General Synthetic Route to Substituted Bis(cyclopentadienyl)- and Bis(indenyl)methanes

Ilya E. Nifant'ev,*[a] Pavel V. Ivchenko,[a] Lyudmila G. Kuz'mina,[b] Yuri N. Luzikov,[a] Alexander A. Sitnikov,[a] Oleg E. Sizan[a]

[a] Department of Chemistry, Moscow University, Moscow 119899, Russia

[b] N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, 31 Leninskii Prospect, V-71 Moscow 117907, Russia

Fax +7(95)9395546; E-mail inif@org.chem.msu.su

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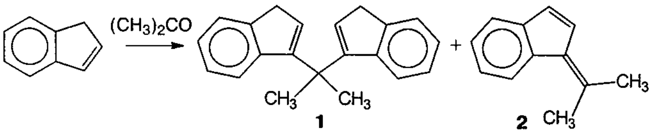
Several substituted bis(cyclopentadienyl)- and bis(indenyl)methanes were synthesized directly from the corresponding cyclopentadienes (indenes) and ketones in KOH/DME two-phase mixture.

Bis(cyclopentadienyl)- and bis(indenyl)*ansa*-metallocenes of group IV transition metals have been extensively investigated in the last ten years within the search for the new-generation catalysts of α-olefin homo- and copolymerization.[1,2] The main focus has been directed towards the study of complexes containing short bridges and the derivatives with $-SiMe_2-$[3] and $-CH_2CH_2-$[1,4] bridges are better known due to the general availability of the starting ligands. On the contrary, the derivatives with a single carbon bridge are known to a lesser extent due to the absence of good methods for the synthesis of the starting bis(cyclopentadienyl)methanes and bis(indenyl)methanes. Usually such ligands were synthesized from the corresponding fulvenes and the lithium and sodium salts of the corresponding cyclopentadienes and indenes with moderate yields.[5-7]

Recently[8] we found that the same process can be carried out without the preceding preparation of alkali metal organic derivatives. 6,6-Dimethylfulvene reacts with several cyclopentadienes and indene in a two-phase NaOH/THF mixture to give corresponding bis(cyclopentadienyl)methanes with considerable yields (18–72%).[8a] Since the fulvenes could be easily synthesized from cyclopentadienes and ketones under the same basic conditions, we tried to prepare symmetrical bis(cyclopentadienyl)methanes from corresponding cyclopentadienes and ketones in a one-pot procedure. It was found that the simplest 2,2-bis(cyclopentadienyl)propane only, could be prepared by this method with high yield and substituted cyclopentadienes and indene were inactive in this reaction. The goal of the present contribution is to overcome such limitations and to elaborate a good and general protocol for the preparation of several bis(cyclopentadienyl)methanes substituted onto cyclopentadienyl rings as well as on the carbon bridge atom.

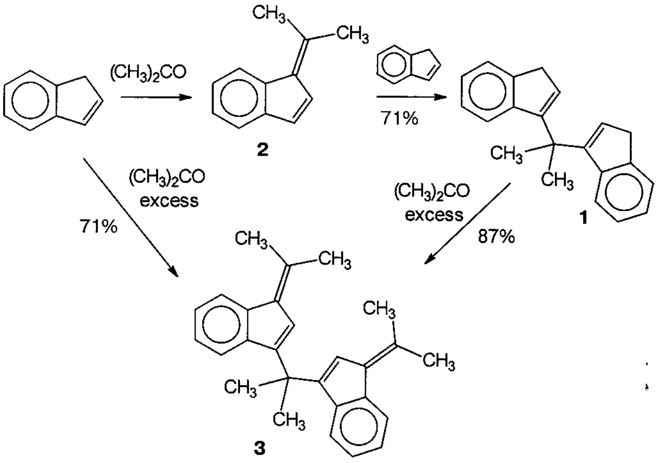
As an initial hypothesis we supposed that the reactivity of cyclopentadienes towards electrophiles (e.g. ketones, fulvenes etc.) depends on the correct tuning of the acidity of the cyclopentadiene and the basicity of the medium. It seems reasonable that the basicity of alkali metal hydroxides increases when the selective solvation of the alkali metal cation is improved. Several alkali hydroxide/solvent mixtures were tested for the reaction between indene and acetone (see Scheme 1).

The best results were obtained using KOH/DME system. This result can be explained by the efficient solvation of the metal cation and the good solubility of KOH. We found that the system KOH/DME is so effective, that in the reaction of indene even with excess of acetone not the corresponding fulvene **2**, but only bisfulvene **3** is formed. The same product was also synthesized from bis(indene) **1**.



Base/solvent	Yield of **1**, %	Yield of **2**, %
NaOH/Et₂O	-	-
NaOH/THF	-	25
NaOH/DME	33	20
KOH/THF	-	31
KOH/DME	71	7

Scheme 1

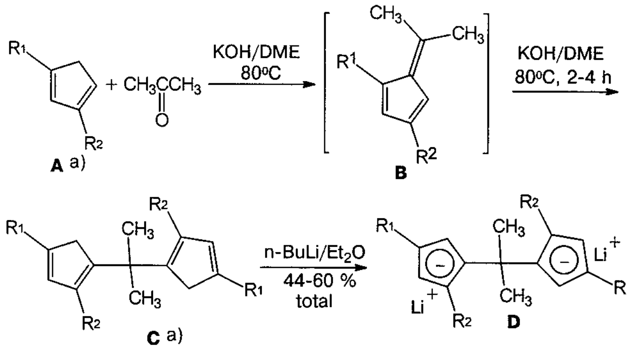


Scheme 2

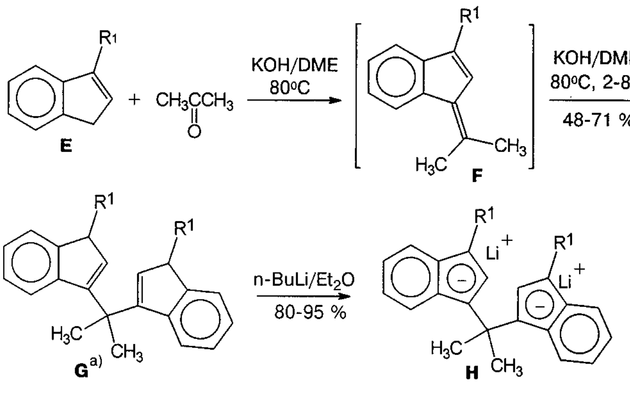
When the reaction between indene and the equivalent amount of acetone was carried out in THF no traces of 2,2-bis(indenyl)propane **1** were found. If 3 equivalents excess of indene were used the fulvene **2** was the only isolated product. No reaction takes place if diethyl ether is used as a solvent.

Several differently substituted bis(cyclopentadienyl)- **C** and bis(indenyl)methanes **G** **4–9** for the *ansa*-metallocene synthesis were prepared by condensation of substituted cyclopentadienes **A** and indenes **E** with acetone in the KOH/DME system. (Scheme 3; Table 1).

Compounds **C**, **G** (**4–9**) represent mixtures of double bond isomers with different positions of double bonds. Thus, these were converted to the lithium derivatives **D**, **H** (**4a–9a**).



C	D	R^1	R^2
4	4a	$CH(CH_3)_2$	H
5	5a	$C(CH_3)_3$	H
6	6a	$C(CH_3)_3$	CH_3



G	H	R
7	7a	CH_3
8	8a	$CH(CH_3)_2$
9	9a	$C(CH_3)_3$

a) double bond isomers, only one is shown

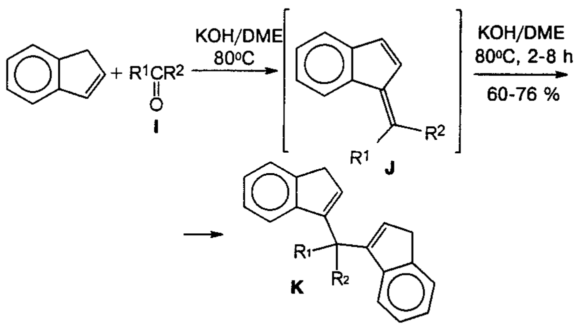
Scheme 3

The reaction of indene with several ketones **I** has some limitations with respect to **I** (see Scheme 4; Table 2). Bulky ketones such as pinacolone do not react; even the corresponding fulvene **J** was not isolated.

We also examined an alternative possibility for the synthesis of 3,3′-disubstituted bis(indenyl)methanes by alkylation of dilithium derivative **1a**, and nucleophilic addition to difulvene **3**.

Alkylation of Dilithium Derivative 1a:

It was found that this approach could be used for the synthesis of the derivatives with primary alkyl radicals (e.g. methyl group, **7**, 75 % yield) and with organoelement groups (Me_3Si- **14**, Me_3Ge- **15**). As to the corresponding substances with secondary (*i*-Pr, **8**) and tertiary (*t*-Bu-, **9**) substituents the yields seem unsatisfactory: 14 and 0 %, respectively (Scheme 5).



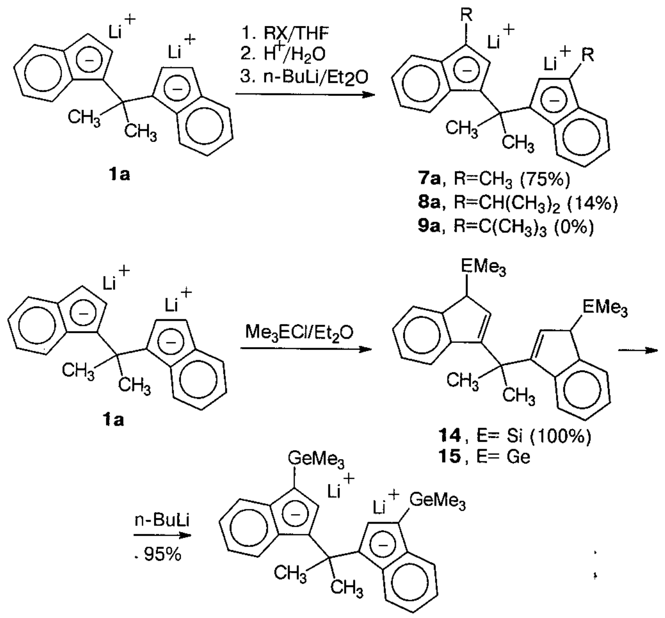
Substituent key see table 2

Scheme 4

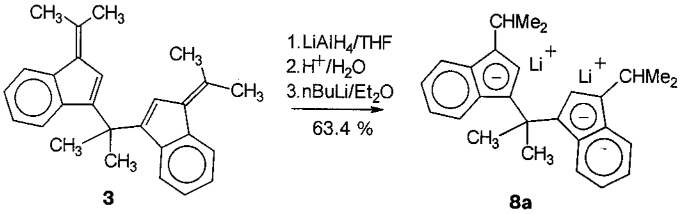
Nucleophilic Addition Reactions to Difulvene 3:

It was found that difulvene **3** is in fact a very stable compound. It reacts with $LiAlH_4$ under reflux in THF within 10 hours to give after workup **8** and does not react with MeLi at all.

a) Alkylation of lithium derivative **1a**

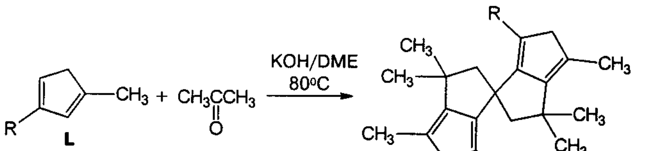


b) Nucleophylic addition to difulvene **3**



Scheme 5

The reaction course of 1,3-dimethylcyclopentadiene and 1-methyl-3-phenylcyclopentadiene **L** towards acetone differs from that of simple cyclopentadienes. Under standard conditions these cyclopentadienes did not yield the corresponding bis(cyclopentadienyl)methanes. In the first case we isolated a complicated mixture of hydrocarbons; from that only the spiro compound **16** was isolated in pure form in 7% yield. No reaction of 1-methyl-3-phenylcyclopentadiene with the stoichiometric amount of acetone takes place under standard conditions. By using a 100-fold excess of acetone, the spiro compound **17** was isolated in 60% yield as the only product of the reaction (Scheme 6). Mass-spectral investigation of **16** and **17** as well as the X-ray analysis of **16** (Figure 1) led us to the structure of the spiro compounds.



16, R=CH_3; 7%
17, R=C_6H_5; 60%

Scheme 6

We propose that **16** and **17** are formed by a sequence of Michael addition and aldol reactions with the diene **L** via intermediate ketone **N** (Scheme 7). Phorone **M** arises from aldol condensation of acetone.[9]

When using *tert*-butylcyclopentadiene **Lc**, no condensation was recorded under these conditions. Presumably, this is a result of the high steric restrictions.

X-ray Structure of 16:

The experimental reflections were measured on an Enraf Nonius CAD4 diffractometer using MoK_α radiation and graphite monochromator. No absorption correction was applied. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2. All of the hydrogen atoms were found in the difference Fourier synthesis. The final full-matrix least-squares refinement in the anisotropic approximation for the non-hydrogen atoms and in the isotropic one for the hydrogen atoms converged to $R_1 = 0.0480$ and $wR_2 = 0.1378$ for $F^2 > 2\sigma(F^2)$. Residuals are 0.280 and -0.216 e/A^3.

All of the calculations were performed using SHELX76[10] and SHELX93[11] software. The ORTEP program (with probability 0.5) was used for drawing the molecules. The details of the X-ray experiment and crystallographic parameters are given in Table 3.

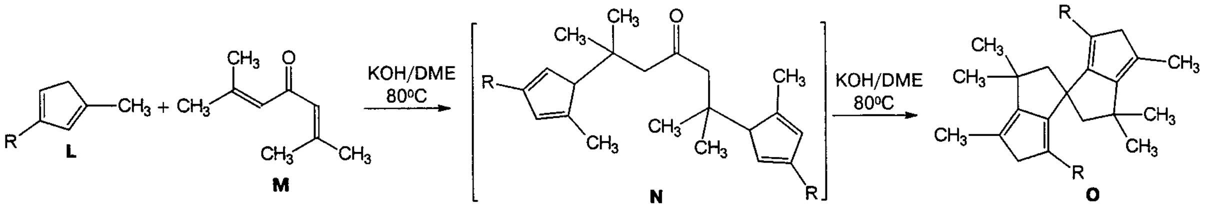
The molecule of **16** is shown in Figure 1. It represents a spirocyclic system with the C(6) spiro atom situated at a two-fold axis. This axis passes through the bisectrix of the angles C(7)C(6)C(7a) and C(4)C(6)C(4a). Unsaturated cycle C(1)C(2)C(3)C(4)C(5) is planar and saturated cycle C(4)C(6)C(7)C(8)C(5) has an envelope conformation with the C(7) atom deviated from the plane of the remaining atoms of the cycle. The dihedral angle between the planes C(6)C(7)C(8) and C(6)C(4)C(5)C(8) is equal to 27.2° and the dihedral angle between the latter plane and the plane of unsaturated cycle is 179.3°.

All the geometrical parameters of the molecule were found with high accuracy. The lengths of the C(sp^2)-C(sp^3) bonds C(2)-C(3) and C(2)-C(1) in unsaturated cycle 1.509(2) and 1.507(2) Å as well as C(4)-C(6) and C(5)-C(8) in saturated on 1.509(2) and 1.508(2) Å) are very close to each other. Two double bonds C(1)-C(5) and C(3)-C(4) are 1.340(2) and 1.346(2) Å, and the central bond C(4)-C(5) of the bicyclic system is 1.458(2) Å. The distances between the C(1) and C(3) atoms in the sp^2 hybridization state and C atoms of the corresponding Me groups are 1.493(2) and 1.495(2) Å, whereas the distances between the C(8) atom in the sp^3 hybridization state and the C atoms of its Me groups are 1.532(2) and 1.529(2) Å. All the bond distances considered fit a standard bond length typical of appropriate bonds. A single bond that is somewhat elongated is the C(6)-C(7) one (1.564(2) Å). The reason for such an elongation is, probably, steric hindrance at the C(6) spiro atom although it does not affect the second bond length (C(6)-C(4)).

In the bicyclic system, the bond angles are symmetrical with respect to the C(2) ... C(7) line. The angles at spiro atom C(6) are a little distorted due to occurrence of two cycles with the endocyclic angles (100.6(7)°) less than exocyclic ones (114.1(2) and 116.5(2)^2).

In the crystal, the molecules are packed due to Van der Waals interactions.

The ethereal solvents (DME, THF, Et_2O) used in this work were supplied by Merck and distilled under Ar from Na/benzophenone. Other solvents were used without special purification. KOH powder was supplied by Merck. Isopropylcyclopentadiene,[12] *tert*-butylcyclopentadiene,[13] methyl-*tert*-butylcyclopentadiene,[14] methylindene,[15] isopropylindene,[16] tert-butylindene,[12] and 1-methyl-3-phenylcyclopentadiene[17] were prepared by usual methods. Synthetic procedures were performed under an atmosphere of Ar. Some bis(in-



16, R=CH_3; 7%
17, R=C_6H_5; 60%
18, R=t-Bu; 0%

Scheme 7

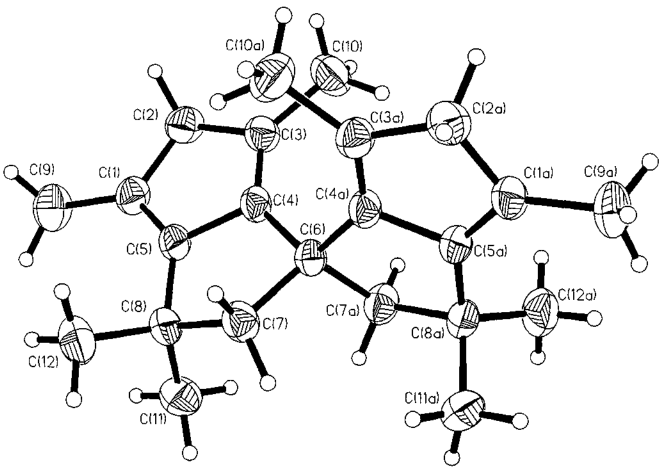


Figure 1. Molecular Structure of compound **16** with 50% probability ellipsoids depicted.

denyl) "ligands" and all the dilithio derivatives were prepared and characterized using the Schlenk technique.[18]

^1H and ^{13}C NMR spectra were registered on a Varian XR-300 and Varian XR-400 spectrometers. Chemical shifts were referenced against internal H-impurities in the deuterated solvents.

Synthesis of Compounds 1, 4–13 by Direct Condensation of Cyclopentadienes or Indenes and Ketones:

Method A: 200 mmol of corresponding cyclopentadiene or indene were added over 0.5 h under vigorous stirring to the suspension of KOH powder (15 g) in DME (150 mL). The mixture was heated until reflux. Then the carbonyl compound (100 mmol) was added dropwise over 1 h and the mixture was stirred under reflux for an additional 1–6 h. Then the resulting mixture was cooled, treated with H_2O (200 mL) and Et_2O (100 mL). The organic layer was separated, washed with H_2O and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was distilled. The broad fraction was collected, then was dissolved in Et_2O (50 mL), cooled to −20 °C and treated with 1.6 M BuLi in hexane (13.8 mL, 22 mmol) over 5 minutes. After 10 h the resulting precipitate of dilithium salt was isolated, washed with Et_2O (3 × 30 mL), and dried in vacuo. The details of the experiments are presented in Table 1.

Method B: 200 mmol of corresponding cyclopentadiene or indene were added over 0.5 h under vigorous stirring to the suspension of KOH powder (15 g) in DME (150 mL). The mixture was heated until reflux. Then the carbonyl compound (100 mmol) was added dropwise over 1 h and the mixture was stirred under reflux for an additional 1–6 h. Then the resulting mixture was cooled, treated with H_2O (200 mL) and Et_2O (100 mL). The organic layer was separated, washed with H_2O and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was distilled. The broad fraction was collected and recrystallized from Et_2O. All compounds synthesized by Method B were colorless crystalline solids. The details of the experiments are presented in Table 2.

1,1-Bis(inden-1-yl)cyclopentane (**10**):

Anal. Calcd. for $C_{23}H_{22}$, 298.43: C, 92.57; H, 7.43. Found: C, 92.51; H, 7.49.

1,1-Bis(inden-1-yl)cyclohexane (**11**):

Anal. Calcd. for $C_{24}H_{24}$, 312.45: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.88.

1,1-Bis(inden-1-yl)cycloheptane (**12**):

Anal. Calcd. for $C_{25}H_{26}$, 326.48: C, 91.97; H, 8.03. Found: C, 91.89; H, 8.11.

Bis(inden-1-yl)phenylmethane (**13**):

Anal. Calcd. for $C_{26}H_{22}$, 334.46: C, 93.37; H, 6.63. Found: C, 93.25; H, 6.75.

2,2-Bis[1-(1-isopropylidene)(1*H*)inden-3-yl]propane (3):

Indene (11.8 mL, 100 mmol) was added over 0.5 h under vigorous stirring to the suspension of KOH powder (8 g) in DME (150 mL). The mixture was heated until reflux. Then acetone (30 mL, 400 mmol) was added dropwise over 1 h and the mixture was stirred under reflux for an additional 4 h. Then the resulting mixture was cooled, treated with H_2O water (200 mL) and Et_2O (100 mL). The arising white organic precipitate was isolated, washed with H_2O and Et_2O and then dried. Yield of difulvene **3** was 12.5 g (71 %).

The condensation of 2,2-bis(indenyl)propane **1** with acetone at the same conditions gives **3** with the yield 87 %.

^{1}H NMR ($CDCl_3$; 30 °C): δ = 7.68 ("d", 2 H); 7.27 ("d", 2 H); 7.04 ("td", 2 H); 6.94 ("td", 2 H) 6.84 (s, 2 H) {=CH}; 2.42 (s, 6 H); 2.34 (s, 6 H) {=CCH_3}; 1.77 (s, 6 H, $C(CH_3)_2$).

^{13}C NMR ($CDCl_3$; 30 °C): δ = 148.0; 142.9; 140.3; 137.0; 135.2 (=C<) 125.4; 124.1; 123.0; 122.0; 121.0 (=CH) 27.5 (>C<) 28.5; 25.0; 22.9 (CH_3).

Anal. Calcd. for $C_{27}H_{28}$, 352.52: C, 91.99; H, 8.01. Found: C, 91.95; H, 8.05.

Compounds 7,14,15 from Dilithium Salt 1a:

Dilithium Propane-2,2-bis(3-methylindenid-1-yl) (7a):

Dilithium salt **1a** (10.2 g, 35.9 mmol) in THF (50 mL) was treated with MeI (5 mL, 80 mmol) at −30 °C over 30 min. The mixture was allowed to warm to r.t. and solvent was removed. The residue was poured into H_2O (100 mL), treated with Et_2O (100 mL) and the organic layer was separated. The solvent was removed under

Table 1. Synthesis of Substituted Dilithium Propane-2,2-bis(cyclopentadienyl) **D** and -bis(indenes) **H** by Method A (See Scheme 3).

Product	Reaction Time (h)	bp (°C)/ p (Torr)	Educt	Yield (%)	^{1}H NMR (THF-*d*) δ, *J* (Hz)
4	2	155–180/ 0.05–0.1	**4a**	44	5.53 ("t", 2 H), 5.46 ("t", 2 H), 5.30 ("t", 2 H) {Cp-H} 2.61 (sept, 2 H, $-CH(CH_3)_2$), 1.59 (s, 6 H, $>C(CH_3)_2$), 1.12 (d, 12 H, $CH(CH_3)_2$)
5	2	165–190/ 0.05–0.1	**5a**	39	5.63 (br s, 2 H), 5.52 (br s, 2 H), 5.37 (br s, 2 H) {Cp-H} 1.60 (s, 6 H, $>C(CH_3)_2$), 1.13 (s, 18 H, $C(CH_3)_3$)
6	4	170–190/ 0.05–0.1	**6a**	60	5.52 ("d", *J* = 2.8, 2 H), 5.22 ("d", 2 H) {Cp-H} 3.58 (s, 6 H, Cp-CH_3), 1.58 (s, 6 H, $>CMe_2$), 1.18 (s, 18 H, $C(CH_3)_3$)
7	3	165–200/ 0.05–0.1	**7a**	65	7.42 ("d", 2 H), 7.10 ("d", 2 H), 6.26 ("t", 2 H), 6.18 ("t", 2 H) {ABCD, *J* = 9} 6.47 (s, 2 H), 2.33 (s, 6 H, Ind-CH_3), 1.90 (s, 6 H, $>CMe_2$)
8	4	190–210/ 0.05–0.1	**8a**	62	7.45 ("d", 2 H), 7.27 ("d", 2 H), 6.30 ("t", 2 H), 6.23 ("t", 2 H) {ABCD, *J* = 8.0} 6.63 (s, 2 H), 3.30 (sept, *J* = 7.0, 2 H, $-CH(CH_3)_2$), 1.98 (s, 6 H, $>CMe_2$), 1.35 (d, *J* = 7.0, 12 H, $CH(CH_3)_2$)
9	4	170–200/ 0.01–0.03	**9a**	48	8.17 ("t", 4 H), 6.95 (mm, 4 H) {ABCD} 7.36 (s, 2 H), 2.70 (s, 6 H, $>CMe_2$), 2.19 (s, 18 H, CMe_3)

Table 2. Synthesis of Alkanebis[(1*H*)indenyl] **K** from Indene and Various Ketones **I** by Procedure B (See Scheme 4)

Product	Ketone	R_1	R_2	Reaction Time (h)	bp (°C)/ p (Torr)	Yield (%)	^{1}H NMR (acetone-*d*) δ	^{13}C NMR (acetone-*d*) δ
Ka, 1	**Ia**	CH_3	CH_3	1	165–200/ 0.05–0.1	71	7.37 (d, 2H), 7.32 (d, 2H), 6.98 (m, 4H), 6.60 (t, 2H) {=CH} 3.38 (d, 4H, CH_2), 1.74 (s, 6H, CH_3)	151.3, 146.0, 144.9 {=C<} 128.0, 126.2, 124.8, 124.4, 122.1 {=CH} 38.5 (>C<), 37.9 (CH_2-allyl), 28.4 (CH_3)
Kb, 10	**Ib**	$(CH_2)_4$		2	165–200/ 0.05–0.1	62	7.47 (m, 2H), 7.37 (m, 2H), 7.02 (m, 4H), 6.62 (t, 2H) {=CH} 3.38 (d, 4H, CH_2-allyl), 2.37 (m, 4H), 1.80 (m, 4H) {H of cyclopentane}	149.1, 146.1, 145.2 {=C<} 128.6, 126.2, 24.9, 124.3, 122.4 {=CH} 50.5 (>C<), 37.7 (CH_2-allyl), 37.1, 24.2 {CH_2 of cyclopentane}
Kc, 11	**Ic**	$(CH_2)_5$		2	155–180/ 0.03–0.05	76	7.47 (m, 2H), 7.36 (m, 2H), 7.00 (m, 4H), 6.77 (t, 2H) {=CH} 3.41 (d, 4H, CH_2-allyl), 2.40 (m, 4H), 1.70 (m, 4H), 1.58 (m, 2H) {H of cyclohexane}	149.1, 146.1, 144.9 {=C<} 130.4, 126.1, 124.7, 124.4, 122.7 {=CH} 43.0 (>C<), 37.8 (CH_2-allyl), 35.8, 27.5, 23.3 {CH_2 of cyclohexane}
Kd, 12	**Id**	$(CH_2)_6$		2	160–180/ 0.03–0.05	68	7.35 (m, 2H), 6.96 (m, 4H), 6.72 (t, 2H) {=CH} 3.41 (d, 4H, CH_2-allyl), 2.42 (m, 4H), 1.63 (m, 8H) {H of cycloheptane}	150.5, 146.1, 145.1 {=C<} 128.8, 126.1, 24.8, 124.3, 122.4 {=CH} 45.9 (>C<), 37.7 (CH_2-allyl), 37.2, 31.7, 23.7 {CH_2 of cycloheptane}
Kf, 13	**If**	Phenyl	H	5	200–210/ 0.05–0.08	60	7.52–7.18 {mm, 13H} 6.05 (q, 2H, =CH), 5.39 (m, 1H, >CH), 3.40 (br s, 4H, CH_2)	145.6, 145.1, 141.5 (=C<), 131.8, 129.3, 128.7, 127.0, 126.2, 125.0, 124.1, 120.2 (=CH), 44.5 (>CH), 38.1 (CH_2)[a]

[a] CD_2Cl_2 was used.

reduced pressure and the resulting brown oil was dried in vacuo (60–80 °C, 0.01 Torr), dissolved in a mixture of Et_2O (100 mL) and THF (10 mL), cooled to −20 °C, and then treated with 2.2 M BuLi in hexane (33 mL, 72.6 mmol). The precipitate was isolated, washed with Et_2O (3 x 30 mL) and dried. Yield 12.3 g (75 %) of dilithium salt **7a**.

2,2-Bis(3-trimethylsilylinden-1-yl)propane (14):

The suspension of dilithium salt of 2,2-bis(indenyl)propane **1a** (8.77 g, 30.85 mmol) in Et_2O (100 mL) was added to Me_3SiCl (10 mL, 83 mmol) at −40 °C over 10 min. The mixture was allowed to warm to r.t. and the organic layer was separated. Then the solvent was removed under reduced pressure, the resulting yellow oil of **14** (12.75 g, 99 %) was dried in vacuo (60–80 °C, 0.01 Torr).

^{1}H NMR (CD_2Cl_2, 30 °C): $\delta = 7.55$ (m, 4H); 7.18 (mm, 4H) {ABCD}; 6.81; 6.80 (d, $\Sigma = 2H$, =CH); 3.66; 3.62 (d, $\Sigma = 2H$, CH); 1.96; 1.93 (s, $\Sigma = 6H$, CMe_2); 0.197; 0.168 (s, $\Sigma = 18H$, –$SiMe_3$).

Anal. Calcd. for $C_{27}H_{36}Si_2$, 416.75: C, 77.81; H, 8.71. Found: C, 77.44; H, 8.64.

2,2-Bis(3-trimethylgermylinden-1-yl)propane (15):

Isolated in the form of dilithium derivative, dilithium propane-2,2-bis(3-trimethylgermylindenid-1-yl), the suspension of dilithium salt of 2,2-bis(indenyl)propane **1a** (5.25 g, 18.47 mmol) in Et_2O (100 mL) was added to Me_3GeCl (6.1 g, 40 mmol) at −40 °C over 30 min. The mixture was allowed to warm to r.t., the organic layer was separated, and treated with 2.0 M BuLi in pentane (20 mL, 40 mmol). The precipitate was isolated, washed with Et_2O (3 x 30 mL) and dried. Yield 9.1 g, 95 % of **15a**.

^{1}H NMR (THF-d_8, 30 °C): $\delta = 7.63$ (m, 2H); 7.40 (m, 2H); 6.27 (mm, 4H) {ABCD}; 6.81 (s, 2H); 2.00 (s, 6H, >CMe_2); 0.34 (s, 18H, $GeMe_3$).

Anal. Calcd. for $C_{27}H_{36}Ge_2$, 505.76: C, 64.12; H, 7.17. Found: C, 63.89; H, 7.22.

Synthesis of 8 from Difulvene 3:

Difulvene **3** (6.27 g, 17.8 mmol) was dissolved in THF (100 mL) and stirred with $LiAlH_4$ (0.68 g, 17.9 mmol) at reflux for 5 h. The resulting solution was poured into H_2O (200 mL), neutralized and extracted with Et_2O (2 x 50 mL). Then the organic layer was dried (Na_2SO_4), the solvent was removed, the residue was dried in vacuo, dissolved in Et_2O (50 mL), cooled to −20 °C, and added to 2.2 M BuLi in hexane (16.5 mL, 36.3 mmol). The precipitate was isolated, washed with Et_2O (3 x 30 mL) and dried in vacuo. Yield 4.16 g (63 %) of the crystalline product **8a**.

2,2,4,6,2′,2′,4′,6′-Octamethyl-1,2,3,5,1′,2′,3′,5′-octahydro-1,1′-spirobipentalene (16):

1,3-Dimethylcyclopentadiene (18.8 g, 200 mmol) was added over 0.5 h with vigorous stirring to the suspension of KOH powder (15 g) in DME (150 mL). The mixture was heated until reflux. Then acetone (7 mL, 93 mmol) was added dropwise over 1 h and the mixture was stirred under reflux for an additional 4 h. Then the resulting mixture was cooled, treated with 2 M H_3PO_4 (100 mL) until neutralization and then with Et_2O (100 mL). The organic layer was separated, washed with H_2O (2 x 100 mL), evaporated, and the residue was distilled in vacuo. The broad fraction (100–150 °C/ 0.01 Torr) was collected. A part of the distilled oil crystallized. It was collected and recrystallized from hexane. Yield 2.0 g (7 %) of **16**.

^{1}H NMR ($CDCl_3$, 30 °C): $\delta = 2.87$ (br s, 4H, =CCH_2C=); 2.12 (AB, 4H, >CCH_2C<); 1.76 (s, 6H); 1.48 (s, 6H); 1.11 (s, 6H); 1.09 (s, 6H) {CH_3}.

^{13}C NMR ($CDCl_3$, 30 °C): $\delta = 154.2$; 153.1; 126.1; 124.9 (=C<); 63.1; 54.9 (CH_2); 44.2; 37.6 (>C<); 28.9; 28.3; 12.9; 12.4 (CH_3).

Anal. Calcd. for $C_{23}H_{32}$, 308.51: C, 89.55; H, 10.45. Found: C, 89.49; H, 10.51; $M^+ = 308.2504$.

2,2,4,2′,2′,4′-Hexamethyl-6,6′-diphenyl-1,2,3,5,1′,2′,3′,5′-octahydro-1,1′-spirobipentalene (17):

1-Methyl-3-phenylcyclopentadiene (31.2 g, 200 mmol) was added to a suspension of KOH powder (15 g) in DME (150 mL). The mixture was heated until reflux. Then acetone (7 mL, 93 mmol) was added dropwise over 10 min and the mixture was stirred under reflux. After 10 h, no reaction could be detected by TLC. Then a large excess of acetone (500 mL, 6643 mmol) was added. The mixture was stirred for 1 h, poured into ice/water (500 mL), and acidified

Table 3. Crystal Data and Structure Refinement for **16**

Empirical formula	$C_{23}H_{32}$
Formula weight	308.49
Crystal size	0.32 × 0.44 × 0.82 mm
Crystal system	monoclinic
Space group	C2/*c*
Unit cell dimensions	$a = 16.315(5)$ Å $\alpha = 90°$ $b = 8.061(9)$ Å $\beta = 94.46(3)°$ $c = 14.671(6)$ Å $\gamma = 90°$
Volume	1924(2) Å^3
Z	4
Density (calculated)	1.065 g/cm^3
Temperature	293(2) K
Wavelength	0.71069 Å
Absorption coefficient	0.059 mm^{-1}
F(000)	680
Theta range for data collection	2.50 to 29.97°
Index ranges	$-22 \Leftarrow h \Leftarrow 20$, $0 \Leftarrow k \Leftarrow 10$, $-18 \Leftarrow 1 \Leftarrow 19$
Reflections collected	2694
Independent reflections	2275 [R(int) = 0.0417]
Refinement method	Full-matrix least-squares on F^2
Final R indices [I > 2 sigma(I)]	$R_1 = 0.0480$, $wR_2 = 0.1378$
R indices (all data)	$R_1 = 0.0629$, $wR_2 = 0.1461$
Largest diff. peak and hole	0.280 and −0.216 e.A^{-3}

with 2 M H_3PO_4 (100 mL). The resulting solid was recrystallized from MeOH (50 mL) yielding 26 g (60%) of **17**.

^{1}H NMR (CD_2Cl_2, 30 °C): $\delta = 7.12$ (m, 4 H); 7.08 (m, 4 H); 6.96 (m, 2 H) {C_6H_5}; 3.56 (br s, 4 H, =CCH_2C=); 2.62 (2 H); 2.41 (2 H) {AB, $J = 13.2$ Hz, >CCH_2C<}; 1.38 (s, 6 H); 1.36 (s, 6 H) {CH_3}.

^{13}C NMR (CD_2Cl_2, 30 °C): $\delta = 156.6$; 155.8; 136.3; 130.0; 129.9 (=C<); 127.9; 126.9; 124.9 (=CH); 61.5; 52.5 (CH_2); 47.8; 37.5 (>C<); 29.6; 27.9; 13.2 (CH_3).

Anal. Calcd. for $C_{33}H_{36}$, 432.65: C, 91.61; H, 8.39. Found: C, 91.51; H, 8.49; $M^+ = 432.2817$.

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