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Synthesis of highly crowded cyclopentadienes via reactions of Cp_2Ni and $CpSn(CH_3)_3$ with triarylmethylhalogenides. Molecular structure of $1\text{-}(CH_3)_3Si\text{-}(3\text{-}Ph_3C)\text{-}C_5H_4$

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Abstract

Triphenylmethylcyclopentadiene $Ph_3CC_5H_5$ (**1**) and 2-[tris-(2'-methoxyphenyl)methyl]cyclopentadiene $2\text{-}((2'\text{-}CH_3OC_6H_4)_3C)\text{-}C_5H_5$ (**2**) have been prepared in high yields via reactions of the corresponding triarylmethyl-halogenides with Cp_2Ni (and $CpSn(CH_3)_3$ in the case of **1**). It is shown that 3-tritylsubstituted 6,6-dimethylfulvene formed exclusively in the reaction between the lithium salt of **1** and acetone. Cyclopentadiene **2** exists only as the 2-triarylmethylsubstituted isomer in a mixture of two enantiomeric forms caused by the C_{3v}-asymmetry type in the relative orientation of the aryl groups. Cyclopentadiene $1\text{-}Si(CH_3)_3\text{-}(3\text{-}Ph_3C)\text{-}C_5H_4$ was obtained by reaction of the sodium salt of **1** with $(CH_3)_3SiCl$; it crystallizes from hexane in the monoclinic space group $P2_1/c$ with cell dimensions $a = 11.635(5)$, $b = 12.400(7)$, $c = 15.531(7)$ Å, $V = 2240.09(9)$ Å^3 and $Z = 4$; the Si atom is in the allylic position with $d(C_{Cp}\text{–}Si) = 1.891(8)$ Å, Si–C(3)–C(2) = 109.7(6)°, Si–C(3)–C(4) = 110.3(6)°, C(2)–C(3)–C(4) = 100.2(7)°.

Keywords: Nickel; Tin; Silicon

1. Introduction

Only a few examples of highly crowded cyclopentadienes are known to date [1]. Very often attempts at their synthesis have been unsuccessful. For instance, the synthesis of multiphenyl- and multi-tert-butyl-substituted cyclopentadienes is very difficult and nowadays unattractive for organometallic chemists [2]. Today there are two alternative ways of introducing substituents into the Cp-ring: purely organic synthesis and the use of cyclopentadienyl derivatives of active metals.

In this paper we present our results on the synthesis of cyclopentadienes bearing extremely bulky substituents of a triarylmethyl nature, via organometallic derivatives. Synthesis of 1-trimethylsilyl-(3-triphenylmethyl)cyclopenta-2,4-diene (**13**) has been achieved and its crystal structure has been defined.

2. Results and discussion

2.1. Synthesis

In the present work our method for bringing the triarylmethyl group into the Cp-ring is the electrophilic attack of triarylmethylhalogenide on Cp_2Ni or $CpSn(CH_3)_3$. Both these metal derivatives are characterized by a rather covalent M–Cp bond and they are known to be fairly insensitive to oxidation of free radical type.

In this respect these compounds differ greatly from the much more ionic cyclopentadienide derivatives of alkaline metals. The latter are not acceptable for our purpose due to the ease of their electron oxidation transformation.

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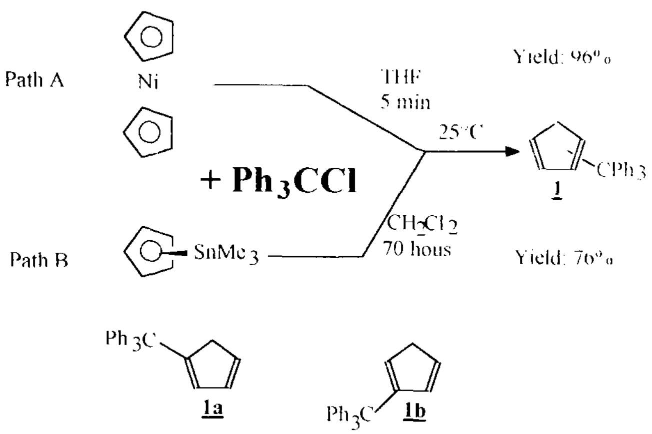


Scheme 1.

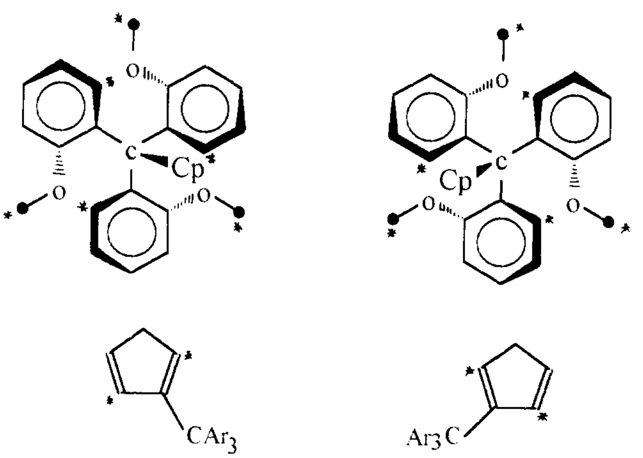


Fig. 1. Enantiomers of 2; diastereotopic carbon atoms are indicated by ★.

We found that both reactions are highly efficient for the preparation of **1**, but there is a great difference in time scale. Reaction of Cp_2Ni (path A) is complete in 5 min, but that of $CpSn(CH_3)_3$ needs no less than 70 h (path B). In the case of Cp_2Ni we used a previously published scheme [3], but we extensively modified the experimental procedure, using THF instead of ether and changing the extraction (see Experimental section). In its present form this synthetic approach provides the highest yield of **1**.

Another path for the synthesis of **1** is based on the interaction of Ph_3CCl with $CpSn(CH_3)_3$ in CH_2Cl_2 solution. The organic phase was washed with water (to extract Me_3SnCl), dried and the solvent was evaporated. Notwithstanding the smaller yield of **1** in this case, the second method assures greater purity of this ligand, especially with regard to traces of nickel.

The ^{1}H-NMR spectrum of **1** is unaffected by synthetic path. The 4/1 ratio of two allylic multiplets at 3.020 and 2.845 ppm illustrates the **1b**/**1a** isomeric ratio in $Ph_3CC_5H_5$ (see Scheme 1).

2-[tris-(2′-methoxyphenyl)-methyl]-cyclopentadiene **2** is another compound with an extremely bulky substituent which was synthesized in this work via reaction with Cp_2Ni. Furthermore we expected that the greater the steric barriers, the less the substituent could provide of the 1-substituted isomer in the resulting mixture. In addition it was also interesting to obtain the cyclopentadiene with a substituent of C_{3v}-asymmetry type (see Fig. 1) for the purpose of subsequent syntheses of this type of transition metal complexes.

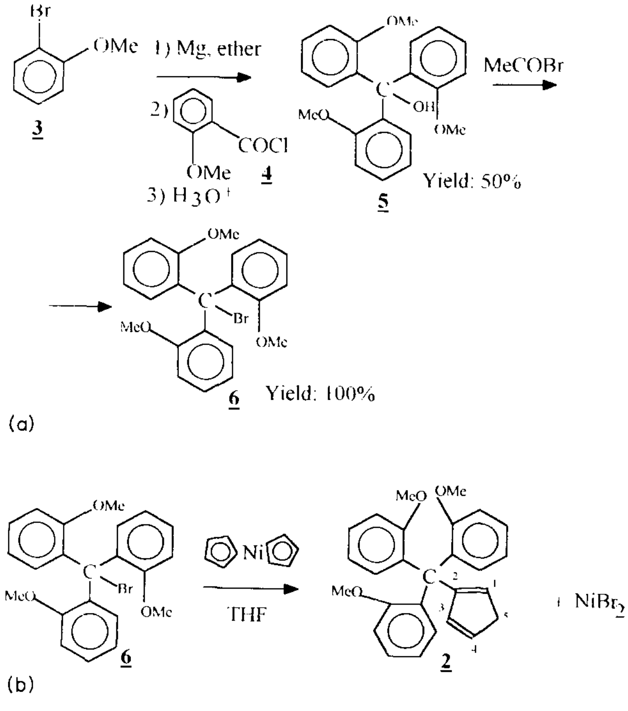
The synthesis of **2** was performed according to Scheme 2a,b.

The appropriate triarylmethylbromide was obtained by a routine method using standard techniques [4]. As **6** has a much more pronounced ionic nature compared to unsubstituted triphenylmethylchloride, its interaction with Cp_2Ni is notably exothermic.

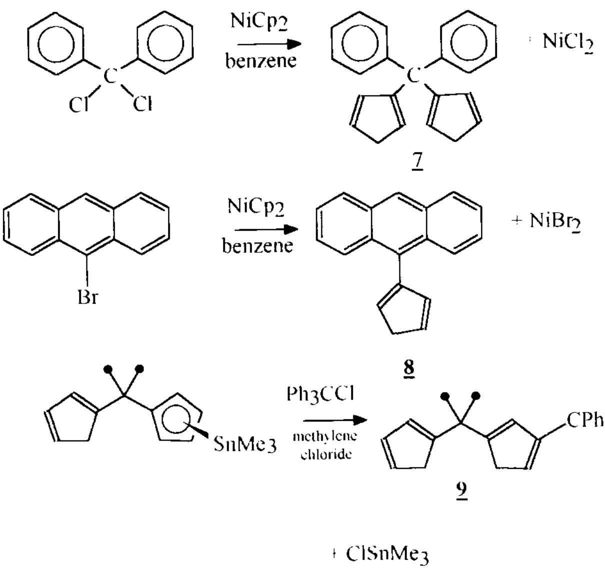
The principal step in this synthesis (see Scheme 2b) produces **2** as an oil easily soluble in THF, and $NiBr_2$ as a colloid solution.

The procedure for the isolation of **2** consists of the evaporation of the reaction mixture to dryness followed by its extraction with boiling heptane. The evaporation of the heptane extract yields a pale-yellow oil that crystallized under methanol over a period of a few days. This procedure gives light-yellow crystals of 2-[tris-(2′-methoxy-phenyl)methyl]cyclopentadiene (**2**) in 75% yield.

The allylic area in the ^{1}H-NMR spectrum of **2** is of particular interest. This area is represented by a single signal at 3.103 ppm of the protons of the $C(5)_{Cp}$-atom



Scheme 2.



Scheme 3.

(see Scheme 2b). It proves that cyclopentadiene **2** exists as the only 2-substituted isomer.

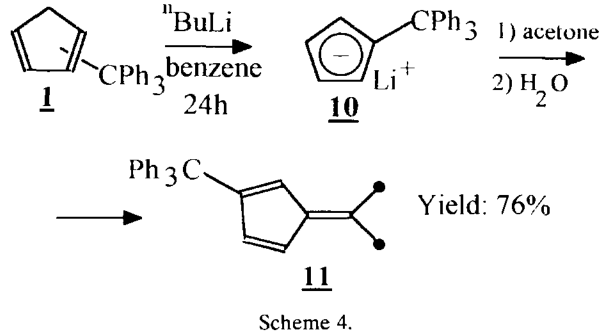
The ^{13}C-NMR-APT{^{1}H} spectrum of **2** provides evidence that this cyclopentadiene is, in reality, the mixture of two enantiomers caused by the C_{3v}-asymmetry type in the relative orientation of the aryl groups. This fact is manifested in the paired signals of diastereotopic carbon atoms (indicated by ⋆, see Fig. 1): 129.207, 129.268 (*C$_{Cp}$(3); 123.216, 120.545 (*C$_{Cp}$(1); 115.979, 111.366 (*C$_{Ar}$(6); 55.676, 55.395 (O-*CH$_3$).

In addition we attempted to synthesize the highly crowded cyclopentadienes **7–9** (see Scheme 3).

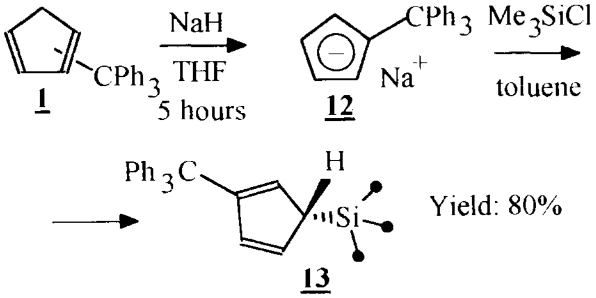
Unfortunately, while these reactions undoubtedly occur the strict identification of the products proved to be impossible.

In order to illustrate the reactivity of **1** we drew on the classic procedure of fulvene synthesis (see Scheme 4).

The white microcrystalline powder of Li-salt **10** was formed only after 24 h. Hereafter **10** was used without isolation and analysis. The interaction of **10** with acetone followed by quenching the reaction mixture with water gives stable bright-yellow crystals of the resulting fulvene **11** in high yield. It is clear that **11** is also a prospective ligand for synthesis of crowded metal complexes.



Scheme 4.



Scheme 5.

The ^{1}H-NMR spectrum of **11** in its vinyl area comprises the multiplet at 6.485 ppm of H(4), triplet at 6.176 ppm of H(2) and multiplet at 6.000 ppm of H(5) with $^3J = 5.2$ Hz and $^4J = 2.0$ Hz.

Finally we succeeded in the synthesis of 1-trimethylsilyl-(3-triphenylmethyl)cyclopenta-2,4-diene (**13**), which was obtained by the reaction of sodium salt **12** with trimethylsilylchloride (see Scheme 5). In contradiction to data reported in [5], the use of **10** in this reaction has been unsuccessful and, in our opinion it lacks potential as a synthetic approach.

The ^{1}H-NMR spectrum of **13** (THF-d^8) shows that at room temperature the Me$_3$Si-group stays exclusively at the allylic site (see Experimental section).

2.2. Structure

The structure of **13** is shown in Fig. 2, the final fractional coordinates for **13** are given in Table 1, and selected bond distances and angles are listed in Table 2.

It should be remarked that there is no interaction between Me$_3$Si- and Ph$_3$C groups. The C(3) atom (see

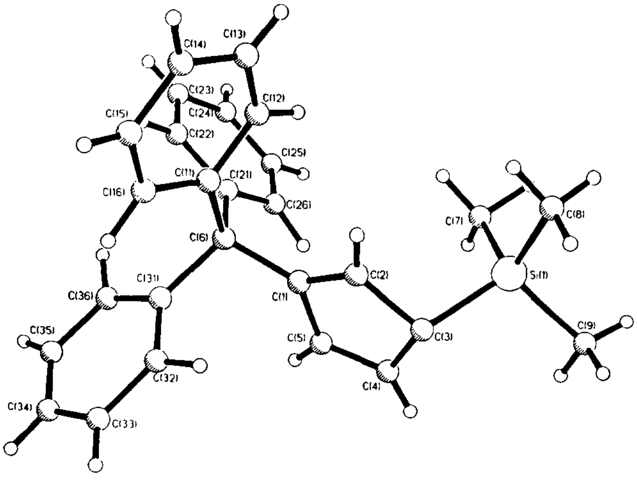


Fig. 2. The crystal structure of $(C_6H_5)_3CC_5H_4Si(CH_3)_3$ (**13**).

Table 1
Atomic coordinates (×10^4) and thermal parameters B_{iso}/B_{eq} for non-hydrogen atoms of **13**

Atom	x	y	z	B_{iso}/B_{eq}
Si(1)	102(2)	7652(2)	171(2)	3.7(1)
C(7)	−72(6)	8590(7)	−1030(8)	6.2(5)
C(8)	589(6)	8364(8)	1420(8)	6.7(6)
C(9)	819(6)	6532(9)	−241(9)	6.0(6)
C(1)	−2230(5)	7988(6)	109(7)	3.7(4)
C(2)	−1572(5)	7920(7)	894(7)	4.5(4)
C(3)	−959(5)	7045(7)	607(7)	3.7(4)
C(4)	−1415(6)	6564(7)	−409(8)	4.6(5)
C(5)	−2125(5)	7105(7)	−704(7)	4.5(5)
C(6)	−2995(5)	8755(6)	66(7)	3.1(4)
C(11)	−2991(5)	9449(7)	1170(7)	3.9(4)
C(12)	−2357(5)	10229(8)	1341(8)	3.9(5)
C(13)	−2335(6)	10835(8)	2327(9)	4.6(5)
C(14)	−2946(7)	10711(8)	3134(9)	6.4(6)
C(15)	−3569(5)	9966(9)	2958(9)	3.2(5)
C(16)	−3610(6)	9338(7)	1993(8)	5.3(5)
C(21)	−2949(5)	9532(7)	−949(7)	4.1(4)
C(22)	−3434(6)	10462(8)	−958(8)	6.5(6)
C(23)	−3422(7)	11197(8)	−1840(10)	7.3(6)
C(24)	−2946(7)	10983(8)	−2800(10)	6.2(6)
C(25)	−2479(6)	10065(9)	−2830(8)	5.5(5)
C(26)	−2475(5)	9339(7)	−1930(8)	3.9(4)
C(31)	−3800(5)	8053(7)	−36(7)	2.8(4)
C(32)	−3874(5)	7160(8)	662(7)	3.3(4)
C(33)	−4599(7)	6486(8)	620(9)	6.1(6)
C(34)	−5239(6)	6726(9)	−140(10)	4.6(6)
C(35)	−5211(6)	7570(10)	−836(9)	4.7(5)
C(36)	−4482(6)	8229(7)	−797(7)	3.5(4)

Table 2
Selected bond lengths (Å) and bond angles (°) for **13**

Bond lengths			
Si(1)–C(7)	1.833(9)	C(2)–H(2)	0.964(8)
Si(1)–C(8)	1.85(1)	C(4)–H(4)	0.926(8)
Si(1)–C(9)	1.85(1)	C(5)–H(5)	0.955(8)
Si(1)–C(3)	1.89(1)	C(7)–H(71)	1.014(9)
C(6)–C(1)	1.52(1)	C(7)–H(72)	1.129(9)
C(6)–C(11)	1.55(1)	C(7)–H(73)	0.870(9)
C(6)–C(21)	1.53(1)	C(8)–H(81)	0.93(1)
C(6)–C(31)	1.53(1)	C(8)–H(82)	0.92(1)
C(1)–C(2)	1.36(1)	C(8)–H(83)	0.928(9)
C(2)–C(3)	1.49(1)	C(9)–H(91)	0.90(1)
C(3)–C(4)	1.49(1)	C(9)–H(92)	0.96(1)
C(4)–C(5)	1.33(1)	C(9)–H(93)	1.01(1)
C(1)–C(5)	1.46(1)		
Bond angles			
C(7)–Si(1)–C(8)	110.2(4)	C(1)–C(2)–C(3)	111.7(7)
C(7)–Si(1)–C(9)	111.0(5)	C(2)–C(3)–C(4)	100.2(7)
C(7)–Si(1)–C(3)	110.1(4)	C(3)–C(4)–C(5)	112.2(8)
C(8)–Si(1)–C(9)	109.0(5)	C(1)–C(5)–C(4)	108.5(8)
C(8)–Si(1)–C(3)	108.8(4)	C(1)–C(6)–C(11)	109.4(6)
C(9)–Si(1)–C(3)	107.7(4)	C(1)–C(6)–C(21)	111.6(6)
C(2)–C(1)–C(5)	107.2(7)	C(1)–C(6)–C(31)	106.5(6)
C(2)–C(1)–C(6)	129.2(6)	C(11)–C(6)–C(21)	107.0(6)
C(5)–C(1)–C(6)	123.2(7)	C(11)–C(6)–C(31)	111.7(6)
Si(1)–C(3)–C(2)	109.7(6)	C(21)–C(6)–C(31)	110.7(6)
Si(1)–C(3)–C(4)	110.3(6)		

Fig. 2) is tetrahedral with angles Si(1)–C(3)–C(2) = 109.7(6)°, Si(1)–C(3)–C(4) = 110.3(6)° and C(2)–C(3)–C(4) = 100.2(7)° (see Table 2). The bond length Si(1)–C(3) (1.89(1) Å) is markedly longer than Si–C the (1.870(5) Å) in tetraalkylsilanes [6]. Unfortunately localization of the H(3) atom connected with C(3) was unsuccessful. The double bonds in the Cp-ring of **13** differ in their length, d(C(1)–C(2)) = 1.36 Å, d(C(4)–C(5)) = 1.33 Å, but the single bonds did not—d(C(2)–C(3)) = d(C(3)–C(4)) = 1.49 Å.

We are now preparing for publication an article concerning the synthesis and crystal structure of new cyclopentadienyl metal complexes using the crowded ligands presented in this paper.

3. Experimental section

All solvents were purified by standard methods and were freshly distilled prior to use. Acetone, trimethylsilylchloride and 2-methoxybenzoylchloride (**4**) were used without special purification. Cyclopentadienyltrimethyltin was distilled twice under argon prior to use. The Grignard reagent and ^{n}BuLi hexane solution were prepared by routine procedures. The NMR spectra were recorded with a Varian-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) NMR spectrometer. The elemental analysis was performed on a Carlo-Erba analyzer. Melting points were determined in sealed capillaries, and are uncorrected.

*3.1. 1- and 2-Triphenylmethylcyclopentadiene (**1a**, **1b**)*

3.1.1. Method A

Nickelocene [7] (9.45 g, 50 mmol) was added to a tetrahydrofuran (250 ml) solution of triphenylmethylchloride [8] (27.9 g, 100 mmol). $NiCl_2$ immediately precipitated in the form of a fine dark-brown powder. The solution was decanted and $NiCl_2$ was washed twice with 50 ml portions of THF. The combined solution was filtered and evaporated to dryness, yielding 29.6 g of a pale-yellow macrocrystalline solid (96%), mp = 201°C. Anal. Found C, 93.78; H, 6.65. $C_{24}H_{20}$ (308.42) calc.: C, 93.51; H, 6.49%. ^{1}H-NMR ($CDCl_3$): δ 7.24–7.16, 7.15–7.08 (m, m, 15H, C_{Ph}-*H*); 6.34–6.21, 6.18–6.14, 6.04–5.99 (m, m, m, 3H, C_{Cp}-*H*, –C*H*=); 3.04–3.00, 2.86–2.83 (m, m′, 2H, –CH_2–, the ratio m/m′ is 4/1). ^{13}C-NMR {^{1}H} ($CDCl_3$): δ 152.265 (C(2), **1b**); 145.675 (C(2), **1a**); 136.849 (*ipso*-C_{Ph}); 131.299 (C(3), **1a**); 130.303 (C(4)); 130.325 (=*C*H–, *meta*-C_{Ph}); 129.522 (C(1), **1b**); 127.193 (=*C*H–, *para*-C_{Ph}); 127.140, 125.738 (=*C*H–, ortho-C_{Ph}); 60.553 (Ph_3*C*-, tert); 40.253 (C(5), **1a**); 30.325 (C(5), **1b**).

3.1.2. Method B

Cyclopentadienyltrimethyltin (2.29 g, 10 mmol) and Ph_3CCl (2.79 g, 10 mmol) were mixed in CH_2Cl_2 (50 ml) and the mixture was allowed to stand at room temperature for three days, then washed seven times with 50 ml portions of water. The organic phase was dried over sodium sulfate and on the column with Al_2O_3. Solvent was removed and the residue was recrystallized from hexane, yielding a pale-yellow macrocrystalline solid (76%), mp = 199°C, whose NMR spectra are identical to those of the product obtained by Method A.

3.2. *3-Triphenylmethyl-6,6-dimethylfulvene (**11**)*

^{n}BuLi (10 ml, 1.0 M, 10 mmol) was mixed with a benzene (50 ml) solution of **1** (0.62 g, 2 mmol). The mixture was stirred overnight, then decanted and the white residue of **10** salt was washed with hexane and dried in a high vacuum for two hours. After that **10** was suspended in hexane (50 ml) and mixed with a great excess of acetone (50 ml). The mixture was stirred for one hour to complete the reaction and hydrolyzed by adding a 1M solution of HCl acid (300 ml). The organic phase was separated and washed twice with water (100 ml). The aqueous phase was extracted three times with hexane (30 ml). The combined organic phase was dried over sodium sulfate and the solvent was evaporated. The yellow oil obtained was crystallized by adding a methanol (3 ml) and dried in high vacuum for three hours to give 0.50 g (76%) of a bright-yellow microcrystalline powder of **11**, which was characterized spectroscopically. ^{1}H-NMR (acetone-d^6): δ 7.28–7.11 (m, 15H, C_{Ph}–H); 6.485 (m, 1H, H(4), ^3J(H(4)–H(5)) = 5.2 Hz); 6.176 (t, 1H, H(2), ^4J(H(2)–H(4)) = ^4J(H(2)–H(5)) = 2 Hz); 6.000 (m, 1H, H(5)); 3.217 (s, 6H, $(CH_3–)_2$).

3.3. *Tris-(2-methoxyphenyl)methanol (**5**)*

An ether (20 ml) solution of 2-methoxybenzoylchloride (**4**) (13.6 g, 100 mmol) was added dropwise to a cooled stirred ether solution (200 ml) of Grignard reagent obtained from 2-methoxyphenylbromide (**3**). The resulting brown suspension was hydrolyzed with ice (50 g) and HCl acid (50 ml, 40% solution). The crude product was filtered off, washed five times with 100 ml portions of hot water and three times with cooled methanol (20 ml), yielding 14.0 g of a snow-white microcrystalline solid (50%). ^{1}H-NMR ($CDCl_3$): δ 7.22–7.09, 6.87–6.78 (m, m, 12H, C_{Ar}–H); 5.413 (s, 1H, O–H); 3.414 (s, 9H, O–CH_3).

3.4. *2-[tris-(2′-methoxyphenyl)methyl]cyclopentadiene (**2**)*

A tetrahydrofuran (50 ml) solution of nickelocene [7] (0.47 g, 2.5 mmol) was added to a cooled THF (100 ml) solution of tris-(2-methoxyphenyl)methylbromide (**6**) (2.07 g, 5 mmol) [4]. The solvent was removed in vacuo and the residual oil was extracted ten times with 25 ml portions of boiling heptane. The combined organic extract was evaporated to give a yellow oil that was allowed to crystallize under methanol in a freezer for one week. Light-yellow crystals were filtered, washed with icy methanol (5 ml), and dried in high vacuum to yield 1.52 g (75%) of (**2**), mp = 81°C. ^{1}H-NMR (THF-d^8): δ 7.25–6.81 (m, 12H, C_{Ar}–H); 6.78–6.62 (m, 3H, C_{Cp}–H, –CH=); 3.624 (s, 9H, O–CH_3); 3.103 (s, 2H, C_{Cp}–H, –CH_2–). ^{13}C-NMR-APT {^{1}H} (THF-d^8): δ 158.461 (CH_3O–C_{Ar}); 155.352 (C_{Cp}(2)); 133.678 ((C_{Ar})$_3$–C–Cp); 130.271 (C_{Ar}(5)); 129.207, 129.268 ($^*C_{Cp}$(3)); 127.631 (C_{Ar}(3)); 126.777 (C_{Cp}(4)); 123.216, 120.545 ($^*C_{Cp}$(1)); 120.434 (C_{Ar}(4)); 115.979, 111.366 ($^*C_{Ar}$(6)); 60.300 ((C_{Ar})$_3$–C–Cp); 55.676, 55.395 (O–$^*CH_3$); 30.623 (C_{Cp},–CH_2–).

3.5. *1-trimethylsilyl-(3-triphenylmethyl)cyclopenta-2,4-diene (**13**)*

To a suspension of 0.96 g (40 mmol) NaH in 50 ml THF, 3.08 g (10 mmol) of **1** was added. The reaction mixture was stirred for 5 h followed by filtering off of excess NaH. Solvent was removed and the residual solid of **12** after drying in high vacuum was mixed with 1.27 ml (1.09 g, 10 mmol) of Me_3SiCl in toluene (30 ml) and refluxed with stirring overnight. NaCl and solvent were then removed and the crude product was recrystallized from hexane, yielding 2.9 g (80%) of light-yellow stable crystals of **13**, mp = 187°C. Anal. Found C 85.73, H 7.68, Si 7.36. $C_{27}H_{28}Si$ (380.60) calcd.: C 85.20, H 7.42, Si 7.38%. ^{1}H-NMR (THF-d^8): δ 7.27–7.10 (m, 15H, C_{Ph}–H); 6.46–6.43, 6.28–6.25, 6.15–6.13 (m, m, m, 1H, 1H, 1H, C_{Cp}–H, –CH=); 3.298–3.291 (m, 1H, Me_3Si–CH<); –0.003 (s, 9H, CH_3–).

3.6. *Structure determination*

Data collection was performed at room temperature on an Enraf-Nonius CAD-4 diffractometer using

Table 3
Crystallographic data for $(C_6H_5)_3CC_5H_4Si(CH_3)_3$ (**13**)

Chemical formular	$C_{27}H_{28}Si$
Crystal system	monoclinic
Mol. wt.	380.60
Cell dimensions	
a, Å	11.635(4)
b, Å	12.400(4)
c, Å	15.531(4)
β, deg	91.42
V, Å^3	2240.09(9)
Scan range 2θ, deg	4–50
Number of reflections	4127
for $\lvert F_o \rvert > 2\sigma(\lvert F_o \rvert)$	946
Spase group	$P2_1/c$
Z	4
R	0.0359
R_w	0.0375

graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and variable ω scans. 4127 unique reflections were measured in the range $4° < 2\theta < 50°$; for 946 observed reflections ($F > 2\sigma(F)$) final R and R_w values were 0.0359 and 0.0375 respectively. Approximate positions for the Si atom were obtained using direct methods (SHELXTL-86 PLUS programs, IBM PC/AT) and all the remaining non-hydrogen atoms were revealed by successive difference Fourier syntheses. Following anisotropic refinement of non-hydrogen atoms, idealized positions for hydrogen atoms were included as fixed contributions using a riding model.

Table 3 lists the crystal data for **13**.

References and notes

[1] H. Schumann, H. Kucht, A. Kucht and F.H. Goerlitz *Z. Naturforsch., B. Chem. Sci., 47* (1992) 1242; H. Schumann, C. Janiak and M.A. Khan *J. Organomet. Chem., 330* (1987) 347; H. Schumann, C. Janiak, M.A. Khan and J.J. Zuckerman *J. Organomet. Chem., 354* (1988) 7; R.T. Klark and S.J. Store *Canadian J. Chem., 50* (1972) 795 and references cited therein; R.L. Halterman, *Chem. Rev., 92* (1992) 965 and references cited therein; Y. Chauvin, S. Heyworth, H. Oliver, F. Robert and L. Saussine *J. Organomet. Chem., 455* (1993) 89; A. Razavi and J.L. Atwood *J. Organomet. Chem., 459* (1993) 117. T. Kinoshita, S. Tsuji, T. Otake and K. Takeuchi *J. Organomet. Chem., 458* (1993) 187 and references cited therein.

[2] U. Thewalt and G. Schmid *J. Organomet. Chem., 412* (1991) 343; M.P. Castellani, S.J. Geib, A.L. Rheingold and W.C. Trogler *Organometallics, 6* (1987) 345; H. Sitzmann, *Z. Naturforsch., B: Chem. Sci., 44* (1989) 1293 and references cited therein.

[3] H. Werner, G. Mattmann, A. Salzer and T. Winkler, *J. Organomet. Chem., 25* (1970) 461.

[4] Ar_3CBr was synthesized in the same way as Ph_3CCl (see Ref. 8).

[5] W. Kläui and H. Werner *Helv. Chem. Acta, 59* (1976) 844.

[6] G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry, Vol. 2*, Pergamon, Oxford 1982. p. 57.

[7] Cp_2Ni was synthesized using the technique described by J.F. Cordes, *Chem. Ber., 95* (1962) 3084.

[8] Ph_3CCl was obtained by the standard method described by H.H. Wasserman and P.S. Wharton *J. Amer. Chem. Soc., 82* (1960) 3457.