, 918 cm^{-1}. Anal. Calc. for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.26; H, 8.51.

***threo*-4,5-Divinyl-1,8-octanediol (8f).** Diester **8e** (3.81 g, 15.0 mmol) was added to a suspension of $LiAlH_4$ (1.42 g, 37.4 mmol) in dry ether (200 mL) at 0 °C. The suspension was allowed to warm to room temperature. After 1 h, the suspension was cooled to 0 °C again. The reaction was quenched by the sequential slow addition of H_2O (1.42 mL), 15% aq. NaOH (1.42 mL), and H_2O (4.26 mL). After warming to room temperature, the suspension was filtered and evaporated to give a colorless oil. The oil solidified upon standing at room temperature, and it was dried in vacuo to give **8f** (2.97 g, 15.0 mmol, 100% yield) as colorless crystals. The crystals began to soften at 51 °C, but they did not lose their shape and flow until 61 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.55 (ddd, 9.1 Hz, 10.3 Hz, 16.9 Hz, 1H), 5.05 (dd, 2.2 Hz, 10.3 Hz, 1H), 4.97 (dd, 2.2 Hz, 16.9 Hz, 1H), 3.61 (broad t, 2H), 2.03 (m, 1H), 1.73 (broad s, 1H), 1.2-1.7 (m, 4H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 139.5, 116.1, 62.9, 48.1, 30.6, 28.8. IR (KBr): 3301, 3077, 2914, 2851, 1838 (w), 1637, 1432, 1074, 1059, 997, 917, 768 cm^{-1}. Anal. Calc. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.67; H, 11.32.

***threo*-4,5-Divinyl-1,8-octanediyl di-*p*-toluenesulfonate (8g).** A solution of **8f** (2.97 g, 15.0 mmol) in pyridine (24 mL, 300 mmol) was cooled to 0 °C, and *p*-toluenesulfonyl chloride (7.09 g, 37.2 mmol) was added. After 2 h, the mixture was diluted with ether and shaken with 3 N HCl. The organic layer was washed with water and sat. aq. $NaHCO_3$, dried over $MgSO_4$, and evaporated. Flash chromatography (16%, then 18%, then 20% EtOAc in petroleum ether as eluant) gave **8g** (6.63 g, 13.1 mmol, 87% yield) as a viscous yellow oil after drying in vacuo with heating. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78 (~d, 8.4 Hz, 2H), 7.34 (d, 8.1 Hz, 2H), 5.40 (dt, J_d = 16.9 Hz, J_t = 10.2 Hz, 1H), 5.00 (dd, 2.1 Hz, 10.2 Hz, 1H), 4.88 (dd, 2.1 Hz, 17.0 Hz, 1H), 3.98 (t, 6.4 Hz, 2H), 2.45 (s, 3H), 1.84 (m, 1H), 1.56 (m, 2H), 1.27 (m, 2H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 144.6, 138.4, 133.1, 129.8 (x2), 127.8 (x2), 116.8, 70.5, 47.7, 28.3, 26.7, 21.6. IR (neat): 3070, 2928, 2873, 1638, 1598, 1356, 1175, 1097, 961, 928, 816, 665 cm^{-1}. Anal. Calc. for $C_{26}H_{34}O_6S_2$: C, 61.63; H, 6.76. Found: C, 61.58; H, 6.87.

***threo*-1,10-Diphenyl-5,6-divinyl-1,9-decadiyne (5a).** *n*-BuLi (2.80 mL of 1.58 M in hexane, 4.4 mmol) was added to a solution of phenylacetylene (480 μL, 4.37 mmol) in dry THF (15 mL) at 0 °C in a sealable

flask under an atmosphere of dry N_2. The solution was allowed to warm to room temperature. Then a solution of **8c** (963 mg, 2.01 mmol) in THF (ca. 6 mL) was added. The flask was sealed, and the mixture was heated to 65-70 °C. After 3 d, the mixture was allowed to cool to room temperature. It was diluted with ether and shaken with 1 N HCl and brine, dried over $MgSO_4$, and evaporated. The material was purified by flash chromatography (7% CH_2Cl_2/ petroleum ether as eluant) and then dried in vacuo with heating to give **5a** (563 mg, 1.66 mmol, 83% yield), 97% pure by GC-MS, as a yellow oil. ^1H NMR (200 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.26 (m, 3H), 5.59 (m, 1H), 5.10 (m, 2H), 2.35 (m, 3H), 1.69 (m, 2H). $^{13}C\{H\}$ NMR and APT (50 MHz, $CDCl_3$): δ 138.3 (odd), 131.5 (odd), 128.1 (odd, x2), 127.5 (odd, x2), 124.0, 117.1 (even), 90.1, 80.7, 47.2 (odd), 31.8 (even), 17.3 (even). IR (neat): 3075, 2925, 2231 (w), 1638, 1598, 1490, 1426, 1070, 995, 916, 755, 691 cm^{-1}. This compound did not give a satisfactory elemental analysis.

***threo*-9,10-Divinyl-5,13-octadecadiyne (5b).** *n*-BuLi (3.1 mL of 1.58 M in hexane, 4.93 mmol) was added to a solution of 1-hexyne (580 μL, 5.05 mmol) in dry THF (15 mL) in a sealable flask at 0 °C. After 15 min, a solution of **8c** (963 mg, 2.01 mmol) in THF (ca. 6 mL) was added. The flask was sealed, and the mixture was heated to 75 °C. After 3 d, the reaction had not yet proceeded to completion, so DMPU (660 μL, 5.46 mmol) was added, and the flask was resealed and heated to 75 °C overnight. The cooled mixture was poured into a mixture of petroleum ether and aq. NaCl and shaken, and the aqueous layer was extracted further with petroleum ether. The combined organic layers were shaken with water, then brine, dried over $MgSO_4$, and evaporated. Flash chromatography (2%, then 2.5%, then 3% CH_2Cl_2/ petroleum ether as eluant) gave **5b** (425 mg, 1.42 mmol, 71% yield) as a nearly colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ 5.52 (m, 1H), 5.03 (m, 2H), 2.14 (m, 5H), 1.44 (m, 6H), 0.91 (t, 7.1 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 138.6, 116.6, 80.3, 79.8, 46.9, 32.1, 31.2, 21.9, 18.4, 16.6, 13.6. IR (neat): 3073 (w), 2956, 2931, 2861, 1638 (w), 1458, 1432, 995, 916 cm^{-1}. This compound did not give a satisfactory elemental analysis.

***threo*-10,11-Divinyl-5,15-eicosadiyne (5c).** A solution of 1-hexyne (4.00 mL, 34.8 mmol, flushed through alumina) in dry THF (80 mL) under N_2 in a sealable flask was cooled to 0 °C, and *n*-BuLi (20.5 mL of 1.59 M in hexane, 32.6 mmol) was added. The solution was allowed to warm to room temperature. Then a solution of **8g** (6.63 g, 13.1 mmol) in THF (ca. 20 mL) was added, followed by DMPU (4.00 mL, 33.1 mmol). The flask was sealed, and the solution was heated to 80 °C overnight. The reaction was quenched with sat. aq. NH_4Cl, and the mixture was transferred to a round-bottom flask and evaporated. The residue was diluted with ether, petroleum ether, water, and brine and shaken. The mixture separated into three layers. The top layer was separated and washed with water and brine. The washes were combined with the bottom two layers and re-extracted with an ether/ petroleum ether mixture. The extract was washed with water, then brine. The combined organic layers were dried over $MgSO_4$ and evaporated. Flash chromatography (3%, then 4% CH_2Cl_2 in petroleum ether as eluant) gave **5c** (2.54 g, 7.77 mmol, 59% yield) as a pale yellow liquid, 99% pure by GC/MS. ^1H NMR (200 MHz, $CDCl_3$): δ 5.54 (ddd, 9.1 Hz, 10.4 Hz, 16.8 Hz, 1H), 5.03 (dd, 2.2 Hz, 10.4 Hz, 1H), 4.97 (dd, 2.2 Hz, 16.8 Hz, 1H), 2.14 (m, 4H), 2.01 (m, 1H), 1.43 (m, 8H), 0.91 (t, 7.1 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 139.7, 115.8, 80.2, 80.0, 47.8, 31.8, 31.2, 27.0, 21.9, 18.7, 18.4, 13.6. IR (neat): 3072, 2932, 2861, 1638, 1457, 1434, 1331, 995, 913 cm^{-1}. This compound did not give a satisfactory elemental analysis.

***(5RS,5'RS,6RS,6'RS)*-Bi(3-oxo-2-phenylbicyclo[3.3.0]oct-1(2)-en-6-yl) (9a).** Dienediyne **5a** (2.15 g, 6.27 mmol) in CH_2Cl_2 (ca. 10 mL) was added to a solution of $Co_2(CO)_8$ containing 1-5% hexane (3.96 g, 13.3-

13.9 mmol) in dry CH_2Cl_2 (ca. 100 mL) under N_2. Gas evolved from the dark brown solution. After 100 min, the solution was cooled to 0 °C, and *N*-methylmorpholine *N*-oxide (9.74 g, 83.1 mmol) was added.[20] Gas evolved again. The ice bath was replaced with a room temperature water bath, and the solution was allowed to stir overnight. The suspension was filtered through Celite to give purple solid and a dark blue filtrate. The filtrate was shaken with a mixture of 3 N HCl and water to give a muddy brown organic layer. The aqueous layer was back-extracted twice with a little CH_2Cl_2, and the combined organic layers were filtered through Celite again, dried over $MgSO_4$, and evaporated. The dark brown solid was transferred to a fritted funnel using EtOAc and washed extensively with EtOAc. TLC showed the complete absence of any of the desired product in the dark brown filtrate. The light gray solid, which showed only one mobile spot by TLC, was redissolved in CH_2Cl_2 and purified by flash chromatography (4%, then 6% ether/ CH_2Cl_2 as eluant) to give 1.23 g **9a** (3.12 mmol, 50% yield) as a white solid. Fine needles were obtained by recrystallization from toluene, mp 229-230 °C (discolors at 227 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (~d, ~8.2 Hz, 2H), 7.40 (~t, ~7.2 Hz, 2H), 7.31 (tt, 7.3 Hz, ~2 Hz, 1H), 2.97 (broad dd, 18.9 Hz, 11.1 Hz, 1H), 2.86 (dd, 17.5 Hz, 6.5 Hz, 1H), 2.70 (m, 2H), 2.33 (dd, 17.5 Hz, 3.3 Hz, 1H), 2.25 (m, 1H), 1.86 (m, 1H), 1.53 (m, 1H). ^{13}C{H} NMR and APT (50 MHz, $CDCl_3$): δ 207.5, 184.3, 134.8, 131.3, 128.3 (odd, x2), 128.2 (odd, x2), 127.9 (odd), 49.7 (odd), 48.6 (odd), 42.9 (even), 31.8 (even), 27.1 (even). IR (KBr): 2980, 2903, 1693 (double peak), 1637, 1077, 1047, 879, 764, 696 cm^{-1}. Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64. Found: C, 85.32; H, 6.84.

***(5RS,5'RS,6RS,6'RS)*-Bi(3-oxo-2-butylbicyclo[3.3.0]oct-1(2)-en-6-yl) (9b).** Dienediyne **5b** (415 mg, 1.39 mmol) in CH_2Cl_2 (ca. 6 mL) was added to a solution of $Co_2(CO)_8$ containing 1-5% hexane (827 mg, 2.92 mmol) in dry CH_2Cl_2 (ca. 50 mL) under N_2. Gas evolved from the dark brown solution. After 100 min, the solution was cooled to 0 °C, and *N*-methylmorpholine *N*-oxide (4.10 g, 35.0 mmol) was added.[20] Gas evolved again. The solution was allowed to warm to room temperature and stir overnight. The suspension was filtered through Celite to give a dark blue filtrate. The filtrate was shaken with 1 *N* HCl, then brine. The aqueous layer was back-extracted with CH_2Cl_2 each time. The combined organic layers were dried over $MgSO_4$ and evaporated. Flash chromatography (20% EtOAc/ petroleum ether as eluant) gave **9b** (281 mg, 0.79 mmol, 57% yield) as a waxy tan solid, mp 69-70 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.45-2.72 (m, 4H), 2.00-2.32 (m, 4H), 1.14-1.36 (m, 1H), 1.20-1.52 (m, 5H), 0.89 (t, 7.0 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 209.6, 182.7, 136.7, 50.3, 48.5, 41.9, 31.7, 30.1, 25.0, 23.4, 22.6, 13.8. IR (KBr): 2955, 2939, 2859, 1701, 1654, 1454, 1349, 1062 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.22; H, 9.81.

***(5RS,5'RS,6RS,6'RS)*-Bi(8-oxo-9-butylbicyclo[4.3.0]non-9-en-5-yl) (9c).** A solution of Cp_2TiCl_2 (549 mg, 2.20 mmol) in dry THF (25 mL) under N_2 was cooled to –78 °C, and a solution of *n*-BuLi (2.75 mL of 1.6 M in hexane, 4.37 mmol) was added.[27] After 5 min, dienediyne **5c** (380 μL, 1.00 mmol) was added, and the solution was allowed to stir overnight at room temperature. The solvent was evaporated, and dry $CHCl_3$ (20 mL) was added. The atmosphere was then immediately flushed with CO. After 4.25 h, the solvent was evaporated. The solid residue was extracted with ether, filtered thru Celite, and evaporated again. Flash chromatography (16%, then 20% EtOAc/ petroleum ether) gave a yellow solid (146 mg) that consisted mostly of **9c**. This material was redissolved in a mixture of ether and petroleum ether and flushed through a short column of silica gel, eluting with 50% ether/ petroleum ether, to give a (less) yellow solid (134 mg). The solid was washed with a minimum amount of ether, then petroleum ether, to give mostly pure **9c** (93 mg, 0.24 mmol, 24% yield) as white crystals, mp 132-134 °C (melts with dec.). The washes were also evaporated to

give a waxy yellow solid (44 mg) that contained more **9c**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.85 (broad d, 13.4 Hz, 1H), 2.54 and 2.44 (~t + dd overlapping, J_d = 6.4 Hz, J_d = 18.0 Hz, 2H), 2.12 (m, 4H), 1.88 (dd + m overlapping, J_d = 1.6 Hz, J_d = 18.0 Hz, 2H), 1.30 (m, 7H), 0.89 (t, 7.0 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 207.7, 175.1, 137.7, 47.6, 42.3, 39.6, 30.9, 28.4, 26.4, 25.4, 22.6, 22.5, 13.9. IR (KBr): 2933, 2856, 1694, 1648, 1444, 1406, 1372 cm^{-1}. The material could not be brought to analytical purity.

***(3RS,3'RS,5RS,5'RS,6RS,6'RS)*-Bi(3-hydroxy-2-phenylbicyclo[3.3.0]oct-1(2)-en-6-yl) (13a).** Bis(enone) **9a** (1.28 g, 3.24 mmol) was dissolved in CH_2Cl_2 (25 mL). Methanol (15 mL) was added, followed by an additional 5 mL CH_2Cl_2 to redissolve the precipitate. Next, $CeCl_3 \cdot 7H_2O$ (3.76 g, 10.1 mmol) was added and allowed to dissolve. The mixture was cooled to 0 °C, and $NaBH_4$ (391 mg, 10.3 mmol) was added all at once.[28] The reaction mixture was then allowed to warm to room temperature. TLC (6% ether/ CH_2Cl_2) showed that the reaction had not proceeded to completion. More $NaBH_4$ (390 mg, 10.3 mmol) was added. The reaction mixture was then poured into a mixture of H_2O and CH_2Cl_2 and shaken. The aqueous layer was extracted with more CH_2Cl_2, acidified, and the extracted once more with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and evaporated. This material was recrystallized from toluene to give 886 mg of the title compound as very fine white needles. The filtrate was evaporated and subjected to flash chromatography (6% ether/ CH_2Cl_2 as eluant) to give more product, which was recrystallized from toluene to give **13a** (1.011 g, 2.54 mmol, 78% yield) as a white solid, mp 149-151 °C (discolors at 149 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, 8.3 Hz, 1.1 Hz, 2H), 7.35 (~t, ~8 Hz, 2H), 7.21 (tt, 1.2 Hz, 7.4 Hz, 1H), 5.47 (broad q, ~6 Hz, 1H), 2.87 (dt, J_d = 12.6 Hz, J_t = 6.9 Hz, 1H), 2.64 (dtt, J_d = 18.0 Hz, J_t = 8.8 Hz, J_t = 2.4 Hz, 1H), 2.55 (broad q, 8.0 Hz, 1H), 2.45 (ddq, $J_d \approx$ 18 Hz, $J_d \approx$ 10 Hz, $J_q \approx$ 2.5 Hz, 1H), 2.23 (m, 1H), 1.74 (d+m, J_d = 7.8 Hz, 2H), 1.50 (m, 2H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 152.6, 135.8, 131.4, 128.4 (x2), 127.1 (x2), 126.4, 83.2, 53.7, 50.9, 41.6, 34.2, 25.2. IR (KBr): 3361, 2946, 2921, 2856, 1496, 1046, 774, 694 cm^{-1}.

***(3RS,3'RS,5RS,5'RS,6RS,6'RS)*-Bi(3-methoxy-2-phenylbicyclo[3.3.0]oct-1(2)-en-6-yl) (14a).** A suspension of 60% sodium hydride in mineral oil (84 mg, 2.10 mmol) was placed in a sealable flask under N_2 and washed twice with dry hexane (2 x 10 mL). Then diol **13a** (199 mg, 0.499 mmol) was added, followed by dry THF (15 mL). Finally, CH_3I (125 μL, 2.01 mmol) was added, and the flask was sealed and placed in an oil bath at 70-80 °C. After 2.5 h, the mixture was allowed to cool. It was then poured into sat. aq. NH_4Cl. Ether was added, and the mixture was shaken. The organic layer was dried over $MgSO_4$ and evaporated. The residue was dried in vacuo to give **14a** (219 mg, 0.513 mmol, 103% yield) as a waxy yellow solid, mp 131.5-133 (discolors). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.54 (d, 7.3 Hz, 2H), 7.33 (~t, 2H), 7.19 (t, 7.1 Hz, 1H), 5.14 (unresolved t, v. small *J*, 1H), 3.35 (s, 3H), 2.75 (dt, J_d = 12.4 Hz, J_t = 6.6 Hz, 1H), 2.56 (m, 3H), 2.22 (m, 1H), 1.45-1.85 (m, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 153.0, 136.1, 129.4, 128.1 (x2), 127.2 (x2), 126.2, 91.6, 54.9, 53.8, 50.5, 36.4, 34.1, 25.2. IR (KBr): 3050 (m), 2962, 2928, 2891, 2818, 1648 (m), 1597 (m), 1494, 1443, 1350, 1111, 1071, 772, 695 cm^{-1}. Flash chromatography of this compound (8%, then 10% ether/ petroleum ether as eluant) gave several fractions from which the title compound crystallized in small, yellow crystals suitable for X-ray analysis. Anal. Calcd for $C_{30}H_{34}O_2$: C, 84.47; H, 8.03. Found: C, 84.47; H, 8.02.

***(4RS,4'RS,5RS,5'RS)*-Bi(8-phenylbicyclo[3.3.0]octa-1(2),7-dien-4-yl) (15a).** A suspension of 60% sodium hydride in mineral oil (147 mg, 3.68 mmol) was placed in a sealable flask under N_2 and washed twice with dry hexane (2 x 10 mL). Then **14a** (161 mg, 0.404 mmol) was added, followed by dry THF (10 mL).

Finally, methyl iodide (100 μL, 1.61 mmol) was added, and the flask was sealed and placed in an oil bath at 80-85 °C. After 2 h, TLC showed that starting material had been consumed completely, and that a new product, presumably the dimethoxy compound, had formed exclusively. The reaction mixture was heated further at 85-90 °C overnight. The suspension was allowed to cool, and it was added to sat. aq. NH_4Cl. This mixture was extracted twice with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and evaporated to give a brown solid. This solid was dissolved in hot $CHCl_3$ and cooled to –30 °C to give very fine needles (61 mg). The filtrate was evaporated, and the solid residue was dissolved in hot toluene and cooled to –30 °C to give another crop of very fine needles. The solids were combined and dried in vacuo overnight to give 81 mg (0.223 mmol, 55% yield) of **15a** as very fine off-white needles. The material decomposed slowly as it was heated above 155 °C, but did not melt up to 200 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (~d, 2H), 7.35 (~t, 2H), 7.27 (tt, 7.5 Hz, 2.2 Hz, 1H), 6.51 (unresolved t, v. small *J*, 1H), 5.65 (unresolved m, v. small *J*, 1H), 3.13 (broad, 1H), 2.68-2.81 (broad m + ddd, J_d = 2.9 Hz, J_d = 8.0 Hz, J_d = 17.0 Hz, m is half of ABX_n pattern, 2H), 2.60-2.60 (broad m, other half of ABX_n pattern, 1H), 2.27 (broad dd, ~6 Hz, ~17 Hz, 1H), 2.19 (m, 1H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 154.8, 139.7, 136.7, 134.9, 128.4 (x2), 127.5, 126.6 (x2), 115.2, 56.5, 53.7, 44.0, 36.5. IR (KBr): 3051 (m), 2931 (s), 2876 (s), 2822 (s), 1601 (w), 1490 (m), 1443 (m), 1245 (w), 979 (w), 803 (s), 756 (s), 692 (s) cm^{-1}. The compound was too unstable to analyze properly.

Potassium *(6RS,6'RS)*-Bi(2-phenylbicyclo[3.3.0]octa-1(2),3-dien-6-yl)-5,5'-diylide (16a). A solution of **14a** (97 mg, 0.23 mmol) and *t*-BuOK (151 mg, 1.35 mmol) in dry THF (15 mL) was heated to 95 °C in a sealed Schlenk tube for 36 h. After solids were allowed to settle, the dark red solution was transferred by cannula into a regular Schlenk flask and evaporated to give **16a** as a dark red powder. ^1H NMR (200 MHz, DMSO-d_6): δ 7.11 (d, 8.2 Hz, 2H), 6.87 (t, 7.2 Hz, 2H), 6.39 (t, 7.1 Hz, 1H), 5.72 (d, 3.3 Hz, 1H), 5.25 (d, 3.4 Hz, 1H), 3.13 (m, 1H), 2.95 (m, 1H), 2.64 (dt, J_d = 13.0 Hz, J_t = 7.4 Hz, 1H), 2.38 (m, 1H). Small amounts of THF, CH_3OK, and *t*-BuOK were also visible in the ^1H NMR spectrum. $^{13}C\{H\}$ NMR (50 MHz, DMSO-d_6): δ 143.5, 130.5, 127.5 (x2), 124.6, 121.4 (x2), 116.9, 109.9, 105.1, 99.4, 46.8, 36.4, 29.1.

***(3RS,3'RS,5RS,5'RS,6RS,6'RS)*-Bi(3-hydroxy-2-butylbicyclo[3.3.0]oct-1(2)-en-6-yl) (13b).** A solution of **9b** (270 mg, 0.76 mmol) and $CeCl_3 \cdot 7H_2O$ (848 mg, 2.28 mmol) in methanol (ca. 30 mL) was cooled to 0 °C, and $NaBH_4$ (292 mg, 7.72 mmol) was slowly added. When the H_2 evolution had ceased, the mixture was diluted with CH_2Cl_2, water, and a little 1 N HCl and shaken. The aqueous layer was extracted with more CH_2Cl_2. The combined organic layers were shaken with brine, dried over $MgSO_4$, and evaporated to give **13b** (264 mg, 0.74 mmol, 97% yield) as a fluffy white solid, mp 135.5-136 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 4.95 (broad, 1H), 2.72 (dt, J_d = 12.4 Hz, J_t = 6.6 Hz, 1H), 1.95-2.40 (m, 6H), 1.15-1.65 (m, 8H), 0.90 (t, 7.0 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 147.8, 133.1, 83.1, 52.2, 51.9, 42.6, 33.4, 30.1, 25.3, 22.7, 22.4, 13.9. IR (KBr): 3225, 2954, 2926, 2861, 1461, 1316, 1038 cm^{-1}. Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.68. Found: C, 80.07; H, 10.92.

***(3RS,3'RS,5RS,5'RS,6RS,6'RS)*-Bi(3-acetoxy-2-butylbicyclo[3.3.0]oct-1(2)-en-6-yl) (14b).** A suspension of **13b** (552 mg, 1.54 mmol) in CH_2Cl_2 (50 mL) was treated with Et_3N (650 μL, 4.66 mmol), DMAP (19 mg, 0.16 mmol), and Ac_2O (360 μL, 3.81 mmol). The solid gradually dissolved. After stirring overnight, the solution was diluted with ether and shaken with dilute HCl, water, brine, and sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, evaporated, and dried in vacuo overnight. Flash chromatography (4%, then 5%, then 6% EtOAc/ petroleum ether as eluant) gave **14b** (600 mg, 1.36 mmol, 88% yield) as a

white crystalline solid, mp 74-75 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.96 (broad t, 1H), 2.72 (dt, J_d = 12.7 Hz, J_t = 6.8 Hz, 1H), 2.36 (m, 1H), 1.92-2.30 (s [d 2.05] + m, 8H), 1.60 (m, 1H), 1.29-1.42 (m, 6H), 0.88 (t, 6.8 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 170.6, 149.6, 129.5, 85.0, 52.7, 51.4, 38.8, 33.4, 30.0, 25.4, 22.5, 22.4, 21.2, 13.8. IR (KBr): 2959, 2926, 2861, 1727, 1377, 1250, 1023 cm^{-1}. Anal. Calcd for $C_{28}H_{42}O_4$: C, 75.98; H, 9.56. Found: C, 76.28; H, 9.52.

***(4RS,4'RS,5RS,5'RS)*-Bi(8-butylbicyclo[3.3.0]octa-1(2),7-dien-4-yl) (15b).** A solution of **14b** (221 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in dry THF (40 mL) was brought to reflux under N_2. The solution turned bright orange. After 20 h, the solution had turned a dull yellow color. The solvent was evaporated, and the residue was dried in vacuo until it no longer smelled of AcOH. The residue was suspended in petroleum ether and flushed through a short column of silica, eluting with petroleum ether. The eluate was evaporated and dried in vacuo to give **15b** (152 mg, 0.47 mmol, 94% yield) as a colorless oil with a mp near room temperature. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.81 (s, 1H), 5.28 (d, 2.8 Hz, 1H), 2.87 (m, 1H), 2.66 (dm, $J_d \approx$ 15 Hz, 1H), 2.45 (m, 2H), 2.18 (~t, 2H), 2.02 (m, 2H), 1.2-1.55 (m, 4H), 0.90 (t, 7.1 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 157.8 (even), 140.9 (even), 135.3 (odd), 111.9 (odd), 55.7 (odd), 54.3 (odd), 43.8 (even), 35.9 (even), 30.2 (even), 27.9 (even), 22.6 (even), 13.9 (odd). IR (neat): 3046, 2926, 2880, 2832, 1459, 800 cm^{-1}. A small amount of a C(sp^2)–H-containing impurity, possibly a regioisomer, can be seen in the ^{1}H NMR spectrum. The compound decomposes over days, even at –30 °C.

***(5RS,5'RS,6RS,6'RS)*-Bi(3-(4-toluenesulfonylhydrazono)-2-butylbicyclo[3.3.0]oct-1(2)-en-6-yl) (24).** A solution of diketone **9b** (796 mg, 2.25 mmol) and hydrazine hydrate (1.3 mL, 23 mmol) in EtOH (~10 mL) was allowed to reflux for 5.5 h. The solvent was evaporated, and the residue was dried in vacuo overnight. The residue was redissolved in CH_2Cl_2 (~10 mL), and Et_3N (1.0 mL, 7.2 mmol) was added. The solution was cooled to 0 °C, and TsCl (1.11 g, 5.84 mmol) was added in portions. After each portion was added, the reaction mixture was allowed to stir for 30 min, and the absence of unreacted TsCl was ascertained by TLC (25% EtOAc/ petroleum ether) before the next portion was added. When unreacted TsCl persisted in the reaction mixture, the CH_2Cl_2 was mostly removed in vacuo, maintaining the mixture below room temperature, and the residue was purified by flash chromatography (20%, then 25% EtOAc/ petroleum ether as eluant). Fractions containing the product were evaporated at or below room temperature to give a pale yellow solid. The solid was rinsed with a little ether/ petroleum ether mixture to remove the yellow color, affording the title compound (547 mg, 0.79 mmol, 35% yield) as a pasty white solid resembling paint chips, mp 118 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.33 (broad, 1H), 7.91 (d, 8.1 Hz, 2H), 7.27 (d, 8.4 Hz, 2H), 2.89 (dd, 6.6 Hz, 17.6 Hz, 1H), 2.51 (m, 1H), 2.42 (s, 3H), 1.95-2.40 (m, 6H), 1.58 (m, 1H), 1.22 (m, 5H), 0.82 (t, 6.8 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 143.5, 135.5, 132.9, 129.2 (x2), 128.5 (x2), 51.5, 50.4, 33.2, 31.4, 29.9, 24.5, 23.2, 22.5, 21.5, 13.8, two C(sp^2) resonances not observed. IR (KBr): 3210, 2955, 2928, 2866, 1623, 1598, 1404, 1330, 1166, 1093, 1037, 920, 813, 706, 670, 550 cm^{-1}. Anal. Calcd for $C_{38}H_{50}N_4O_4S_2$: C, 66.06; H, 7.29. Found: C, 65.87; H, 7.49.

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