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Application of the double Pauson–Khand cyclization to the synthesis of bis(cyclopentadienes): preparation of phenyl-bridged bis(tetrahydroindenyl)titanium and zirconium dichlorides ☆

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Abstract

We have demonstrated a very efficient (5 steps, 28% yield from 1-octen-7-yne and 1,2-diiodobenzene) and novel synthesis of 1,2-bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzene. We utilized for the first time in a bis(cyclopentadiene) synthesis the double Pauson–Khand cyclization and Shapiro-elimination methods. The double Pauson–Khand cyclization is also successful in the preparation of ethylene-bridged bis(cyclopentadienes). A novel iodine-promoted elimination of allyl methyl ethers was also applied in the preparation of bis(cyclopentadienes). The solid state structure of 1,2-bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzenedichlorotitanium (*dl*-**4a**) was obtained and it shows a very obtuse angle between the cyclopentadienyl substituents. The crstallographic data for *dl*-**4a** are as follows: $C_{24}H_{24}Cl_2Ti$, monoclinic, $C2/c$. $a = 15.805(3)$ Å, $b = 11.027(2)$ Å, $c = 13.323(3)$ Å, $\beta = 121.40(3)°$, volume 1981.9 Å^3, $Z = 4$, $R = 4.41$, $R_w = 6.92\%$, goodness of fit 2.96.

Keywords: Phenyl-bridged metallocenes; Pauson–Khand cyclization; Chiral; *Ansa*-metallocene; Titanocene; Zirconocene

1. Introduction

Brintzinger's landmark preparation and applications of the indenyl-derived chiral ansa-metallocene dichloride **1** initiated the vital field of chiral ansa-metallocenes [1,2]. The needed achiral ligand was quickly available through the alkylation of indene with 1,2-dibromoethane and its metalation quickly led to a racemic ansa-metallocene having substituents on the cyclopentadienyl moieties very nicely placed in a C_2-symmetrical orientation about the metal. The ease with which this complex can be prepared has led to its application in a number of stereoselective reactions [2,3]. Along with several other groups [4], our research [5] has been to see whether it is possible to prepare efficiently new ansa-metallocene complexes which would be more stereoselective [6]. Two design features we have concentrated on are (1) removing the bridging-group flexibility exhibited by complex **1** and locking new complexes in the most selective conformation, and (2) optimizing the size and shape of the substituents on the metallocene. In order to be able to carry out efficiently the synthesis of such new complexes, we have been developing new methods for the preparation of bis(cyclopentadienes).

In order to eliminate the conformational flexibility exhibited by complex **1** [7], we and others are preparing ansa-metallocenes containing bridging groups which would lead to rigid metallocenes [8,9]. One class of these metallocenes are the biphenyl- and binaphthyl-briged rigid metallocenes **2** [9] and **3** [8]. Based on the crystal structure of biphenyl-bridged **2**, the substituents on the cyclopentadienyl moieties in biphenyl-bridged complexes are held in a fairly acute orientation, as shown in Fig. 1. By using a 1,2-phenyl-bridge, we anticipated the formation of a rigid metallocene with the much more obtuse angle between the substituents as shown in Fig. 1. The preparation of a conceptually similar, ethylene-bridged, unsubstituted bis(cyclopentadienyl)titanium dichloride has been reported [10], but we desired to develop a more general and perhaps more efficient method for the preparation of rigid two-atom-

☆ Dedicated to Professor Dr. Hans-Herbert Brintzinger on the occasion of his 60th birthday.

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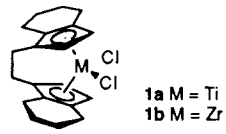


bridged metallocenes. In this paper we describe the preparation of rigid ansa-metallocenes **4** containing a 1,2-phenyl-bridge to which we applied the Pauson–Khand cyclization method [11] to form tethered bis(cyclopentenones) and a Shapiro elimation [12] to convert the bis(cyclopentenones) to the bis(cyclopentadienes) under basic conditions. We also report the use of the Pauson–Khand cyclization in the preparation of ethylene-brigded bis(cyclopentadienes).

2. Results and discussion

2.1. Synthesis of 1,2-phenyl-bridged bis(tetrahydroindene) 17

In order to ascertain the viability of the double Pauson–Khand cyclization method for the formation of phenyl-bridged bis(cyclopentenones), we wanted to prepare and study bis(enynes) **8** and **9**. Our successful ligand synthesis is shown in Scheme 1. Known *o*-diethynylbenzene **7** [13] can be prepared in large quantities through the olefination of commercially available phthalic dicarboxaldehyde **5** with methyltriphenylphosphonium bromide in the presence of potassium *t*-butoxide followed by bromination of intermediate diene **6** and quadruple elimination with potassium *t*-butoxide at room temperature. Diyne **7** can lead to precursors for either five or six and, potentially, even seven membered rings, through its alkylation with available 5-bromo-1-pentene, 6-iodo-1-hexene or 7-iodo-1-heptene [14]. Diyne **7** was deprotonated with *n*-butyllithium at −78 °C followed by sequential addition of HMPA and either

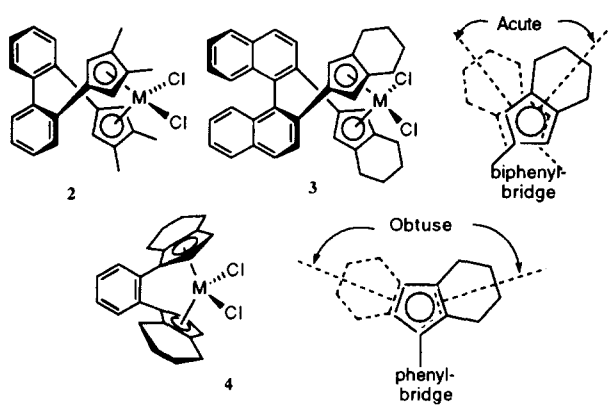
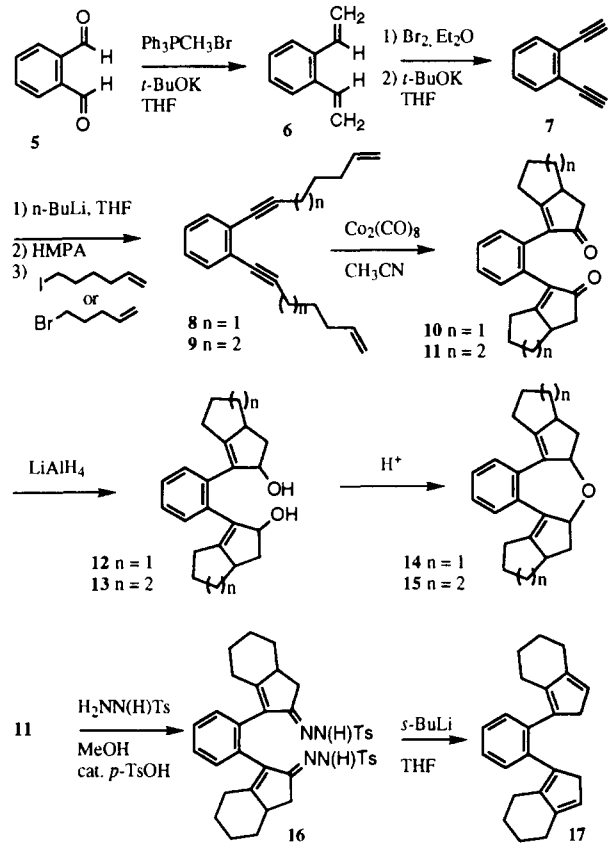


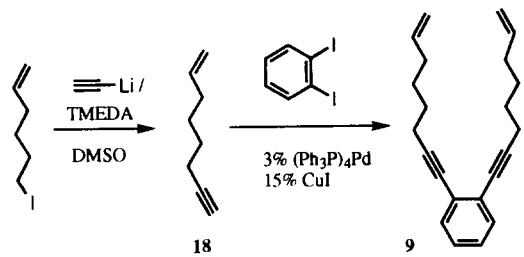
Fig. 1. Angle between substituents in biphenyl- vs. phenyl-bridged metallocenes.



Scheme 1. Synthesis of bis(cyclopentadiene) **17**.

5-bromo-1-pentene or 6-iodo-1-hexene. The resultant solutions were allowed to warm to room temperature over 6 h to give arylbis(enynes) **8** or **9**. We were gratified to find that the double Pauson–Khand reaction of **8** and **9** proceeded in very high yields. Biscyclization occurred through initial complexation of $Co_2(CO)_8$ to the alkynyl moieties at room temperature in acetonitrile with subsequent biscyclization induced by heating the solution under reflux for 8 h to form either bis(hydropentalenone) **10** or bis(hydroindenone) **11** in 81% and 83% yield respectively.

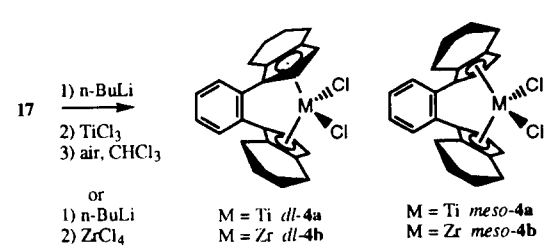
The first significant obstacle in our synthesis was encountered in the conversion of these readily produced bis(cyclopentenones) to the desired bis(cyclopentadienes) under the usual method of reducing the carbonyls and dehydrating the diols. The respective bis(enones) were cleanly reduced with LAH to diols **12** and **13**, but the dehydration with *p*-TsOH in benzene at room temperature resulted in the formation of a mixture of diasteromeric cyclic ethers **14** and **15**. A wide variety of dehydrating conditions [15] including the preparation and elimination of sulfonate esters, led in each case to these ethers as the major products. Apparently, as the first alcohol is being removed (or activated as a sulfonate ester), the second hydroxyl group is in a very favorable position to displace to the allylic oxygen group leading to the ether. Since the yields of acid-in-



Scheme 2. Alternative synthesis of bis(enyne) **9**.

duced dehydrations of other bis(cyclopentenols) are also often poor, we turned to the use of a basic method for conversion of the carbonyl group into an alkene.

Shapiro [12] has shown that cyclic ketones can be derivatized as a tosylhydrazone and, on treatment with alkyllithium, a vinyl anion results. For example, cyclohexenones have been converted to cyclohexadienes. However, to our knowledge, no examples of the formation of bis(cyclopentadienyl) anions as a result of this procedure have been reported. Refluxing a methanol solution of **11**, tosylhydrazide and catalytic *p*-TsOH resulted in the formation of white, solid bis(tosylhydrazone) **16** in good yield. Addition of excess *sec*-butyllithium to a THF solution of **16** at −10 °C and subsequent warming to room temperature and aqueous quenching did indeed produce the desired aryl-bridged bis(tetrahydroindenyl) ligand **17** in 52% yield after purification. Presumably, the very basic vinyl anion aromatizes in situ to the more stable cyclopentadienyl anion which is quenched on workup. The formation of the cyclopentadienyl anion serves to protect the often-sensitive cyclopentadiene from undesired reactions and potentially could lead to an in situ metalation procedure. The spectral and physical data are in agreement with a mixture of double bond isomers of bis(cyclopentadiene) **17** (one symmetric isomer is major). The characteristic tetrahydroindene proton signal for the major isomer appears at 5.95 ppm, the aromatic bridge proton signal at 7.25 ppm and the rest of the alkyl signals come between 2.72 ppm and 0.81 ppm. The expected 12 signals in the ^{13}C NMR spectrum were observed for the symmetrical isomer. We were unsuccessful in applying this method with bis(cyclopentenone) **10** owing to our inability to form the bis(tosylhydrazone) of **10**.



Scheme 3. Metaltation of bis(cyclopentadiene) **17**.

We have also developed a more facile, and potentially more generally applicable, route for the prepartion of the needed arylbis(enyne) **9**. In this route we couple commercially available 1,2-diiodobenzene with readily prepared enyne **18** in the presence of catalytic palladium to give directly the desired bis(enyne) in 99% yield as shown in Scheme 2 [16].

2.2. Metalation of 1,2-phenyl-bridged bis(tetrahydroindene) 17

Both the titanium and zirconium dichloride complexes **4a** and **4b** were prepared from bis(cyclopentadiene) **17** (Scheme 3). Deprotonation of **17** with *n*-butyllithium in THF at −78°C provided a white dianion that was insoluble even at room temperature. Addition of this suspension to $TiCl_3$ [17] at −78 °C followed by refluxing for 6 h and oxidation with air in chloroform afforded a 4:1 mixture of the desired racemic and *meso* isomers of titanocene dichloride **4a** in 89% overall yield. Crystallization from hot toluene resulted in the isolation of *dl*-**4a** in 68% yield. The structure of *dl*-**4a** was assigned initially by ^1H NMR spectroscopy based on Brintzinger's [1a] analogous ethano-bridged tetrahydroindenyl titanocene dichlorides and was later confirmed by X-ray crystallography on crystals obtained from hot toluene. The characteristic cyclopentadienyl proton signals for the C_2-symmetric isomer appear at 6.64 ppm and 4.42 ppm while those of *meso*-**4a** appear at 6.55 ppm and 6.42 ppm.

The zirconocene complex **4b** was synthesized via deprotonation of **17** with *n*-butyllithium at −78 °C in Et_2O followed by the addition of solid $ZrCl_4$ at room temperature via a side arm. A ^1H NMR spectrum of the solid crude reaction mixture showed signals which corresponded to a 60:40 ratio of racemic to meso isomers by comparison of the ^1H NMR spectrum of an analogous ethano-bridged tetrahydroindenyl zirconocene [1b]. Attempts to crystallize selectively the racemic isomer from the meso with hot toluene resulted in observation of the known light-initiated isomerization [18] of the meso to the racemic isomer in a 93:7 ratio of *dl*-**4b** to *meso*-**4b**. The ^1H NMR spectrum of this mixture of the phenyl-bridged bis(tetrahydroindenyl)zirconocene dichloride **4b** consists of characteristic signals for the cyclopentadienyl protons in *dl*-**4b** appearing at 6.43 and 6.07 ppm.

2.3. X-ray diffraction-derived structure of dl-4a

Single crystals were obtained by cooling slowly a hot toluene solution of *dl*-**4a**. The X-ray diffraction of a suitable crystal was measured at room temperature and the structure of *dl*-**4a** was derived according to the data in Table 1. The atomic coordinates and bond lengths are given in Tables 2 and 3. An ORTEP plot of the

structure is shown in Fig. 2(a) and a stereoview of *dl*-**4a** in Fig. 2(b). The structure contains a crystallographically imposed C_2-axis of symmetry bisecting the chlorine atoms, passing through the titanium atom and bisecting the phenyl ring. It appears that this metallocene is rigidly locked into a C_2-symmetrical conformation with the annulated cyclohexane moieties oriented with an obtuse angle with respect to one another.

2.4. Application of the Pauson–Khand cyclization in the preparation of ethano-bridged bis(cyclopentadienes)

In order to ascertain the generality of the cobalt-mediated double Pauson–Khand cyclization of bis(enynes) to afford tethered bicyclic cyclopentenones of various ring sizes, we investigated the preparation of ethano-bridged bis(hydropentalenone) **21** and bis(hydroindenone) **22** (Scheme 4). The bis(enynes) **19** and **20** needed for the cyclization study were readily prepared through the alkylation of 1,5-hexadiyne. Cyclization of **19** and **20** occurred via cobalt complexation of the alkyne moieties with concomitant biscyclization to give ethano-bridged bis(hydropentalenone) **21** in 69% yield and ethano-bridged bis(hydroindenone) **22** in 68% yield. Bis(cyclopentenone) **22** was eliminated through the tosylhydrazone **25** as with bis(enone) **11** to give ethano-bridged bis(tetrahydroindene) **26** in 42% yield.

As with the 1,2-phenyl-bridged bis(hydropentalene) **10**, we had difficulty forming the bis(tosylhydrazone) derivative of **21**. Enones **21** and **22** could both be cleanly reduced to their corresponding diols. Attempted dehydration of **21** under a variety of conditions resulted primarily in the formation of a mixture of cyclic ethers. We speculated that conversion of the bis(allylic alcohol)

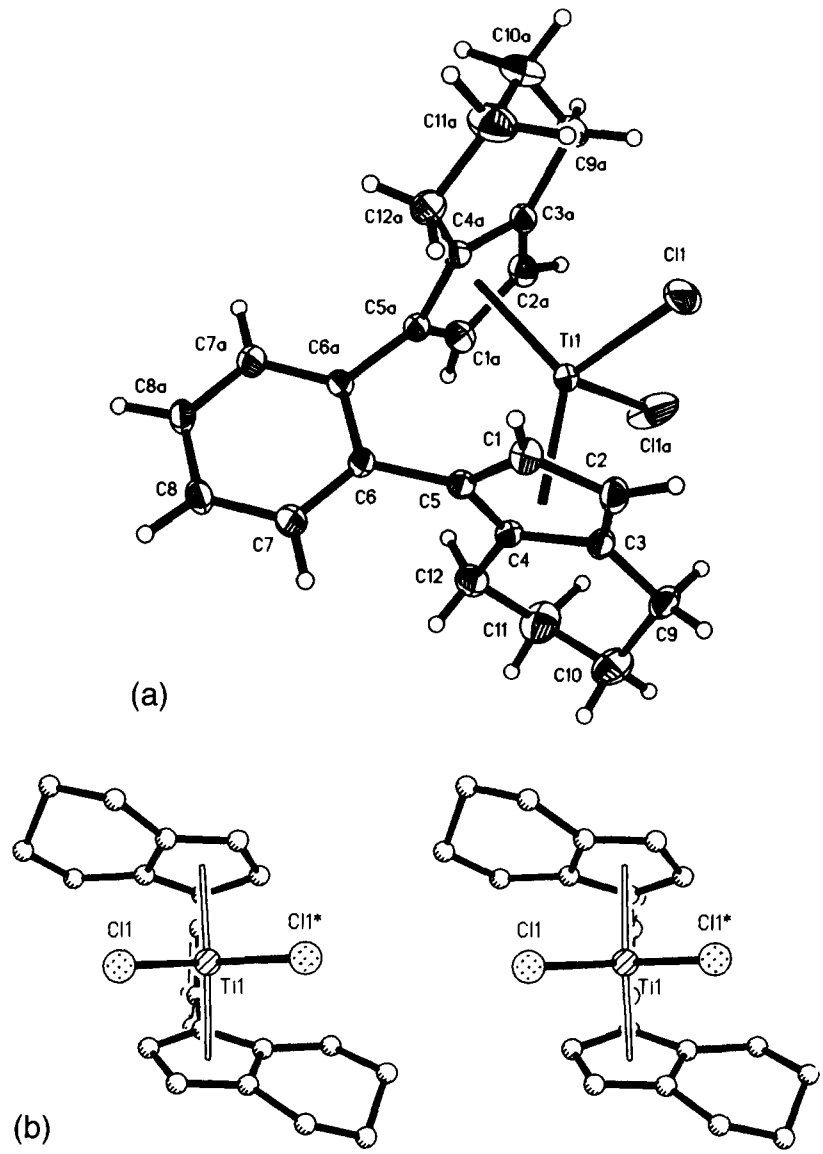


Fig. 2. Structure of *dL*–**4a**: (a) ORTEP plot, (b) stereoview.

Table 1
Summary of structure determination

Crystal data	
Empirical formula	$C_{24}H_{24}Cl_2Ti$
Color habit	Red prismatic
Crystal size (mm)	0.3 × 0.3 × 0.5
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 15.805(3)$ Å
	$b = 11.027(2)$ Å
	$c = 13.323(3)$ Å
	$\beta = 121.40(3)°$
volume (Å^3)	1981.9(7)
Z	4
Formula weight	431.2
Density(calculated) (mg m^{-3})	1.445
Absorption coefficient (mm^{-1})	0.708
$F(000)$	896
Data collection	
Diffractometer	Enraf Nonius CAD-4
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	295
Monochromator	Highly oriented graphite crystal
2θ range	1.5°–46.0°
Scan type	$2\theta - \theta$
Scan speed	Variable. 1.00° to 5.00° min^{-1} in ω
Scan range (ω)	0.90° plus Kα separation
Background measurement	Moving crystal and moving counter at beginning and end of scan, each for 12.5% of total scan time
Standard reflections	3 measured every 120 min
Index ranges	$0 \le h \le 18$, $0 \le k \le 13$, $-15 \le l \le 13$
Reflections collected	1806
Independent reflections	1746 ($R_{int} = 2.08\%$)
Observed reflections	1484 ($F > 4.0\sigma(F)$)
Absorption correction	N/A
Solution and refinement	
System	Siemens SHELXTL, TRIS
Solution	Patterson method
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Absolute structure	N/A
Extinction correction	N/A
Hydrogen atoms	Located and refined
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$
Number of parameters refined	171
Final R indices (observed data)	$R = 4.41\%$, $R = 6.92\%$
R indices (all data)	$R = 5.77\%$, $R = 7.10\%$
Goodness-of-fit	2.96
Largest and mean Δ/σ	0.029, 0.004
Data-to-parameter ratio	8.7 : 1
Largest difference peak (eÅ^{-3})	0.54
Largest difference hole (eÅ^{-3})	−0.58

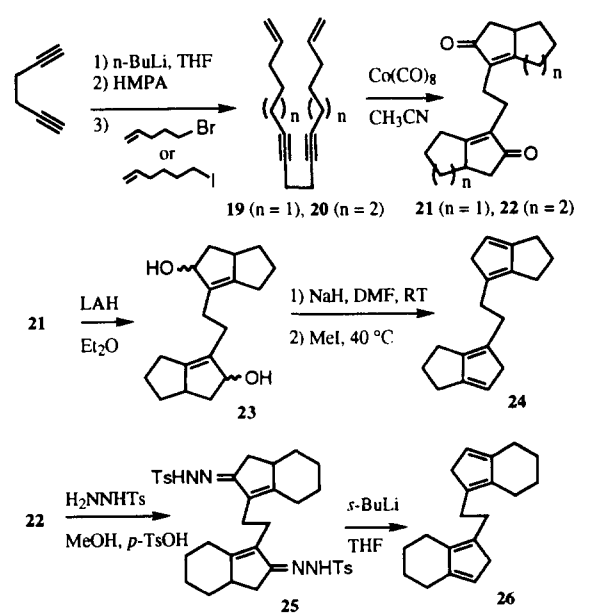
Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	U_{eq}
Ti(1)	0	1968(1)	7500	31(1)
Cl(1)	1279(1)	541(1)	8305(1)	92(1)
C(1)	840(2)	3020(3)	9274(3)	38(1)
C(2)	481(2)	1968(3)	9540(3)	39(1)
C(3)	−540(2)	2039(3)	8966(2)	33(1)
C(4)	−838(2)	3134(2)	8304(2)	31(1)
C(5)	23(2)	3751(2)	8531(2)	29(1)
C(6)	30(2)	4960(2)	8038(2)	28(1)
C(7)	67(3)	6050(3)	8582(3)	40(1)
C(8)	37(2)	7134(2)	8040(3)	39(1)
C(9)	−1273(3)	1231(3)	9056(3)	45(2)
C(10)	−2193(3)	1941(4)	8750(5)	67(2)
C(11)	−2601(3)	2649(5)	7614(5)	68(2)
C(12)	−1881(2)	3583(3)	7657(3)	43(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å)

Ti(1)–Cp(1)	2.103(3)	Ti(1)–Cl(1)	2.335(2)
Ti(1)–C(1)	2.329(3)	Ti(1)–C(2)	2.411(4)
Ti(1)–C(3)	2.508(4)	Ti(1)–C(4)	2.457(4)
Ti(1)–C(5)	2.388(3)	C(1)–C(2)	1.416(5)
C(1)–C(5)	1.402(4)	C(2)–C(3)	1.382(5)
C(3)–C(4)	1.422(4)	C(3)–C(9)	1.514(6)
C(4)–C(5)	1.406(5)	C(4)–C(12)	1.492(4)
C(5)–C(6)	1.489(4)	C(6)–C(7)	1.389(4)
C(6)–C(6A)	1.387(7)	C(7)–C(8)	1.384(5)
C(8)–C(8A)	1.381(8)	C(9)–C(10)	1.509(7)
C(10)–C(11)	1.516(8)	C(11)–C(12)	1.513(7)



Scheme 4. Pauson–Khand route to ethano-bridged bis(cyclopentadienes) **24** and **26**.

to the dimethoxy derivative would reduce the nucleophilicity and hopefully prevent this etherification in subsequent acid-promoted dehydrations. To our surprise, deprotonation of **23** with sodium hydride in DMF at room temperature followed by addition of iodomethane and heating to 40 °C for 12 h resulted directly in the formation of the desired diene **24** in 30% yield. The mechanism of this fortuitous reaction probably involves the formation of the dimethoxy compound and, as the excess iodomethane is heated evolving iodine in solution, iodine-promoted elimination [19] ensues. When the reaction was stopped after 3 h only the dimethylether of **23** was isolated. The ^{1}H NMR spectrum of bis(cyclopentadiene) **24** reveals a signal at 5.93 ppm corresponding to the vinyl proton and a bisallylic proton signal at 3.00 ppm. The ^{13}C NMR spectrum reveals the nine expected signals with appropriate chemical shifts. To test the generality of this elimination method, 7,7-dimethyltetrahydropentalenol, tetrahydroindenol and hexahydroazulenol were subjected to the same conditions. Elimination occurred in low to moderate yields in each case. These conditions will probably only seem attractive when intramolecular etherification is a likely side product and the tosylhydrazone formation fails.

2.5. Summary

We have demonstrated a very efficient (five steps, 28% yield from 1-octen-7-yne and 1,2-diiodobenzene) and novel synthesis of 1,2-bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzene. We utilized for the first time in a bis(cyclopentadiene) synthesis the double Pauson–Khand cyclization and Shapiro elimination methods. The double Pauson–Khand cyclization is also successful in the preparation of ethylene-bridged bis(cyclopentadienes). A novel iodine-promoted elimination of allyl methyl ethers was also applied in the preparation of bis(cyclopentadienes). The solid state structure of 1,2-bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzenedichlorotitanium was obtained and it shows a very obtuse angle between the cyclopentadienyl substituents.

3. Experimental details

3.1. General

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Ether, THF, hexanes, toluene and benzene were distilled under N_2 from sodium and benzophenone. C_6D_6 was distilled from calcium hydride. Transfer of air- and moisture-sensitive compounds was carried out in a Vacuum Atmospheres Dri-Box under N_2. Routine solvent removal was performed on a Büchi RE-111 rotary evaporator using a water aspirator. All ^{1}H NMR spectra were obtained using a Varian XL-300 or Varian VXR-500S. Data are reported as follows: chemical shifts (δ scale) in parts per million (ppm) relative to residual solvent peaks (multiplicity, coupling constants in hertz (rounded to 0.5 Hz), number of hydrogens. For ^{1}H NMR spectra, the peaks due to residual $CHCl_3$ or C_6H_6 are listed at 7.24 ppm or 7.15 ppm respectively and for ^{13}C NMR spectra, the central peak of the $CDCl_3$ or C_6D_6 multiplets are assigned chemical shifts of 77.0 ppm or 128.0 ppm respectively. Unless otherwise noted, multiplicities and compound ratios are deduced from electronic integration. IR spectra were recorded on a Bio-Rad FTS-7 FT-IR with a dedicated Bio-Rad 3240-SPC computer. Low-resolution mass spectra (reported as m/z, relative intensity at 12, 40 or 70 eV) were recorded on either a Finnegan MAT-90 or a Hewlett Packard 5985 instrument. Melting points were determined in Pyrex capillary tubes with a Thomas-Hoover Unimelt or Mel-Temp apparatus and are uncorrected.

Preparative chromatography was performed on flash silica gel (E. Merck Reagents silica gel 60 Å, 230–400 mesh ASTM or Whatman silica gel 60 Å, 70–230 mesh ASTM) or neutral alumina IV (E. Merck Reagents alumina F-20, 80-200 mesh). Analytical thin layer chromatography was performed on 0.2 mm Kieselgel silica gel 60 F-254. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

3.2. 1,2-Bis(1-hepten-6-yne)benzene 8

To a THF solution (10 ml) of 1,2-diethynyl benzene (380 mg, 3.0 mmol) at −78 °C was slowly added *n*-butyllithium (2.68 m in heptane, 2.4 ml, 6.3 mmol) under N_2 to obtain a lavender-colored solution. After 0.5 h, HMPA (1.57 ml, 9.03 mmol) was added at the same temperature and the solution was stirred an additional 0.5 h whereupon the color of the solution became dull red. 5-bromo-1-pentene (787 μl, 6.9 mmol) was added dropwise to obtain a colorless solution. After allowing the solution to warm to room temperature over 4 h, the reaction was quenched with H_2O (10 ml), the mixture extracted with Et_2O (3 × 5 ml), dried ($MgSO_4$) and concentrated. The crude oil was distilled to yield **8** as a colorless oil (552 mg, 71%), bp 115 °C, $P = 0.001$ mm Hg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, $J = 3.0$, 6.0 Hz, 2H), 7.14 (dd, $J = 3.0$, 6.0 Hz, 2H), 5.80 (ddt, $J = 10.0$, 17.5, 7.5 Hz, 2H), 5.05 (dd, $J = 2.5$, 17.5 Hz), 4.98 (dd, $J = 2.5$, 10.0 Hz, 2H), 2.44 (t, $J = 7.5$ Hz, 4H), 2.22 (q, $J = 7.5$ Hz, 4H), 1.69 (dt, $J = 15.0$, 7.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.91, 131.82, 127.15, 126.26, 115.14, 93.61, 79.94, 32.77, 27.93, 19.03; IR (neat) 3068, 2933, 2858, 2228, 1639, 1479, 1440, 1329 cm^{-1}; MS, m/z (12 eV, relative intensity) 262 (3%), 261 (12), 247 (22), 234 (12), 220 (18), 193 (48), 181 (100).

3.3. 1,2-Bis(1-octen-7-yne)benzene 9

To a THF solution (30 ml) of 1,2-diethynylbenzene (1.59 g, 12.6 mmol) at −78 °C was slowly added *n*-butyllithium (2.68 m in heptane, 9.9 ml, 26.5 mmol) under N_2 to obtain a purple-colored solution. After 0.5 h, HMPA (6.6 ml, 37.8 mmol) was added at the same temperature and the solution was stirred an additional 0.5 h whereupon the color became red. 6-Iodo-1-pentene (6.05 g, 28 mmol) was added dropwise at −78 °C to obtain a colorless solution. The solution was allowed to warm to room temperature over 3 h. H_2O (20 ml) was added and the mixture extracted with Et_2O (3 × 10 ml), dried ($MgSO_4$) and concentrated. The crude oil was distilled to yield **9** as a colorless oil (3.0 g, 83%), bp 125 °C, $P = 0.001$ mm Hg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, $J = 6.0$, 3.0 Hz, 2H), 7.15 (dd, $J = 6.0$, 3.0 Hz, 2H), 5.80 (ddt, $J = 10.0$, 17.5, 7.5 Hz, 2H), 5.05 (dd, $J = 2.5$, 17.5 Hz, 2H), 4.98 (dd, $J = 2.5$, 10.0 Hz, 2H), 2.44 (t, $J = 7.5$ Hz, 4H), 2.22–2.12 (m, 4H), 1.60–1.55 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.65, 131.85, 127.18, 126.35, 114.67, 98.89, 79.77, 33.38, 28.20, 28.13, 19.56; IR (neat) 3070, 2972, 2932, 2857, 2227, 1638, 1479, 1440, 1329 cm^{-1}; MS, *m/z* (70 eV, thermal spray, relative intensity) 291 (12%), 219 (14), 207 (17).

3.4. 1,2-Bis(2-bicyclo[3.3.0]-oct-1(2)-en-3-one)benzene 10

To a round bottom flask equipped with a condenser and charged with dicobalt octacarbonyl (1.49 g, 4.36 mmol) was added a CH_3CN solution (8.7 ml) of 1,2-bis(1-hepten-6-yne)benzene (520 mg, 1.98 mmol) under N_2. When the bubbling ceased, the solution was heated under reflux for 12 h. The resulting solution was cooled to room temperature and Al_2O_3 (activity IV) (1 g) was added to the crude solution and the solvent evaporated. The dark red solid was transferred to a column of silica gel and eluted (5%–50% ethyl acetate/petroleum ether) to afford **10** as a white solid (420 mg, 67%), mp 132–133 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, $J = 9.0$, 3.0 Hz, 2H), 7.18 (dd, $J = 9.0$, 3.0 Hz, 2H), 2.80–2.77 (m, 2H), 2.71–2.67 (m, 4H), 2.42 (dd, $J =$ 7.5, 4.0 Hz, 4H), 1.93–2.21 (m, 4H), 1.26–1.02 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.27, 136.55, 131.75, 130.12, 129.69, 127.73, 44.39, 42.73, 31.21, 25.68, 25.18; IR (thin film) 2932, 2856, 1700, 1639, 1443, 1406, 1362, 1319, 1148 cm^{-1}; MS, *m/z* (70 eV, relative intensity) 319 (M^{+1}, 10%), 160 (3).

3.5. 1,2-Bis(2-bicyclo[4.3.0]-non-1(9)-en-8-one)benzene 11

To a round bottom flask equipped with a condenser and charged with dicobalt octacarbonyl (7.8 g, 22.8 mmol) under N_2 was added a CH_3CN solution (50 ml) of 1,2-bis(1-hepten-7-yne)benzene (3.0 g, 10.3 mmol). When the bubbling ceased, the solution was heated to reflux for 12 h. The red solution was cooled to room temperature and Al_2O_3 (activity IV) (2 g) was added to the crude solution and the solvent evaporated. The solid was transferred to a column of silica gel and eluted (5%–50% ethyl acetate/petroleum ether) to afford **11** as a white solid (2.67 g, 75%), mp 174–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, $J = 9.0$, 3.0 Hz, 2H), 7.26 (dd, $J = 9.0$, 3.0 Hz, 2H), 2.70–2.68 (m, 6H), 2.44–2.42 (m, 4H), 1.82–1.77 (m, 8 H), 1.02–1.21 (m 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.57, 178.70, 131.7, 131.47, 130.27, 130.21, 130.17, 127.73, 127.68, 42.14, 42.00, 40.61, 40.33, 35.12, 34.71, 29.53, 29.15, 27.04, 26.68, 25.66, 25.34; IR (thin film) 2933, 2851, 1700, 1639, 1456 cm^{-1}; MS, *m/z* (70 eV, thermal spray, relative intensity) 347 (26%), 346 (1).

3.6. 1,2-Bis(2-bicyclo[3.3.0]-oct-1-en-3-ol)benzene 12

To an Et_2O suspension (20 ml) of $LiAlH_4$ (191 mg, 5.03 mmol) at 0 °C under N_2 was slowly added an Et_2O solution (8 ml) of 1,2-bis(2-bicyclo[3.3.0]-oct-1-en-3-one)benzene (400 mg, 1.26 mmol) and the solution was allowed gradually to come to room temperature for 1 h. The solution was cooled again to 0 °C and the reaction was slowly quenched with Rochelle's salt (665 μl). The mixture was stirred for 0.5 h and filtered. The solution was concentrated to provide **12** as a white solid (300 mg, 75%) as a mixture of isomers, mp 120–123 °C. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of isomers) δ 7.02–7.37 (m, 4H), 5.34 (m, 2H), 2.59–2.71 (m, 6H), 1.80–2.00 (m, 4H), 1.14–1.64 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, mixture of isomers) δ 147.66, 130.18, 129.95, 126.68, 126.65, 110.12, 110.107, 84.47, 63.95, 58.00, 48.10, 42.86, 42.21, 32.45, 32.40, 31.55, 26.99, 26.92, 23.67, 23.63; IR (thin film) 3365, 2948, 1694, 1445, 1314, 1064 cm^{-1}; MS, *m/z* (70 eV, thermal spray, relative intensity) 322 (70%) 305 (28), 287 (4).

3.7. 1,2-Bis(9-bicyclo[4.3.0]-non-1(9)-en-8-ol)benzene 13

To an Et_2O suspension (50 ml) of LAH (219 mg, 5.78 mmol) at 0 °C under N_2 was slowly added an Et_2O solution (12 ml) of 1,2-bis(2-bicyclo[4.3.0]-non-1(9)-en-8-one)benzene (500 mg, 1.44 mmol) and the solution was allowed gradually to come to room temperature for 1 h. The solution was cooled again to 0 °C and the reaction was slowly quenched with Rochelle's salt (757 μl). The mixture was stirred for 0.5 h and then filtered. The solvent was evaporated to provide **13** as a white solid (352 mg, 70%) as a mixture of isomers, mp 163–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of isomers) δ 7.21 (m, 2H), 7.13 (m, 2H), 5.21 (m, 2H), 2.21–2.66 (m, 3H), 1.51–2.15 (m, 5H), 0.94–1.48 (m,

4H); ^{13}C NMR (75 MHz, $CDCl_3$, mixture of isomers) δ 138.00, 137.97, 135.10, 130.51, 126.93, 126.77, 126.56, 65.88, 45.01, 45.00, 43.83, 43.73, 43.70, 40.09, 35.76, 35.72, 27.68, 27.02, 26.93, 26.75, 26.59, 26.04, 25.87, 25.73; IR (thin film) 3320, 2921, 2841, 1501, 1487, 1291 cm^{-1}; MS *m/z* (70 eV, thermal spray, relative intensity) 350 (5%), 333 (30), 315 (27).

3.8. 1,2-Bis(9-bicyclo[4.3.0]-non-1(9)-en-8-one-4-methylbenzenesulfonylhydrazone)benzene **16**

To a round bottom flask equipped with a stirbar and charged with *p*-toluenesulfonylhydrazide (269 mg, 1.44 mmol), *p*-toluenesulfonic acid (12.5 mg, 0.065 mmol) and 1,2-bis(9-bicyclo[4.3.0]-non-1(9)-en-8-one)benzene (227 mg, 0.65 mmol) was added anhydrous methanol (21 ml). The colorless solution was purged with nitrogen and refluxed for 8 h, whereupon a white precipitate evolved. The pale yellow solution was cooled to −32 °C to encourage further precipitation and was subsequently filtered and the solid washed with cold methanol providing **16** as a white solid (327 mg, 73%), mp 218–220 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 4H), 7.25 (m, 4H), 7.15 (m, 4H), 6.66 (m, 4H), 2.61–2.23 (m, 5H), 2.16 (br s, 6H), 2.05–0.93 (m, 6H); IR (thin film) 3205, 2927, 2852, 1625, 1593, 1441, 1401, 1335, 1164, 1090 cm^{-1}.

3.9. 1,2-Bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzene **17**

To a flask charged with ethylene-bis(bicyclo[4.3.0]-non-1(9)-en-8-one-4-methylbenzenesulfonylhydrazone) (900 mg, 1.32 mmol) dissolved in THF (120 ml) at −10 °C under N_2 was added slowly *sec*-butyllithium (6.6 ml, 10 mmol, 1.6 M in ether) resulting in a deep red color. The cold bath was removed and the solution allowed to warm gradually to room temperature. After 3 h, the mixture was cooled to 0 °C and the reaction quenched with aqueous $NaHCO_3$. The mixture was extracted with Et_2O (3 × 10 ml), dried with $MgSO_4$ and concentrated to a brown red oil. The crude product was purified (SiO_2, pentane) resulting in **17** as a white solid (213 mg, 52% yield), mp 88–90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (br s, 4H), 5.94 (br s, 2H), 2.79 (d, J = 2.5 Hz, 4H), 2.29 (m, 4H), 1.95 (m, 4H), 1.60 (m, 4H), 1.51 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.00, 130.51, 126.93, 126.77, 126.56, 65.88, 45.01, 43.83, 40.09, 35.72, 26.75, 25.87; IR (thin film) 3320, 2921, 2841, 1501, 1487, 1291 cm^{-1}; MS *m/z* (70 eV, thermal spray, relative intensity) 350 (5), 333 (30), 315 (27).

3.10. 1,2-Bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzenedichlorotitanium **4a**

To a THF solution (4 ml) of 1,2-bis(9-bicyclo[4.3.0]-non-1(9)-1,6-diene)benzene (54.0 mg, 0.172 mmol) at −78 °C under Ar was added *n*-butyllithium (79 μl, 0.20 mmol, 2.5 M in heptanes) to obtain a pale yellow color. The cooling bath was removed and the solution allowed to warm to room temperature whereupon a white precipitate evolved. The suspension was stirred for 1.5 h at room temperature and then was added to a suspension of $TiCl_3$ (28.0 mg, 0.18 mmol) in THF (1 ml) at −78 °C. The purple solution was allowed to warm to room temperature and was then heated under reflux for 6 h. After cooling to room temperature, the solution was concentrated in vacuo to a green solid which was dissolved in $CHCl_3$ (10 ml) and air was gently bubbled through the solution for 1.5 h. To the resultant bright red solution was added 6 M HCl and the product extracted with $CHCl_3$ (3 × 5 ml) affording **4a** as a red solid (66.0 mg, 89%) on solvent evaporation as a 20:80 mixture of *meso* to *dl* isomers. Crystallization with hot toluene resulted in pure *dl*-**4a** (68% overall yield), mp 242 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.26–7.21 (m, 2H), 6.70 (d, J = 2.5 Hz, 2H), 5.49 (d, J = 2.5 Hz, 2H), 3.25 (ddd, J = 17.0, 6.5, 6.5 Hz, 2H), 2.70 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 2.42 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 2.09 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 1.99–1.90 (m, 2H), 1.79–1.67 (m, 2H), 1.62–1.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.06, 132.00, 129.35, 128.78, 128.36, 125.89, 113.99, 24.53, 24.23, 21.85, 21.49; IR (thin film) 2926, 2852, 1737, 1610, 1466, 1430, 1260 cm^{-1}; MS, *m/z* (70 eV, relative intensity) 430 (17), 395 (21), 360 (16), 358 (100); Anal. Calc. for $C_{24}H_{24}TiCl_2 \cdot H_2O$: C, 61.81; H, 6.07. Found: C, 61.79; H, 6.05.

3.11. 1,2-Bis(9-bicyclo[4.3.0]-non-1,6-dienyl)benzenedichlorozirconium **4b**

To a Et_2O solution (15 ml) of 1,2-bis(9-bicyclo[4.3.0]-non-1(9)-1,6-diene)benzene (266 mg, 0.847 mmol) at −78 °C under Ar was added *n*-butyllithium (713 μl, 1.86 mmol, 2.6 M in heptanes) to obtain a pale yellow colored solution. The solution was allowed to warm to room temperature and was stirred for 9.5 h. Solid $ZrCl_4$ (233 mg, 1.0 mmol) was added to the solution via an attached side arm resulting in a white suspension which was stirred for 48 h. The solvent was evaporated and methylene chloride (8 ml) added. The milky suspension was filtered under Ar to remove LiCl and the solvent was again evaporated. A ^{1}H NMR spectrum of the crude residue showed a 60:40 ratio of suspected racemic to meso isomers of **4b** and no starting material hydrogen signals. Crystallization with hot toluene failed to crystalize one isomer selectively, but did result in the isomerization of some of the meso isomer to the racemic (93:7, racemic:meso). Evaporation of the solvent provided **4b** as a lavender solid (369 mg, 92% yield) as a mixture of meso and racemic isomers, mp 195–197 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.25–7.22 (m, 2H), 6.43 (d,

J = 2.5 Hz, 2H), 6.07 (d, J = 2.5 Hz, 2H), 3.11 (ddd, J = 17.0, 6.5, 6.5 Hz, 2H), 3.05 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 2.71 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 2.65 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 2.38–2.28 (m, 2H), 2.09–1.94 (m, 2H), 1.91–1.83 (m, 2H), 1.65–1.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.99, 131.58, 129.63, 127.96, 127.94, 122.22, 119.21, 108.58, 23.93, 22.84, 22.07, 21.80; IR (thin film) 2933, 2856, 1453, 1433, 1259, 1094, 1028, 909 cm^{-1}; MS, m/z (12 eV, relative intensity) 474 (78%), 438 (69), 436 (100).

3.12. Alternative preparation of 1,2-Bis(1-octen-7-yne)benzene 9

To a flask charged with $Pd(PPh_3)_4$ (0.70 mmol, 0.83 g) and CuI (3.50 mmol, 0.68 g) at room temperature under Ar was added a solution of 1,2-diiodobenzene (24.0 mmol, 7.80 g) and 1-octen-7-yne (71.0 mmol, 7.70 g) in Et_3N (16.7 ml) and THF (460 ml). The mixture was stirred at room temperature for 48 h, and then water (200 ml) and diethyl ether (100 ml) were added to the dark green solution. The layers were separated and the aqueous portion extracted with diethyl ether (3 × 50 ml). The combined organic portion was dried over $MgSO_4$, concentrated and purified by chromatography (SiO_2, 1% ethyl acetate in petroleum ether) to give **9** as a pale yellow oil (7.0 g, 99%). The spectroscopic data for **9** obtained in this manner were identical with those obtained above.

3.13. 1,15-Hexadecadien-6,10-diyne 19

To a THF solution (100 ml) of 1,5-hexadiyne (1.75 mg, 22 mmol) at −78 °C under N_2 was slowly added *n*-butyllithium (2.86 M, 16.2 ml, 46 mmol) and the resulting solution was stirred for 1 h. HMPA (8.4 ml, 48 mmol) was added and the solution was stirred for an additional 15 min. A THF solution (9 ml) of 5-bromo-1-pentene (5.1 ml, 48 mmol) was added dropwise to give a pale yellow colored solution. This solution was allowed to come gradually to room temperature over 8 h. The reaction was quenched with H_2O (100 ml), the mixture was extracted with petroleum ether (4 × 20 ml) and rinsed with brine (10 ml). The organic extracts were dried ($MgSO_4$) and concentrated to a pale yellow oil. The crude product was distilled to yield **19** as a colorless oil (3.2 g, 68%), bp 82 °C, P = 0.002 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (ddt, J = 10.0, 17.5, 7.5 Hz, 2H), 5.10 (dd, J = 2.5, 17.5 Hz, 2H), 5.00 (dd, J = 2.5, 10.0 Hz, 2 H), 2.36 (br s, 4H), 2.20 (t, J = 7.5 Hz, 8H), 1.60 (dt, J = 15.0, 7.5 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.97, 114.89, 80.64, 79.05, 32.70, 28.13, 19.47, 18.09; IR (neat) 2928, 2856, 1710, 1639, 1457, 1436, 1352, 1256, 1162 cm^{-1}; MS, m/z (70 eV, rel intensity) 214 (M^+, 6%), 199 (12), 171 (13), 159 (13), 145(32), 131 (42).

3.14. 1,17-Octadeca-7,11-diyne 20

To a THF solution (10 ml) of 1,5-hexadiyne (1.39 g, 7.49 mmol) at −78 °C under N_2 was slowly added *n*-butyllithium (2.68 M, 6.4 ml, 15.7 mmol) to achieve a white suspension. After 15 min, HMPA (3.9 ml, 22.5 mmol) was added dropwise to yield a faintly yellow solution and was stirred at −78 °C for 0.5 h. A THF solution (2 ml) of 6-iodo-1-hexene (3.75 ml, 16 mmol) was added dropwise and the solution allowed to come to room temperature over 8 h. The reaction was quenched with H_2O (10 ml) and the mixture extracted with petroleum ether (3 × 10 ml) before drying over $MgSO_4$. After concentrating, the crude product was distilled to provide **20** as a colorless oil (1.26 g, 70%), bp 95 °C, P = 0.001 mm Hg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (ddt, J = 10.0, 17.5, 7.5 Hz, 2H), 4.95 (dd, J = 2.5, 17.5 Hz, 2H), 4.91 (dd, J = 2.5, 10.0 Hz, 2H), 2.29 (br s, 4H), 2.11 (t, J = 5.0 Hz, 4H), 2.02 (t, J = 6.0 Hz, 4H), 1.47–1.44 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.72, 114.49, 83.08, 81.33, 33.52, 31.49, 28.93, 26.87, 18.93; IR (neat) 3073, 2928, 2855, 1709, 1640, 1458, 1350 cm^{-1}; MS, m/z (70 eV, relative intensity) 242 (1%), 233 (9), 219 (25), 203 (34), 193 (25), 179 (73).

3.15. 1,2-Ethylene-bis(2-bicyclo[3.3.0]-oct-1(2)-en-3-one) 21

To a round bottom flask equipped with a condenser and charged with dicobalt octacarbonyl under N_2 at room temperature was added a CH_3CN solution (110 ml) of 1,15-hexadecadien-6,10-diyne (3.04 g, 14.2 mmol) and the resulting solution was stirred until the bubbling had ceased. The deep red solution was then heated for 8 h under reflux. The solution was cooled to room temperature and Al_2O_3 (IV) was added before concentrating. The product, adhered to the alumina, was poured onto a column of SiO_2 and eluted with 5%–50% ethylacetate/petroleum ether to provide **21** as a white solid (2.6 g, 68%), mp 95–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.58 (dd, J = 18.5, 6.0 Hz, 4H), 2.44 (dd, J = 7.5, 4.0 Hz, 4H), 2.25–2.41 (m, 4H), 2.07–2.16 (m, 2H), 1.94–2.02 (m, 4H), 0.98 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.11, 184.40, 135.09, 44.24, 41.59, 31.09, 25.45, 24.92, 22.01; IR (thin film) 2945, 2923, 1696, 1643, 1427, 1356, 1288, 1166 cm^{-1}; MS, m/z (70 eV, relative intensity) 270 (38%), 243 (27), 163 (31), 149 (40), 136 (83).

3.16. 1,2-Ethylene-bis(9-bicyclo[4.3.0]-non-1(9)-en-8-one) 22

To a round bottom flask equipped with a condenser and charged with dicobalt octacarbonyl (3.8 g, 11 mmol) under N_2 was added a CH_3CN solution (22 ml) of

1,17-heptadeca-7,11-diyne (1.26 g, 5.2 mmol). When the bubbling ceased, the solution was heated under reflux for 12 h before cooling to room temperature. Al_2O_3 (IV) (1 g) was added to the crude solution and concentrated. The solid was transferred to a column of silica gel and eluted with 5%–50% ethyl acetate/petroleum ether to afford **22** as a white solid (1.07 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77–2.74 (m, 2H), 1.72–2.52 (m, 16H), 1.48–1.44 (m, 2H), 1.25–1.10 (m, 4H), 1.01–0.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.26, 196.98, 156.00, 61.29, 60.12, 54.88, 48.54, 46.69, 45.36, 41.07; IR (thin film) 2927, 2854, 1696, 1645, 1443, 1373, 1298, 1067 cm^{-1}; MS, *m/z* (70 eV, relative intensity) 299 (M^+, 68%).

3.17. 1,2-Ethylene-bis(2-bicyclo[3.3.0]-oct-1(2)-en-3-ol) 23

To an Et_2O suspension (15 ml) of $LiAlH_4$ (710 mg, 18.7 mmol) at 0 °C under N_2 was slowly added an Et_2O solution (5 ml) of ethylene-bis(bicyclo[3.3.0]-oct-1-en-3-one) (505 mg, 1.87 mmol) and the resulting solution was allowed to come gradually to room temperature. After stirring for 1 h at room temperature, the solution was cooled again to 0 °C and Rochelle's salt (2.43 ml) slowly added. The solution was stirred for 20 min and then filtered. The solvent was evaporated to leave **23** as a white solid (384 mg, 75%), mp 101–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (br s, 2H), 2.54–2.62 (m, 10H), 2.06–2.20 (m, 4H), 1.84–1.95 (m, 4H), 0.986–1.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, mixture of two isomers) δ 148.07, 148.66, 133.35, 133.26, 83.64, 83.24, 47.78, 47.58, 42.48, 42.37, 32.52, 32.43, 27.23, 27.21, 27.12, 24.95, 24.88, 22.80, 22.72; IR (thin film) 3258, 2941, 2857, 1448, 1321, 1266, 1055 cm^{-1}; MS, *m/z* (70 eV, relative intensity) 274 (6%), 256 (10), 238 (5).

3.18. 1,2-Ethylene-bis(9-bicyclo[4.3.0]-non-1(9)-en-8-ol)

To an Et_2O suspension (10 ml) of $LiAlH_4$ (112 mg, 2.96 mmol) at 0 °C under N_2 was slowly added an ether solution (6 ml) of ethylene-bis-(bicyclo[4.3.0]non-1-en-3-one) (441 mg, 1.48 mmol) and the solution was allowed to come gradually to room temperature. After stirring for 1 h at room temperature the solution was cooled again to 0 °C and Rochelle's salt (388 μl) slowly added. After stirring for 20 min the solution was filtered. The solution was concentrated to provide the title compound as a white solid (385 mg, 85%) as a mixture of isomers, mp 108–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of isomers) δ 5.15 (br s, 2H), 2.65 (m, 8H), 1.82–2.21 (m, 10 H), 1.13–1.33 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, mixture of isomers) δ 141.73, 141.70, 134.66, 134.55, 79.27, 78.51, 43.83, 43.80, 40.93, 40.59, 36.026, 35.87, 26.81, 26.75, 26.62, 26.48, 26.44, 26.39, 24.51 23.60; IR (thin film) 3339, 2921, 2848, 1442, 1332, 1049 cm^{-1}; MS, *m/z* (70 eV, relative intensity) 302 (1%), 285 (11), 267 (25).

3.19. 1,2-Ethylene-bis(2-bicyclo[3.3.0]-1,4-octadiene) 24

To a flask purged with N_2, equipped with a condenser and charged with de-oiled NaH (46 mg, 1.9 mmol) was added a DMF solution (10 ml) of ethylene-bis(bicyclo[3.3.0]-oct-1-en-3-ol) (131 mg, 0.482 mmol) and the resulting solution was stirred at room temperature for 1 h. Iodomethane (300 μl, 4.82 mmol) was added and the solution was heated to 45 °C for 15 h. H_2O (10 ml) was added at 0 °C and the solution was extracted with Et_2O (4 × 5 ml) and dried over $MgSO_4$ before concentrating. The crude yellow solid was chromatographed (SiO_2, pentane) to yield **24** as a white solid (33 mg, 29%), mp 85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (br s, 2H), 2.99 (m, 4H), 2.37 (m, 4H), 2.30 (br s, 8H), 1.26 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.44, 149.43, 141.69, 113.57, 32.99, 30.36, 28.52, 28.01, 25.68; IR (thin film) 2951, 2921, 2865, 1460, 1440, 1376, 1243 cm^{-1}; MS, *m/z* (70 eV, relative intensity) 236 (7%), 209 (11), 169 (10), 155 (12).

3.20. 1,2-Ethylene-bis(9-bicyclo[4.3.0]-non-1(9)-en-8-one-4-methylbenzene sulfonylhydrazone) 25

To a round bottom flask equipped with a stirbar and charged with *p*-toluenesulfonylhydrazide (469 mg, 2.56 mmol), *p*-toluenesulfonic acid (22 mg, 0.117 mmol) and ethylene-bis(bicyclo[4.3.0]-non-1(9)-en-8-one) (348 mg, 1.17 mmol) was added anhydrous methanol (40 ml). The colorless solution was purged with N_2 and refluxed for 8 h, whereupon a white precipitate evolved. The pale yellow solution was cooled to −32 °C to encourage further precipitation and was subsequently filtered. The solid was washed with cold methanol to obtain **25** as a white solid (332 mg, 64%), mp 131–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.81 (m, 4H), 6.71–6.80 (m, 4H), 2.33 (s, 6H), 0.65–2.49 (m, 13H); IR (neat) 3205, 2927, 2852, 1625, 1593, 1441, 1401, 1335, 1164, 1090 cm^{-1}.

3.21. 1,2-Ethylene-bis(9-bicyclo[4.3.0]-nona-1(6),6-diene) 26

To a THF (14 ml) solution of ethylene-bis(bicyclo[4.3.0]-non-1(9)-en-8-one-4-methylbenzene-sulfonylhydrazone) (166 mg, 0.370 mmol) at −10 °C was slowly added *sec*-butyllithium (1.6 M, 1.80 ml, 2.89 mmol) resulting in a red colored solution. On completion of the addition, the solution was allowed to

warm to room temperature and was stirred at room temperature for 3.5 h. At 0 °C, the reaction was quenched with aqueous $NaHCO_3$, the mixture extracted with Et_2O (3×10 ml), dried over $MgSO_4$ and the solvent evaporated. The crude product was purified (SiO_2, pentane) to give **26** as a white solid (46 mg, 47% yield), mp 154–158 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 5.81 (s, 2H), 2.70 (br s, 4H), 2.41 (t, 4 Hz, 4H), 2.24 (br s, 4H), 2.12 (br s, 4H), 1.60 (m, 8H); IR (neat) 3052, 3015, 1600, 1590, 1505, 1457, 1384, 1367 cm^{-1}; MS, m/z (70 eV, relative intensity) 266 (10%), 235 (13).

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