The Effect of Phenyl Substituents on the Activity of Some Zirconocene Photoinitiators[‡]

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In this paper we report the synthesis of several unbridged zirconocenes, **1a**–**c**, **2** and **5**, each bearing a phenyl substituent in the 2-position of the cyclopentadienyl ring. We also report their photochemical behaviour and we compare the results with those obtained with the corresponding unsubstituted metallocenes **3a**–**c** and **4**. Study of their electronic spectra and EPR/spin trapping experiments showed photogeneration of ligand- and zirconium-centred radicals, thus making these complexes suitable as photoinitiators for radical polymerisation processes. The substitution of the hydrogen atom in the 2-position with a phenyl group had positive effects both on the absorption coefficients, improving the light absorption efficiency, and on the reaction yields of *tert*-butyl acrylate polymerisation. These results can be explained in terms of the combined effects of greater persistence of the radical in solution and/or increased efficiency of the radical in initiating the polymerisation process.

Introduction

A growing area of interest in photochemistry is the design of new photoinitiators for use in pigmented coatings, photoresists, adhesives, and holography;[2–4] of these, initiators with absorption peaks at wavelengths longer than 300 nm are of particular interest since they can be used with the visible light produced by continuous wave lasers.[5]

Since the absorption of a photon generates an electronically excited state that does not occur thermally or occurs only at very high temperatures, photoinitiated reactions and thermally activated processes can induce different reaction pathways. Light can be used as a clean, tuneable and versatile "reagent", thus allowing selective activation of a photoinitiator, also in the presence of organic solvents and chemical contaminants. Another advantage offered by photoinitiation is that the light can be spatially directed and turned on or off simply.

The desirability of expanding the application of photoinitiated chemistry has recently resulted in the discovery of several classes of inorganic and organometallic photoinitiators.[6–9] Among these, metallocenes have attracted increasing interest due to the "tuneability" of their structures and because they leave few toxic residues and photobleach with high efficiency, thus leaving clear or colourless coatings after exposure to argon lasers.

In the context of our research into metallocenes suitable as photoinitiators in radical polymerisation processes, we have recently[1] explored the possible use of several known and new zirconocenes. In the light of the encouraging results obtained, we then investigated possible improvements to their activity as photoinitiators through the introduction of particular substituents in the cyclopentadienyl moiety to modify the electronic distribution.

In this paper we report the photochemical behaviour of several unbridged zirconocenes, each bearing a phenyl substituent in the 2-position of the cyclopentadienyl ring. This substitution should help in stabilising the radical of the polymerisation initiator and enhance the polymerisation efficiency, due to the potential delocalisation of the spare electron offered by the phenyl ring, thus prolonging its life in solution. The introduction of this substituent should increase the absorption coefficients, thus improving the light absorption efficiency.

Several zirconium complexes were synthesised and studied: bis[η^5-(2-phenyl-4,5,6,7-tetrahydro-1*h*-indenyl)]zirconium dichloride [**1a**, $(C6Ph)_2ZrCl_2$], bis[η^5-(2-phenyl-4,5,6,7,8-hexahydroazulenyl)]zirconium dichloride [**1b**, $(C7Ph)_2ZrCl_2$], bis[η^5-(2-phenyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulenyl)]zirconium dichloride [**1c**, $(C8Ph)_2ZrCl_2$] and bis[η^5-(2-phenylindenyl)]zirconium dichloride [**2**, $(IndPh)_2ZrCl_2$]. The results were compared with those obtained with the corresponding unsubstituted

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[‡] Zirconocenes as Photoinitiators for Free Radical Polymerisation of Acrylates, 2. Part 1: Ref.[1]

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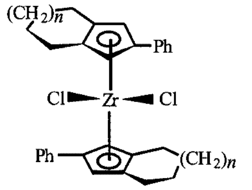
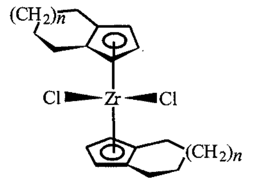
metallocenes: bis[η^5-(4,5,6,7-tetrahydro-1*H*-indenyl)]zirconium dichloride [**3a**, $(C6)_2ZrCl_2$], bis[η^5-(4,5,6,7,8-hexahydroazulenyl)]zirconium dichloride [**3b**, $(C7)_2ZrCl_2$], bis[η^5-(4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulenyl)]zirconium dichloride [**3c**, $(C8)_2ZrCl_2$], and bis(η^5-indenyl)zirconium dichloride (**4**, Ind_2ZrCl_2).



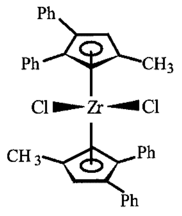
1a–c



3a–c

a: *n* = 1
b: *n* = 2
c: *n* = 3

Another similar complex, bis(4-methyl-1,2-diphenylcyclopentadienyl)zirconium dichloride [**5**, $(CpMePh_2)_2ZrCl_2$], was also synthesised and tested. It should combine the above advantages with a shorter and cheaper synthetic procedure.



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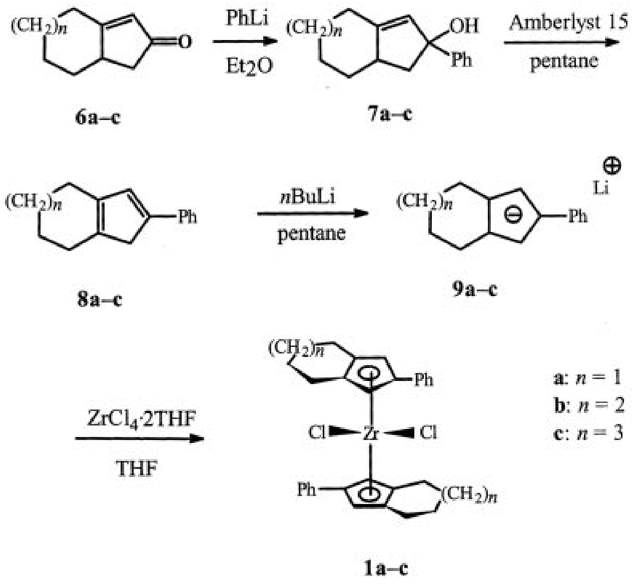
Results and Discussion

Ligand and Complex Synthesis

The synthetic approach is outlined in Scheme 1. The starting enones **6a−c** were obtained by a synthetic procedure previously designed in our laboratories.[10]

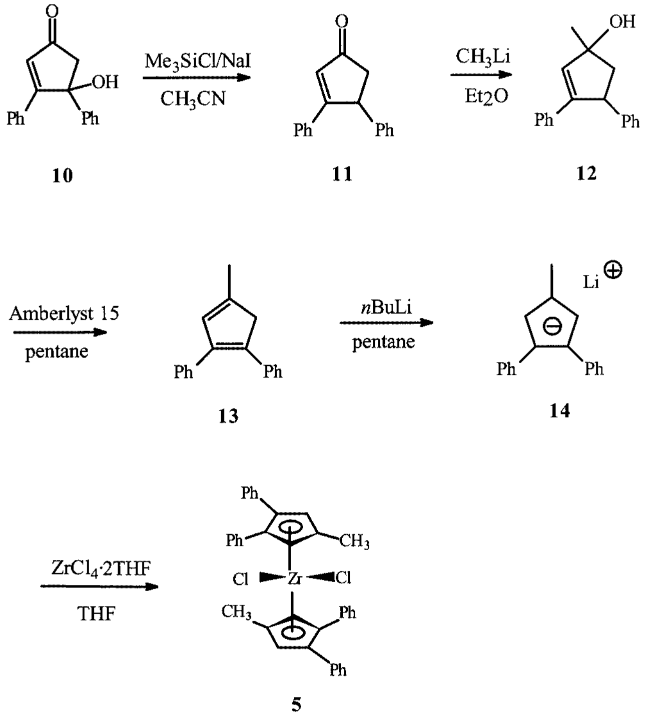


Scheme 1

2-Phenyl-substituted ligands can easily be obtained in three steps from the enones **6a−c**. Treatment of **6a−c** with phenyllithium gave the allyl alcohols **7a−c**, which were dehydrated under very mild conditions by treatment at room temp. with Amberlyst 15, a strongly acidic ion-exchange resin. Since the resulting dienes **8a−c** polymerise quite easily, it is crucial to use low temperatures and short workup times for the dehydration step in order to improve the reaction yields. The use of an ion-exchange resin gave better yields than the usual acid workup, since the reagent can be easily and rapidly removed from the reaction medium by simple filtration. Furthermore, in the case of these phenyl-substituted ligands, filtration through Florisil afforded only one of the three possible isomeric dienes, thus making the hydrogen abstraction easier, since only the isomer bearing an allylic $-CH_2-$ group can easily be dehydrogenated.[11]

Treatment of the dienes with a slight excess of *n*-butyllithium gave the corresponding lithium salts **9a−c**, with overall yields over the three preceding steps ranging from 60 to 70%. Treatment of the lithium salts **9a−c** with $ZrCl_4\cdot 2THF$ in THF in a 2.3:1 molar ratio resulted in the formation of the corresponding metallocenes **1a−c**, in yields ranging from 68 to 72%.

The synthesis of the complex **5** was performed according to Scheme 2, starting from 4-hydroxy-3,4-diphenylcyclopent-2-en-1-one.



Scheme 2

The synthesis of the ligand **14**[12,13] and of the corresponding metallocenes have already been described by others,[14,15] but we have found that the reaction yields were hardly reproducible. Our modified procedure proved more reliable and gave higher yields both of the intermediates and of the metallocene **5**.

The starting compound was converted into the enone **11** by treatment with the reagent Me_3SiCl/NaI in acetonitrile (a synthetic equivalent of Me_3SiI)[16,17] under very mild conditions. Treatment with methyllithium, followed by dehydration with Amberlyst 15, gave the diene **13** as the sole isomer, if Florisil treatment was used. Treatment with *n*-butyllithium and metallation with $ZrCl_4·2THF$ gave the metallocene **5**.

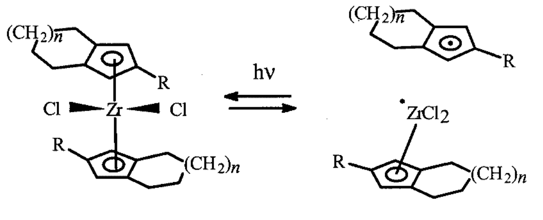
Photochemistry

UV/Vis spectra of the complexes **1a−c**, **2** and **5** were recorded in benzene and compared with those obtained previously[1] for the complexes **3a−c** and **4**. While we did not observe significant variations in the position of the λ maxima (just a slight shift towards shorter wavelengths), we did see that the substituents in the cyclopentadienyl ring increased the extinction coefficients by more than one order of magnitude (Table 1), a feature particularly interesting for the efficiency of the process.

Table 1. Spectroscopic properties of the complexes in benzene

Complex		λ_{max} [nm]	ε_{max} [$mol^{-1}·L·cm^{-1}$]
1a	$(C6Ph)_2ZrCl_2$	320	23500
1b	$(C7Ph)_2ZrCl_2$	300	18000
1c	$(C8Ph)_2ZrCl_2$	300	14000
2	$(IndPh)_2ZrCl_2$	300	60500
		310	60500
		330	41000
3a	$(C6)_2ZrCl_2$	310	1600
		350	1100
3b	$(C7)_2ZrCl_2$	310	2380
		345	1540
3c	$(C8)_2ZrCl_2$	305	2920
		345	1720
4	$(Ind)_2ZrCl_2$	310	1475
		380	720
5	$(CpMePh_2)_2ZrCl_2$	290	12000

These zirconium(IV) complexes possess d^0 configuration, so any dominant effect of Ligand-Field (LF) and/or Metal-to-Ligand Charge Transfer (MLCT) transitions can reasonably be excluded. Since the free ligand shows absorption bands at lower energies ($\lambda \geq 330$ nm), the observed shift supports the hypothesis of a prevalent Ligand-to-Metal Charge Transfer (LMCT) character for the electronic transition, consistent with the formation of ligand- and metal-centred radicals (Scheme 3). The photochemistry of the complexes strongly supports the LMCT assignment.[18,19]



Scheme 3

Selective photolysis was carried out on the complexes in benzene at the wavelengths corresponding to their LMCT transitions, in order to test their photoreactivity in solution and whether they might be possible candidates for free radical photopolymerisation. The nature of the complexes has a significant influence on their photoreactivity in solution; in particular, the introduction of the phenyl substituent seems to accelerate the initial decomposition of the complexes, but only to a certain extent. In the cases of complexes **1a−c**, **4** and **5**, we observed percentages of degradation (estimated by UV/Vis spectroscopy) varying from 10 to 40% with respect to the initial values after only 10 min (Figure 1). After that time, though, a sort of plateau was reached, and this persisted for the rest of the irradiation time, as if a photostationary equilibrium had been established. The photodecomposition was reversible; after 24 h of storage in the dark, the initial spectral pattern and absorbance values were almost completely recovered. In contrast, only 15% of the unsubstituted complexes **3a−c** was degraded even after 1 h of irradiation.

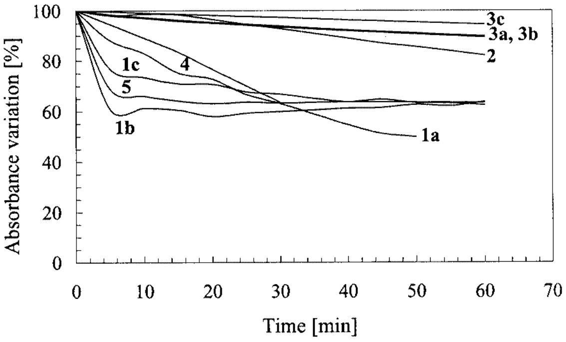
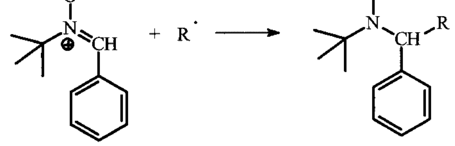


Figure 1. Percentage variation of the absorption band maxima of complexes in benzene as a function of the irradiation time

A particular case is represented by complex **2**, which shows a similar photostability to the complexes **3a−c**, despite its phenyl substituent. This effect can be attributed to the extra stabilisation given by the indenyl aromatic system.

EPR Spin Trapping Investigation

To establish the nature of the species produced upon irradiation, EPR/spin trapping experiments were carried out by direct irradiation of benzene solutions of the zirconocenes inside the spectrometer cavity. The spin trap *N*-*tert*-butyl-α-phenylnitrone (PBN) was used to identify the nature of the radical species (Scheme 4).[20,21]



Scheme 4

Besides the signals already recorded with the reference complexes **3a−c** and **4**, the spectra of the phenyl-substituted complexes **1a−c**, **2** and **5** showed the presence of a second radical species, consistent with the presence of a cyclopentadienyl radical.[22] Since the hyperfine coupling constant (*hfcc*) values are common to all the phenyl-substituted complexes, including the metallocene **5**, which does not possess a second ring, they can reasonably be assigned to a radical delocalised on the phenyl ring.

Table 2. *hfcc* values of the radical spin adducts with PBN in benzene

Complex		Species I			Species II		
		a_N [G]	a_H [G]	[%]	a_N [G]	a_H [G]	[%]
1a	$(C6Ph)_2ZrCl_2$	14.6	2.4	61	15.3	2.6	39
1b	$(C7Ph)_2ZrCl_2$	14.2	2.1	60	15.0	4.7	40
1c	$(C8Ph)_2ZrCl_2$	14.6	2.7	70	15.0	3.8	30
2	$(IndPh)_2ZrCl_2$	14.5	2.6	66	15.4	3.3	34
3a	$(C6)_2ZrCl_2$	14.6	3.2	100	−	−	−
3b	$(C7)_2ZrCl_2$	14.5	2.9	100	−	−	−
3c	$(C8)_2ZrCl_2$	14.7	3.0	100	−	−	−
4	$(Ind)_2ZrCl_2$	14.6	2.5	100	−	−	−
5	$(CpMePh_2)_2ZrCl_2$	14.6	2.3	71	14.9	3.5	29

Polymerisation Activity

The polymerisation of acrylates has great industrial significance and has been the subject of intensive experimental investigations and practical applications. On the basis of the photochemical findings, polymerisation tests were performed on *tert*-butyl acrylate (*t*BA), the least reactive monomer in the acrylates series. For this reason, the commercial product does not contain stabilisers as the other acrylates do, and its chemical sluggishness makes it a good terminating agent for the polymerisation of the other acrylate monomers. A positive result obtained in *t*BA polymerisation can be considered evidence of a high efficiency of a metallorganic complex as a radical initiator and can rule out the possibility that the polymer obtained may have come from direct photochemical activation of the monomer.

The polymerisation tests were carried out in benzene and the tacticity of the polymer formed was estimated by deconvolution of the methine peaks of poly(*t*BA) at $\delta \approx 42$ ppm in the $^{13}C\{^1H\}$ NMR spectra.

The final result of the polymerisation might be due to the combined effects of two factors: i) the photoreactivity of the complex in solution, and ii) the efficiency of the radical in promoting the polymerisation process.

The polymer yields obtained with the complexes **1a**,**b**, **2** and **5** were at least twice as high as those obtained with the corresponding unsubstituted metallocenes **3a**−**c** and **4**. This improvement in the polymerisation outcome can be explained by better persistence of the radical initiating species in solution. The extra stabilisation provided by the phenyl ring can slow down recombination and fragmentation processes, thus guaranteeing higher concentrations of radical initiators in solution. Particularly interesting is the bis(2-phenylindenyl)zirconium dichloride (**2**), which offers the highest percentage in conversion combined with the best photostability in solution. Complex **5** also deserves more studies, since it combines good monomer conversion with a shorter synthetic preparation.

Another interesting feature is that the polymerisation yields are linear with the irradiation time. This result could be a possible sign of a living radical process.[23] Further studies in order to ascertain the nature of this process unambiguously are currently in progress.

As was to be expected, the stereochemical outcome of the reaction was quite independent of the complex used and the data were quite similar to those reported with the unsubstituted complexes, with a content of syndiotactic triads [rr] ranging from 30 to 35% and of isotactic triads [mm] around 6%. This result is consistent with the radical nature of the process.

Table 3. *tert*-Butyl acrylate polymerisation data

Complex		20% (v/v) *t*BA in C_6H_6 [a]			
		Yield [%][b]	Stereochemistry [%][c]		
			[rr]	[mr]	[mm]
1a	$(C6Ph)_2ZrCl_2$	46	30	65	05
1b	$(C7Ph)_2ZrCl_2$	46	34	60	06
1c	$(C8Ph)_2ZrCl_2$	39	36	58	06
2	$(IndPh)_2ZrCl_2$	56	35	59	06
3a	$(C6)_2ZrCl_2$	24	37	52	11
3b	$(C7)_2ZrCl_2$	22	40	45	15
3c	$(C8)_2ZrCl_2$	24	35	50	15
4	$(Ind)_2ZrCl_2$	25	36	51	13
5	$(CpMePh_2)_2ZrCl_2$	40	35	60	05

[a] Polymerisation conditions: a 20% (v/v) monomer solution in benzene in a 4-mL cuvette was irradiated ($\lambda > 320$ nm) for 1 h in the presence of 7 mg of the metallocene. [b] Degree of polymerisation: (weight of polymer obtained/weight of starting monomer) × 100. [c] Percentage composition of syndiotactic [rr], atactic [mr], and isotactic [mm] triads in the polymer, calculated from deconvolution of the ^{13}C NMR peaks at $\delta = 41-43$ ppm.

Conclusion

On the basis of their photochemical behaviour in solution, known and new phenyl-substituted metallocene complexes **1a**−**c**, **2** and **5** have been used here for the first time as photoinitiators for radical polymerisation processes.

An interesting feature is the high extinction coefficients of these new complexes, which improve the light absorption efficiency of the irradiation process, and the possibility to shift their λ maxima towards lower energies by a judicious choice of phenyl substituents without the necessity to modify the entire synthetic procedure.

The radical species involved in the photoinduced cleavage of the metal−ligand bond have been identified and *t*BA polymerisation has been studied in detail and the results compared with those obtained with the complexes **3a**−**c** and **4**, already described in the first paper of this series.[1]

The substitution of the hydrogen atom in position 2 of the cyclopentadienyl ring with a phenyl group increased the polymerisation yields significantly, due to the combined effects of a longer persistence of the radical in solution and/

or increased efficiency of the radical in initiating the polymerisation process.

Experimental Section

General Remarks: All manipulations of air- and/or moisture-sensitive materials were carried out under an inert gas by use of a dual vacuum/argon line and standard Schlenk techniques. All solvents were thoroughly dehydrated and deoxygenated under argon before use. They were dried and purified by heating at reflux under argon in the presence of a suitable drying agent (pentane, petroleum ether, diethyl ether, benzene, toluene and THF: Na/benzophenone ketyl or potassium; CH_2Cl_2: CaH_2) followed by distillation and storage under argon in Young's ampoules. CH_3CN was dried with 4 Å molecular sieves. Solvents and solutions were transferred under positive argon pressure through stainless steel cannulas (diameter 0.5−2.0 mm) and mixtures were filtered in a similar way with modified cannulas that could be fitted with glass fibre filter disks (Whatman GFC). Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich and Fluka) and used without further purification. Reaction courses and product mixtures were routinely monitored by thin layer chromatography (TLC) on pre-coated silica gel F_{254} plates. Preparative flash chromatography was carried out with 60 Å silica gel (230−400 mesh ASTM). Anhydrous magnesium sulfate was used for drying. Elemental analyses were performed with a Carlo Erba 1106 Elemental Analysis apparatus.

NMR Spectra: ^1H (200.13 MHz) and ^{13}C (50.32 MHz) NMR spectra were recorded at room temperature with a Bruker AC 200 spectrometer. Spectra were referenced internally to the residual protio solvent resonance relative to tetramethylsilane ($\delta = 0$ ppm). Deuterated solvents were dried and distilled under argon in the presence of a suitable drying agent ($CDCl_3$: CaH_2; C_6D_6: K) and stored under argon in Young's ampoules.

EPR Studies: The spin trap PBN was purchased from Sigma−Aldrich Chem. Co. and used without further purification. The EPR/spin trapping experiments were performed with a Bruker EMX spectrometer, operating in the X-band (microwave frequency = 9.74 GHz, microwave power = 20 mW, magnetic field modulation frequency = 100 kHz, magnetic field modulation amplitude = 1 G). Sample solutions were freeze-pump-thaw-degassed and then irradiated with a 350-W medium-pressure Hg lamp directly in the EPR spectrometer cavity (Bruker ER-4104OR, TE102). Hyperfine coupling constants (*hfcc*s) were calculated by best-fit simulation of experimental spectra with NIEHS WinSim software.[24]

Photochemical Experiments: Irradiation was performed with an Oriel 500-W high-pressure Hg lamp equipped with cut-off filters for wavelength selection and a water filter to prevent thermal processes. UV/Vis spectra were recorded with a Perkin−Elmer Lambda 40 double-beam spectrophotometer.

Polymerisation Tests: *tert*-Butyl acrylate was dehydrated with CaH_2 and vacuum-distilled immediately before sample preparation. In a typical experiment, a 20% (v/v) monomer solution in benzene in a 4-mL cuvette was irradiated at $\lambda > 320$ nm for 1 h in the presence of 7 mg of the metallocene. All polymerisations were carried out at 20 °C. The reaction was quenched by addition of a small amount of aqueous hydrochloric acid, and the polymer was precipitated by pouring CH_3OH/HCl (10:1) into the reaction mixture. The polymer was collected by filtration and dried overnight under high vacuum.

Preparation of the Complexes: The enones **6a−c**,[11] 4-hydroxy-3,4-diphenylcyclopent-2-en-1-one (**10**),[13] the metallocenes Ind_2ZrCl_2 (**3**)[25] and (2-phenylindenyl)$_2ZrCl_2$ (**4**)[26] were prepared as described in the literature.

Allylic Alcohols 7. General Procedure: Enone **6** (8.80 mmol) in anhydrous diethyl ether (20 mL) was cooled to 0 °C under nitrogen. Phenyllithium (6.5 mL, 10.4 mmol, 1.6 M in cyclohexane/ether) was slowly added, and the yellow solution became brown. The cooling bath was removed and the mixture was stirred at room temp. until TLC (eluent: diethyl ether/petroleum ether, 1:1) showed only traces of the starting material (about 2 h). The reaction mixture was then cooled to 0 °C, the excess of alkylating agent was decomposed by careful addition of iced water, and the separated organic phase was washed several times with diethyl ether. The collected organic fractions were dried and the solvent was evaporated under reduced pressure. The crude alcohol **7** was obtained in quantitative yield as a mixture of two diastereoisomers.

2-phenyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-2-ol (7a). Major Isomer: ^1H NMR ($CDCl_3$): δ = 1.20−1.50 (m, 3 H), 1.60 (s, 1 H, exchanged on D_2O addition, O*H*), 1.70−2.20 (m, 6 H), 2.40−2.65 (m, 2 H, C*H*$_2$Cp), 5.40 (m, 1 H, =C*H*Cp), 7.10−7.60 (m, 5 H, Ar*H*) ppm. **Minor Isomer:** ^1H NMR ($CDCl_3$): δ = 1.20−1.50 (m, 3 H), 1.60 (s, 1 H, exchanged on D_2O addition, O*H*), 1.70−2.20 (m, 6 H), 2.40−2.65 (m, 2 H, C*H*$_2$Cp), 5.50 (m, 1 H, =C*H*Cp), 7.10−7.60 (m, 5 H, Ar*H*) ppm.

2-phenyl-1,2,4,5,6,7,8,8a-octahydroazulen-2-ol (7b). Major Isomer: ^1H NMR ($CDCl_3$): δ = 1.35−1.95 (m, 11 H), 2.35−2.60 (m, 2 H), 2.65−2.81 (m, 1 H), 5.48 (m, 1 H, =C*H*Cp), 7.15−7.60 (m, 5 H, Ar*H*) ppm. **Minor Isomer:** ^1H NMR ($CDCl_3$): δ = 1.35−1.95 (m, 11 H), 2.35−2.60 (m, 2 H), 2.65−2.81 (m, 1 H), 5.58 (m, 1 H, = C*H*Cp), 7.15−7.60 (m, 5 H, Ar*H*) ppm.

2-phenyl-2,4,5,6,7,8,9,9a-octahydro-1*H*-cyclopenta[8]annulen-2-ol (7c). Major Isomer: ^1H NMR ($CDCl_3$): δ = 1.38−2.40 (m, 13 H), 2.40−2.60 (m, 2 H), 2.62−2.70 (m, 1 H), 5.52 (m, 1 H, =C*H*Cp), 7.10−7.65 (m, 5 H, Ar*H*) ppm. **Minor Isomer:** ^1H NMR ($CDCl_3$): δ = 1.38−2.40 (m, 13 H), 2.40−2.60 (m, 2 H), 2.62−2.70 (m, 1 H), 5.60 (m, 1 H, =C*H*Cp), 7.10−7.65 (m, 5 H, Ar*H*) ppm.

Dienes 8. General Procedure: Crude alcohol **7** (max, 8.80 mmol), partially dissolved in pentane (30 mL), was stirred at room temp. with Amberlyst 15 (1.27 g). After 1 h, the reaction was complete (TLC: diethyl ether/petroleum ether, 2:1). Magnesium sulfate was added and, after a further 5 min of stirring, the suspension was filtered through a short column (*h* = 6 cm; i.d. = 3 cm) of Florisil (100−200 mesh) and the solvents were evaporated under reduced pressure, keeping the temperature below 30 °C. A yellow solid was obtained.

2-phenyl-4,5,6,7-tetrahydro-1*H*-indene (8a): ^1H NMR ($CDCl_3$): δ = 1.60−1.80 (m, 4 H, CCH$_2$C*H*$_2$), 2.20−2.45 (m, 4 H, CC*H*$_2$CH$_2$), 3.25 (d, *J* = 1.17 Hz, 2 H, C*H*$_2$Cp), 6.70 (d, *J* = 1.17 Hz, 1 H, = C*H*Cp), 7.10−7.70 (m, 5 H, Ar*H*) ppm.

2-phenyl-4,5,6,7,8-hexahydroazulene (8b): ^1H NMR ($CDCl_3$): δ = 1.55−1.82 (m, 6 H, CCH$_2$C*H*$_2$), 2.40−2.52 (m, 4 H, CC*H*$_2$CH$_2$), 3.25 (d, *J* = 1.08 Hz, 2 H, C*H*$_2$Cp), 6.70 (d, *J* = 1.08 Hz, 1 H, = C*H*Cp), 7.15−7.20 (m, 1 H, Ar*H*), 7.20−7.35 (m, 2 H, Ar*H*), 7.35−7.50 (m, 2 H, Ar*H*) ppm.

2-phenyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene (8c): ^1H NMR ($CDCl_3$): δ = 1.40−1.60 (m, 4 H, CCH$_2$C*H*$_2$), 1.60−1.80 (m, 4 H, CCH$_2$C*H*$_2$), 2.45−2.60 (m, 4 H, CC*H*$_2$CH$_2$), 3.25 (s, 2 H, C*H*$_2$Cp), 6.72 (s, 1 H, =C*H*Cp), 7.10−7.65 (m, 5 H, Ar*H*) ppm.

Lithium Salts 9. General Procedure: Diene **8** (max, 8.80 mmol) was placed in a Schlenk flask, degassed, dissolved in anhydrous petroleum ether (30 mL) and cooled to 0 °C. *n*-Butyllithium (5 mL, 2.5 M solution in hexanes, 12.5 mmol) was added dropwise, and the solution was stirred at 0 °C for 30 min, then allowed to reach room temp. and stirred overnight. Lithium salt **8** separated from the solution as powdery solid, which was filtered through a cannula and washed twice with petroleum ether. The residual solvent was pumped off, leaving the lithium salt **9** as yellow pyrophoric powder.

2-Phenyl-4,5,6,7-tetrahydro-1*H*-indenyllithium (9a): 1.07 g. Yield over three steps: 60%; average yield per step 84%.

2-Phenyl-4,5,6,7,8-hexahydroazulenyllithium (9b): 1.24 g. Yield over three steps: 65%; average yield per step 87%.

2-Phenyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulenyllithium (9c): 1.44 g. Yield over three steps: 71%; average yield per step 89%.

Metallocene Dichlorides 1. General Procedure: $ZrCl_4 \cdot 2THF$ (4.5 mmol) in THF (20 mL) was added dropwise to solutions of the lithium salts **9** (9.6 mmol) in anhydrous THF (20 mL). The reaction mixtures were stirred overnight. The solvent was then removed under vacuum, and the residues were extracted with toluene, filtered, concentrated and layered with pentane. Fine, deep yellow solids precipitated and were isolated by filtration, washing with pentane and concentration under high vacuum.

Bis[η^5-(2-phenyl-4,5,6,7-tetrahydro-1*H*-indenyl)]zirconium Dichloride (1a): 1.80 g. Yield 68%. $C_{30}H_{30}Cl_2Zr$ (552.69): calcd. C 65.2, H 5.5, Cl 12.8; found C 65.8, H 5.7, Cl 12.4. ^{1}H NMR ($CDCl_3$): δ = 1.2−1.5 (m, 4 H, CCH$_2$C*H*$_2$), 1.6−1.9 (m, 4 H, CC*H*$_2$CH$_2$), 2.1−2.4 (m, 8 H, CC*H*$_2$CH$_2$), 6.1 (s, 4 H, C*H*Cp), 7.0−7.4 (m, 10 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.0 (CCH$_2$*C*H$_2$), 23.8 (C*C*H$_2$CH$_2$), 113.7 (*C*H Cp), 123.9 (*C*=CH Cp), 125.2 (*m*CH Ar), 127.3 (*p*CH Ar), 129.0 (*o*CH Ar), 130.8 (CH$_2$*C*=CCp), 133.3 (*C*C=Ar) ppm.

Bis[η^5-(2-phenyl-4,5,6,7,8-hexahydroazulenyl)]zirconium Dichloride (1b): 2.17 g. Yield 78%. $C_{32}H_{34}Cl_2Zr$ (580.74): calcd. C 66.2, H 5.9, Cl 12.2; found C 65.8, H 6.2, Cl 12.0. ^{1}H NMR ($CDCl_3$): δ = 1.6−2.1 (m, 12 H, CCH$_2$C*H*$_2$), 2.2−2.7 (m, 8 H, CC*H*$_2$CH$_2$), 6.3 (s, 4 H, C*H* Cp), 7.1−7.6 (m, 10 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.6 (*C*H$_2$), 30.0 (*C*H$_2$), 32.0 (*C*H$_2$), 116.4 (*C*H Cp), 124.4 (*C*=CH Cp), 125.3 (*m*CH Ar), 127.2 (*p*CH Ar), 129.0 (*o*CH Ar), 133.3 (*C*C=Ar), 134.6 (CH$_2$*C*=C Cp) ppm.

Bis[η^5-(2-phenyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulenyl)]zirconium Dichloride (1c): 2.10 g. Yield 72%. $C_{34}H_{38}Cl_2Zr$ (608.80): calcd. C 67.1, H 6.3, Cl 11.7; found C 66.8, H 6.8, Cl 11.3. ^{1}H NMR ($CDCl_3$): δ = 1.0−1.5 (m, 12 H, CCH$_2$C*H*$_2$), 1.6−1.9 (m, 4 H, CCH$_2$C*H*$_2$), 2.0−2.3 (m, 4 H, CC*H*$_2$CH$_2$), 2.3−2.6 (m, 4 H, CC*H*$_2$CH$_2$), 5.6 (s, 4 H, C*H* Cp), 7.0−7.5 (m, 10 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 25.9 (*C*H$_2$), 26.4 (*C*H$_2$), 31.1 (*C*H$_2$), 32.3 (*C*H$_2$), 107.6 (*C*H Cp), 124.3 (*m*CH Ar), 124.7 (*C*=CH Cp), 126.0 (*p*CH Ar), 127.5 (CH$_2$*C*=C Cp), 128.6 (*o*CH Ar), 134.9 (*C*C=Ar) ppm.

3,4-Diphenylcyclopent-2-en-1-one (11): The alcohol **10** (0.5 g, 2 mmol), dissolved in dry benzene (10 mL), and Me_3SiCl (12 mmol, a slightly exothermic reaction occurs) were added to a suspension of NaI (12 mmol) in anhydrous CH_3CN (0.6 mL, 12 mmol). The mixture was stirred at room temp. in the dark until TLC (eluent: diethyl ether/petroleum ether, 1.5:1), showed only traces of the starting alcohol (about 1 h). The reaction mixture was then cooled to 0 °C, quenched with water and extracted several times with diethyl ether. The collected organic fractions were washed with aqueous sodium thiosulfate, water and brine and dried. The solvent was evaporated under reduced pressure to give a deep yellow solid, which was purified by flash chromatography (eluent: diethyl ether/petroleum ether, 1:1.5) to give the enone **11** (0.44 g, 1.86 mmol). (Yield 93%). M.p. 108−110 °C. ^{1}H NMR ($CDCl_3$): δ = 2.46 (dd, *J* = 2.0, 18.8 Hz, 1 H, *cis*-PhCHC*H*$_2$), 3.14 (dd, *J* = 7.3, 18.8 Hz, 1 H, *trans*-PhCHC*H*$_2$), 4.65 (dt, *J* = 7.3, 1.7 Hz, 1 H, PhC*H*CH$_2$), 6.77 (d, *J* = 1.5 Hz, 1 H, COC*H*), 7.11−7.42 (m, 8 H, Ar*H*), 7.47−7.61 (m, 2 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 46.68, 46.75, 126.96, 127.06, 127.90, 128.70, 129.06, 129.11, 130.79, 133.18, 141.22, 142.41, 175.12, 208.12 ppm.

1-Methyl-3,4-diphenylcyclopent-2-en-1-ol (12): Methyllithium (2.15 mmol, 1.5 M in diethyl ether) was added dropwise to a solution of enone **11** (0.44 g, 1.86 mmol) in anhydrous THF (20 mL), cooled to 0 °C. The yellow solution turned orange. The mixture was stirred for 30 min at 0 °C and for 30 min at room temperature (TLC: diethyl ether/petroleum ether, 1.5:1). The reaction mixture was then again cooled to 0 °C, the excess of alkylating agent was decomposed by careful addition of iced water, and the separated organic phase was washed several times with diethyl ether. The collected organic fractions were dried and the solvent was evaporated under reduced pressure. The crude alcohol **12** was obtained in quantitative yield as a mixture of two diastereoisomers. **Major Isomer:** ^{1}H NMR ($CDCl_3$): δ = 1.59 (s, 3 H, C*H$_3$*), 1.68 (s, 1 H, O*H*), 1.96−2.12 (m, 1 H, *cis*-PhCHC*H*$_2$), 2.63−2.82 (m, 1 H, *trans*-PhCHC*H*$_2$), 4.27−4.42 (m, 1 H, PhC*H*CH$_2$), 6.34 (d, *J* = 1.5 Hz, 1 H, COC*H*), 7.18−7.41 (m, 10 H, Ar*H*) ppm. **Minor Isomer:** ^{1}H NMR ($CDCl_3$): δ = 1.50 (s, 3 H, C*H$_3$*), 1.72 (s, 1 H, O*H*), 1.96−2.12 (m, 1 H, *cis*-PhCHC*H*$_2$), 2.63−2.82 (m, 1 H, *trans*-PhCHC*H*$_2$), 4.27−4.42 (m, 1 H, PhC*H*CH$_2$), 6.78 (d, *J* = 1.5 Hz, 1 H, COC*H*), 7.08−7.41 (m, 10 H, Ar*H*) ppm.

4-Methyl-1,2-diphenylcyclopentadiene (13): The crude alcohol **12** (max. 1.56 mmol) in diethyl ether (30 mL) was stirred at room temp. with Amberlyst 15 (1.27 g). After 1 h, the reaction was complete (TLC: diethyl ether/petroleum ether, 2:1). Magnesium sulfate was added and, after a further 5 min of stirring, the suspension was filtered and the solvents were evaporated under reduced pressure. The residue was dissolved in petroleum ether and filtered through a short column (*h* = 6 cm; i.d. = 3 cm) of Florisil (100−200 mesh) and the solvents were evaporated under reduced pressure, keeping the temperature below 30 °C. A yellow solid (0.30 g, 1.31 mmol) was obtained (yield over two steps: 80%; average yield per step: 89%). ^{1}H NMR ($CDCl_3$): δ = 2.19 (d, *J* = 1.5 Hz, 3 H, C*H*$_3$), 3.49 (d, *J* = 1.1 Hz, 2 H, C*H*$_2$Ph), 6.37 (d, *J* = 1.3 Hz, 1 H, C=C*H*), 7.11−7.46 (m, 10 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.2, 48.8, 126.0, 126.9, 127.7, 128.2, 128.35, 132.1, 137.6, 137.5, 136.6, 141.4, 144.0 ppm.

4-Methyl-1,2-diphenylcyclopentadienyllithium (14): The diene **13** (0.30 g, 1.31 mmol) was placed in a Schlenk flask, degassed, dissolved in anhydrous petroleum ether (30 mL) and cooled to −20 °C. *n*-Butyllithium (2.20 mmol, 2.5 M solution in hexanes) was added dropwise, and the solution was stirred at −20 °C for 2 h and then allowed slowly to reach room temp. and stirred overnight. The lithium salt **14** separated from the solution as a powdery solid, which was filtered through a cannula and washed twice with petroleum ether. The residual solvent was pumped off, leaving the lithium salt **14** (0.30 g, 1.24 mmol) as a pale yellow pyrophoric powder (yield 95%).

Bis(1,2-diphenyl-4-methylcyclopentadienyl)zirconium Dichloride (5): The lithium salt **14** (0.30 g, 1.24 mmol) was dissolved in anhydrous THF (20 mL), and a solution of $ZrCl_4 \cdot 2THF$ (4.5 mmol) in THF

(20 mL) was added dropwise. The reaction mixture was stirred overnight. The solvent was then removed under vacuum, and the residue was extracted with toluene, filtered, concentrated and layered with pentane. A powdery, deep yellow solid (0.62 g, 0.99 mmol) precipitated and was isolated by filtration and washing with pentane (yield 80%). $C_{36}H_{30}Cl_2Zr$ (624.35): calcd. C, 69.2, H 4.8; Cl, 11.4; found C 69.1, H 4.9; Cl, 11.3. ^1H NMR ($CDCl_3$): δ = 1.73 (s, 6 H, C*H₃*), 6.38 (s, 4 H, Cp*H*), 7.11−7.49 (m, 20 H, Ar*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.2, 118.9, 127.4, 128.0, 128.8, 129.4, 133.2 ppm.

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