Mono-, Bis- and Tris(cyclopentadienyl) Compounds - Syntheses of New Polydentate Ligands and their Molybdenum and Tungsten Complexes

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Condensation reactions of cyclopentadienyl-substituted chlorosilanes $CpSiMe_2Cl$ ($Cp = C_5H_5$, C_5HMe_4) with a number of phenols [C_6H_5OH, 1,3-$C_6H_4(OH)_2$, 1,4-$C_6H_4(OH)_2$, 1,3,5-$C_6H_3(OH)_3$] in the presence of excess base led to six novel molecules containing up to three cyclopentadienyl groups {e.g. 1,3,5-$C_6H_3[OSiMe_2(C_5Me_4H)]_3$}. The dynamic behavior of 1,4-$C_6H_4[OSiMe_2(C_5H_5)]_2$ (**2**) was investigated by temperature-variable ^1H NMR and the reaction rate of the degenerate 1,2-silicon shift determined. $C_6H_5OSiMe_2(C_5H_5)$ (**1**) and (**2**) were treated with NaH, $(MeCN)_3M(CO)_3$ (M = Mo, W), and MeI to give the η^5-complexes $C_6H_5OSiMe_2-(C_5H_4)M(CO)_3Me$ (**8**: M = Mo, **9**: M = W) and 1,4-$C_6H_4[OSiMe_2-(C_5H_4)M(CO)_3Me]_2$ (**10**: M = Mo, **11**: M = W) in good yields. The X-ray crystal structure of **11** was determined.

The importance of the cyclopentadienyl ligand in organometallic chemistry can hardly be overestimated[1]. Ever since the discovery of bis(cyclopentadienyl)iron(II), cyclopentadienyls have been among the most common ligands in transition metal chemistry[2]. Replacing protons on C_5H_6 by organic groups further widened this field, leading to numerous substituted cyclopentadienes[3], for example $HC_5H_4(Me)$[4], $HC_5H_4(SiMe_2H)$[5], $Ph_2P[CH_2]_nC_5Me_4H$[6], $HC_5H_2(SiMe_3)_3$[7], $HC_5H_2(t\text{-}C_4H_9)_3$[8], HC_5Ph_5[9], $HC_5(CH_2Ph)_5$[9,10], and asymmetric units[11]. Spectacular results were obtained by using the fully methylated cyclopentadienyl C_5Me_5[12], its remarkable steric and electronic properties led to the synthesis of a number of interesting transition metal and main group element[17] compounds: Cp^*ReO_3[13], Cp^*_2ScMe[14], Cp^*_2Yb[15], $Cp^*TaN(Cl)]_3$[16], and Cp^*_2Si[18]. The chemistry of linked bis(cyclopentadienyl) compounds is much less developed, the most prominent - among others[19] - being $Me_2Si(Cp)_2$[20]. Organic molecules incorporating three cyclopentadiene moieties are rare, examples being trindene[21], truxene[22], and $HC(C_5H_5)_3$[23]. Only few examples of related metal complexes are known[24]. Ligands of this type will be able to hold several metals in close proximity thereby allowing to investigate whether cooperative effects can enhance or modify the chemical reactivity of metal complexes with regard to the mono-Cp analogs. This could result in new multimetal catalysts[25], organometallic polymers[26], heterodimetallics[27], or redox active crown ethers[28].

In this paper I describe the syntheses of several new mono-, bis-, and tris(cyclopentadienyl) compounds and a DNMR investigation of one of the silylcyclopentadienes. Furthermore, the synthesis of molybdenum and tungsten η^5-complexes with some of the new ligands is reported.

Results and Discussion

Bis-cyclopentadienes usually are prepared according to (1)[19,20].

$$X-E-X + 2Cp^- \xrightarrow[-2X^-]{} Cp-E-Cp \qquad (1)$$

This approach however is limited, especially to cyclopentadienes that carry bulky substituents. Their anions display a high basicity, but only a low nucleophilicity[6]. We therefore chose a different approach by attaching a reactive fragment to a cyclopentadiene, see (2).

$$Cp^- + Me_2SiCl_2 \xrightarrow[-Cl^-]{} Me_2SiCpCl \qquad (2)$$

This reaction had been described previously only for $Cp = C_5H_5$[29]. We were able to prepare the related compound with $Cp = C_5Me_4H$ in high yields (80%). Such cyclopentadiene derivatives contain a highly reactive silicon–chlorine bond that can be used to couple these reagents to a large number of nucleophiles. The high affinity of silicon to oxygen makes alcohols the reagents of choice for the preparation of molecules that contain several cyclopentadienyl groups. A wide range of alcohols with two, three, or even more OH groups are suitable and easily available candidates for which this type of condensation ought to work.

The phenols C_6H_5OH, 1,2-$C_6H_4(OH)_2$, 1,3-$C_6H_4(OH)_2$, 1,4-$C_6H_4(OH)_2$, and 1,3,5-$C_6H_3(OH)_3$ react with the chlorosilanes $CpSiMe_2Cl$ ($Cp = C_5H_5$, HC_5Me_4) in the presence of excess triethylamine according to equation (3).

$$n\,CpSiMe_2Cl + C_6H_{6-n}(OH)_n \xrightarrow[-\,HCl]{Et_3N} C_6H_{6-n}(OSiMe_2Cp)_n \quad (n = 1, 2, 3) \quad (3)$$

Table 1. Reactions of phenols with chloro(cyclopentadienyl)silanes

	$C_5H_5SiMe_2Cl$	$(HC_5Me_4)SiMe_2Cl$ **3**
C_6H_5OH	$C_6H_5OSiMe_2(C_5H_5)$ **1**	$C_6H_5OSiMe_2$-(HC_5Me_4) **4**
1,3-$C_6H_4(OH)_2$	–	1,3-$C_6H_4[OSiMe_2$-$(HC_5Me_4)]_2$ **5**
1,4-$C_6H_4(OH)_2$	1,4-$C_6H_4[OSiMe_2(C_5H_5)]_2$ **2**	1,4-$C_6H_4[OSiMe_2$-$(HC_5Me_4)]_2$ **6**
1,3,5-$C_6H_4(OH)_3$	–	1,3,5-$C_6H_4[OSiMe_2$-$(HC_5Me_4)_3$ **7**

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Six new mono-, bis-, and tris(cyclopentadienyl) compounds are isolated (Table 1). Not surprisingly though, for sterical reasons, the reactions of 1,2-$C_6H_4(OH)_2$ with the chlorosilanes do not go to completion, as is evidenced in the IR spectrum by the presence of strong vOH absorptions. Compounds **4**, **5**, and **7** are non-volatile, highly lipophilic oils that darken on exposure to air and are difficult to purify. However, due to the mild reaction conditions employed, these compounds are reasonably pure ($>90\%$ based on ^{29}Si NMR) when filtered through a thin layer of silica gel. The two crystalline *para*-substituted derivatives **2** and **6** can be recrystallized from pentane to give compounds of analytical purity. Compound **2** crystallizes solely in the form of the bis allyl isomer and isomerizes slowly in solution, having (almost) reached equilibrium after 48 h. This mixture contains 70% of the allyl and 30% of the two vinyl isomers (Scheme 1), as is determined by the integral ratios of the CH_2 to the CHSi part of the cyclopentadienyl group. This result is in line with the series $(C_5H_5)SiMe_nCl_{3-n}$ where the isomer ratios depend on the number of electron-withdrawing groups (allyl:vinyl, $n = 3$ 90:10, $n = 2$ 79:21, $n = 1$ 50:50, $n = 0$ 35:65)[30].

The reactions of 1,3-$C_6H_4(OH)_2$ and 1,3,5-$C_6H_3(OH)_3$ with $CpSiMe_2Cl$ go to completion (IR), but no stable products are isolated. The reaction product of 1,3-$C_6H_4(OH)_2$ analyzes correctly for 1,3-$C_6H_4(OSiMe_2C_5H_5)_2$, but its ^1H-NMR spectrum is not in agreement with this formulation. This can be attributed to the fact that *intra*molecular Diels-Alder reactions are possible, in contrast to **1** and **2** where only intermolecular reactions of this type can occur. These appear to be slow enough to make **1** and **2** stable compounds.

Reactions of this type usually are extremely slow with cyclopentadienes bearing sterically demanding substituents and pose no problem for their long-term stability. On the other hand, compounds **4**, **5**, **6**, and **7** being dienes rich in electrons are sensitive to oxygen and light.

To prove whether these siloxycyclopentadienes can act as η^5-ligands for transition metals we prepared some molybdenum and tungsten complexes. In a one-pot reaction the substituted cyclopentadiene is first deprotonated by a twofold excess of NaH, followed by addition of $(CH_3CN)_3M(CO)_3$ (M = Mo, W) and finally by MeI [eq. (4), (5)].

$$\underset{\mathbf{1}}{C_6H_5OSiMe_2(C_5H_5)} \xrightarrow[3)\ +2\ MeI]{1)\ +2\ NaH \quad 2)\ +(MeCN)_3M(CO)_3} \underset{\mathbf{8}:\ M = Mo \quad \mathbf{9}:\ M = W}{C_6H_5OSiMe_2-(C_5H_4)M(CO)_3Me} \tag{4}$$

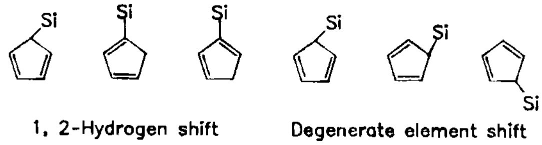
$$\underset{\mathbf{2}}{1,4\text{-}C_6H_4[OSiMe_2(C_5H_5)]_2} \xrightarrow[3)\ +4\ MeI]{1)\ +4\ NaH \quad 2)\ +2\ (MeCN)_3M(CO)_3} \underset{\mathbf{10}:\ M = Mo \quad \mathbf{11}:\ M = W}{1,4\text{-}C_6H_4[OSiMe_2-(C_5H_4)M(CO)_3Me]_2} \tag{5}$$

Complexes containing one or two metals are isolated in good yields as yellow, air-stable powders. Upon chromatographic purification two side products can be separated in small yields (10–15%), which are identified as $(C_5H_5)M(CO)_3Me$ (M = Mo, W). These products obviously result from the splitting of the silicon–C_5H_5 bond[31]. Most likely this occurs during the deprotonation of the cyclopentadiene with NaH {a reaction of $(MeCN)_3W(CO)_3$ in refluxing DME leaves the ligand intact and yields red $[C_6H_5OSiMe_2(C_5H_4)W(CO)_3]_2$[32]}. The use of equimolar amounts of NaH leads to slightly lower yields but also to cleavage of the silicon–C_5H_5 bond. Changing the base gives either a low overall yield (BuLi) of the metal complexes or results in quantitative cleavage $[NaN(SiMe_3)_2]$ of the silicon–C_5H_5 bond.

NMR Spectra

It is a well-known phenomenon that silicon and other main group cyclopentadienyl compounds display fluxional behavior[33]. Two different processes are known to occur simultaneously: A 1,2-hydrogen shift producing isomers with the element in the allyl- and two different vinyl positions and a degenerate element shift (Scheme 1).

Scheme 1



The activation energy for the degenerate element shift usually is lower than for the 1,2-hydrogen shift[33]. The rate constants being in the range between 10 and 10^5 s^{-1} (activation energies between 20 and 100 kJ/mol) are therefore accessible by dynamic NMR spectroscopy. We recorded ^1H-NMR spectra of **2** between 243 and 370 K. The high-temperature solvent 99% $[D_8]$toluene exhibits several inconvenient signals in the region of the vinyl protons, therefore $CDCl_3$ was used for temperatures below 300 K. The cyclopentadienyl group of the allyl isomer of **2** displays an AA'BB'X spectrum. The coalescence of the AA'BB' signal around 370 K was evaluated according to the Eyring equation. The activation energy for the silicon migration in **2** was calculated to be 75.5 ± 2 kJ/mol[34].

The ^{13}C- and ^{29}Si-NMR data for the compounds **1**–**11** are listed in Table 2. The dynamic processes mentioned above also influence the ^{13}C NMR of **1** and **2**. The three resonances associated with the cyclopentadiene ring are severely broadened. The CHSi resonances have a $v_{1/2}$ of ca. 100 Hz at 300 K. In an equilibrated mixture of **2** three peaks in the in the $Si(CH_3)_2$ region are observed (−3.14 allyl and −2.4, −1.07). It is tempting to assign these peaks to the two vinyl isomers, but in the ^{29}Si-NMR spectrum no additional peaks show up. The ^1H-NMR spectra of the metal complexes (**8**–**11**) display sharp signals, coupling between ^{183}W (spin = 1/2, 14%) ($^2J_{WH} = 3.6$ Hz) and ^{29}Si ($^3J_{SiH} = 6.8$ Hz) can be observed. Two different sets of sharp CO resonances are observed in the ^{13}C-NMR spectrum close to $\delta = 227$ and 240 (Mo) and 216 and 230 (W), corresponding to the two magnetically inequivalent sites in the square-pyramid complexes. The ^{29}Si-NMR resonances are located at δ = 6.64, 6.74 (Mo) and 6.90, 7.05 (W), with the different metals still having a small influence on the shifts.

Table 2. ^{13}C- and ^{29}Si-NMR data (δ values)

	1	**2**[b]	**3**	**4**	**5**
Cp	a)	131.64	131.31	131.67	131.71
		131.88	137.65	136.93	137.08
CpMe			11.25	11.39	11.46
			14.34	14.28	14.39
CpSi	52.76	52.15	46.43	55.75	55.75
$SiMe_2$	-2.90	-3.14	0.56	-2.76	-2.66
Ar	a)	120.80		120.20 (2,6)	112.36 (4,6)
				121.69 (4)	113.54 (2)
				129.86 (3,5)	130 38 (5)
ArO	155.40	149.00		155.70	156.98
$M(CH_3)$					
^{29}Si-NMR	9.73	13.59	26.13	14.56	14.83

	6	**7**	**8**	**9**	**10**	**11**
Cp	131.72	131.46	97.37	96.24	97.40	95.84
	136.86	137.07	97.76	96.76	97.69	96.44
CpMe	11.42	11.37				
	14.34	14.25				
CpSi	55.82	55.61	96.20	94.98	96.10	94.57
$SiMe_2$	-2.72	-2.68	-0.86	-0.66	-0.95	-1.03
Ar	120.79	105.84	120.37	120.68	120.89	120.92
			122.22 (4)	122.61 (4)		
			129.82	130.17		
ArO	149.93	157.45	155.00	155.24	149.46	149.47
$M(CH_3)$			-21.58	-33.96	-21.61	-34.33
M(CO) (1,3)			227.01	216.80	226.82	216.33
(2)			240.03	229.86	239.87	229.43
^{29}Si	14.48	15.01	6.64	6.90	6.74	7.05

[a] Compound 1 is a mixture of isomers and is therefore difficult to purify by distillation. It is impossible to unambigously assign peaks in the regions denoted by a). — [b] Recorded at 230 K in $CDCl_3$.

Crystal Structure of 11

The results of an X-ray crystal structure analysis are presented in Figure 1 and in Tables 3–6.

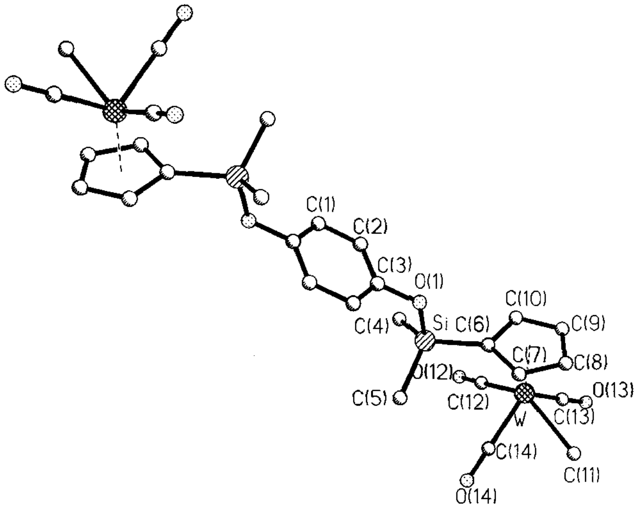


Figure 1. Crystal structure of compound **11** (without H atoms); selected bond distances [pm] and angles [°]: W–CO (mean) 198.8; W–CH_3 230.3(10); W–Cp–Cent. 200.9; C(3)–O(1)–Si 126.1(5); O(1)–Si–C(6) 101.6(3)

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (pm^2 × 10^{-1}) for **11**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
W	713(1)	4026(1)	3370(1)	36(1)
Si	331(3)	6300(3)	1587(1)	42(1)
O(1)	141(11)	8584(9)	1373(3)	59(2)
C(1)	1881(14)	10997(13)	-228(4)	55(3)
C(2)	1952(14)	10289(13)	462(4)	56(3)
C(3)	81(14)	9251(11)	678(4)	46(3)
C(4)	2697(15)	5915(16)	1313(5)	66(4)
C(5)	-2179(15)	4122(14)	1132(5)	66(4)
C(6)	604(12)	6644(10)	2612(4)	41(3)
C(7)	-1102(13)	6322(11)	2996(4)	44(3)
C(8)	-182(17)	6977(12)	3767(4)	59(4)
C(9)	2061(17)	7646(12)	3867(4)	60(4)
C(10)	2596(13)	7426(10)	3168(4)	48(3)
C(11)	-1720(15)	2480(16)	4082(5)	67(4)
C(12)	2606(13)	2903(14)	2846(4)	53(3)
O(12)	3722(10)	2289(11)	2575(4)	71(3)
C(13)	2333(14)	3074(12)	4202(5)	55(3)
O(13)	3223(12)	2588(12)	4726(4)	83(3)
C(14)	-1440(12)	1458(11)	2760(4)	47(3)
O(14)	-2746(10)	43(9)	2398(4)	69(3)

Table 4. Bond lengths [pm] of **11**

W-C(6)	233.0 (7)	O(1)-C(3)	138.5 (9)
W-C(7)	231.0 (9)	C(1)-C(2)	138.6 (12)
W-C(8)	235.7 (10)	C(1)-C(3A)	137.1 (12)
W-C(9)	237.1 (7)	C(2)-C(3)	136.4 (12)
W-C(10)	232.4 (7)	C(3)-C(1A)	137.1 (12)
W-C(11)	230.3 (10)	C(6)-C(7)	141.2 (12)
W-C(12)	200.9 (10)	C(6)-C(10)	144.7 (10)
W-C(13)	197.6 (9)	C(7)-C(8)	142.6 (10)
W-C(14)	198.0 (6)	C(8)-C(9)	138.9 (15)
Si-O(1)	164.7 (7)	C(9)-C(10)	141.1 (12)
Si-C(4)	182.4 (11)	C(12)-O(12)	112.9 (13)
Si-C(5)	185.4 (8)	C(13)-O(13)	116.3 (12)
Si-C(6)	186.2 (7)	C(14)-O(14)	113.9 (8)

In the solid-state structure of the bismetallocene **11**, the two half-sandwich units are symmetry-related through an inversion center, which is located in the middle of the benzene hexagon. The two (cyclopentadienyl)tungsten moieties lie on opposite faces of the planar $C_6H_4O_2$ unit, giving the molecule a dumb bell-like appearance. This linear shape is also reflected in the dimensions of the unit cell, which contains one molecule. In the solid state there can be no interaction between the two metal sites. However, the conformative flexibility of the O(1)–Si–C(6) unit will allow a much closer approach of the two tungsten atoms in solution and the observation of cooperative effects. The coordination sphere around tungsten can be viewed as a pseudo square-pyramid, with the three carbonyls (mean W–C 198.8, C–O 114.4 pm) and the CH_3 group (W–C 230.3 pm) forming the base. The tungsten atom is located 200.4 pm above the plane of the cyclopentadienyl ring. The C–C distances in

Table 5. Bond angles [°] for **11**

C(6)-W-C(7)	35.4(3)	C(13)-W-C(14)	106.9(3)
C(6)-W-C(8)	58.8(3)	O(1)-Si-C(4)	110.0(4)
C(7)-W-C(8)	35.6(3)	O(1)-Si-C(5)	110.0(4)
C(6)-W-C(9)	59.0(2)	C(4)-Si-C(5)	110.9(4)
C(7)-W-C(9)	58.5(3)	O(1)-Si-C(6)	101.6(3)
C(8)-W-C(9)	34.2(4)	C(4)-Si-C(6)	112.7(4)
C(6)-W-C(10)	36.2(2)	C(5)-Si-C(6)	111.3(4)
C(7)-W-C(10)	59.2(3)	Si-O(1)-C(3)	126.1(5)
C(8)-W-C(10)	58.0(3)	C(2)-C(1)-C(3A)	119.8(8)
C(9)-W-C(10)	35.0(3)	C(1)-C(2)-C(3)	120.3(8)
C(6)-W-C(11)	128.1(4)	O(1)-C(3)-C(2)	120.5(7)
C(7)-W-C(11)	92.8(4)	O(1)-C(3)-C(1A)	119.5(8)
C(8)-W-C(11)	80.2(4)	C(2)-C(3)-C(1A)	119.8(7)
C(9)-W-C(11)	104.0(3)	W-C(6)-Si	124.8(4)
C(10)-W-C(11)	137.3(3)	W-C(6)-C(7)	71.5(4)
C(6)-W-C(12)	95.4(3)	Si-C(6)-C(7)	126.4(5)
C(7)-W-C(12)	128.9(3)	W-C(6)-C(10)	71.7(4)
C(8)-W-C(12)	147.7(3)	Si-C(6)-C(10)	127.0(6)
C(9)-W-C(12)	117.7(3)	C(7)-C(6)-C(10)	106.4(6)
C(10)-W-C(12)	89.7(3)	W-C(7)-C(6)	73.0(5)
C(11)-W-C(12)	131.7(4)	W-C(7)-C(8)	74.0(5)
C(6)-W-C(13)	148.2(3)	C(6)-C(7)-C(8)	108.3(7)
C(7)-W-C(13)	147.2(3)	W-C(8)-C(7)	70.4(5)
C(8)-W-C(13)	111.7(3)	W-C(8)-C(9)	73.5(6)
C(9)-W-C(13)	95.5(3)	C(7)-C(8)-C(9)	108.7(8)
C(10)-W-C(13)	112.0(3)	W-C(9)-C(8)	72.4(5)
C(11)-W-C(13)	73.2(4)	W-C(9)-C(10)	70.7(4)
C(12)-W-C(13)	79.3(4)	C(8)-C(9)-C(10)	108.3(7)
C(6)-W-C(14)	102.6(3)	W-C(10)-C(6)	72.1(4)
C(7)-W-C(14)	96.3(3)	W-C(10)-C(9)	74.3(4)
C(8)-W-C(14)	123.0(3)	C(6)-C(10)-C(9)	108.2(8)
C(9)-W-C(14)	154.7(4)	W-C(12)-O(12)	177.6(7)
C(10)-W-C(14)	136.3(3)	W-C(13)-O(13)	175.0(9)
C(11)-W-C(14)	72.7(3)	W-C(14)-O(14)	176.4(8)
C(12)-W-C(14)	78.6(3)		

Table 6. X-ray diffraction data for **11**[4)]

Formula: $C_{28}H_{30}O_8Si_2W_2$; mol. mass 918.4; crystal size 0.35 x 0.25 x 0.10 mm; yellow rhombic plates; a = 665.3(1), b = 672.7 (1), c = 1847.9(4) pm, α = 93.60(3)°, β = 100.30(3)°, γ = 108.44 (3)°; V = 7.656(2) x 10^8 pm^3; $d_{calcd.}$ = 1.992 gcm^{-3}; linear absorption coefficient = 7.791 mm^{-1}; absorption correction: empirical, psi-scans ($R_{int.}$ = 0.13 ⟶ 0.04); space group P$\bar{1}$; Z = 1; F(000) = 438; radiation Mo-K_α; diffractometer: four-circle Stoe-Siemens, graphite monochromator; scan technique ω-2Θ; measured reflections 6865 (h ±8, k ±8, l +20); independent reflections 3506; observed reflections 3185 [I > 4.0 σ(I)]; solution: heavy-atom method; full matrix least squares refinement; H atoms: riding-model, fixed isotropic U; refined parameters 181; data to parameter ratio 17.6 : 1; R = 0.0348, R_w = 0.0388; Goof 1.59; final residual electron density max. 1.04 eA^{-3}, min. -1.67 eA^{-3}; Structure solution and refinement: SHELXTL PLUS (PC Version)[36)]

the aromatic five-membered ring (mean 141.7 pm, 138.9–144.7 pm) are not unusual.

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Experimental

All reactions were carried out under dry argon using standard Schlenk techniques. Commercially available solvents and reagents were purified according to literature procedures[35)]. The phenols were distilled (C_6H_5OH) or dried in vacuo [1,2-$C_6H_4(OH)_2$, 1,3-$C_6H_4(OH)_2$, 1,4-$C_6H_4(OH)_2$, 1,3,5-$C_6H_3(OH)_3$] prior to use. – Chromatography: silica MN 60. – NMR: recorded at 300 K (^{13}C and ^{29}Si NMR in C_6D_6 unless stated otherwise), Bruker AC 200 F spectrometer (DNMR measurements in $CDCl_3$ and $C_6D_5CD_3$ with a Eurotherm temperature controling unit). ^1H NMR (200 MHz), ^{13}C NMR (50 MHz) (ligands) and Varian Unity 300, ^{13}C NMR (75 MHz) (metal complexes), ^{29}Si NMR [59 MHz, Cr(acac)$_2$ relaxation reagent, ext. TMS]. – IR: Bruker IFS 25, oils neat, solids as nujol mulls between NaCl plates with intensities estimated. – Elemental analyses: Mikroanalytisches Laboratorium der Chemischen Laboratorien Universität Freiburg. – Melting points: Meltemp melting point apparatus in sealed capillaries. – Starting materials were prepared according to literature procedures: $(C_5H_5)SiMe_2Cl$[29)], $(CH_3CN)_3M(CO)_3$ (M = Cr, Mo, W[37)]), Tetramethylcyclopentenon[38)], Tetramethylcyclopentadiene[39)].

$(C_5H_5)SiMe_2(OC_6H_5)$ (**1**): To a stirred solution of 9.4 g of C_6H_5OH (100 mmol) and 15.2 g of Et_3N (150 mmol) in 200 ml of toluene at 0°C is added 16.4 g of $Me_2(C_5H_5)SiCl$ (0.110 mol) in 20 ml of toluene, whereupon the hydrochloride starts to precipitate. After 2 h at room temp. the $(C_2H_5)_3NHCl$ is filtered off and washed with 50 ml of hexane. The solvents are removed in vacuo, and the residue distilled over a 30-cm Vigreux column (b.p. 67–70°C/0.1 Torr) to yield 17.3 g (80%) of a colorless liquid. – ^1H NMR ($CDCl_3$): δ = 0.16 ($SiMe_2$), 0.32 ($SiMe_2$), 0.50 ($SiMe_2$), 3.16 (s, CH), 3.76 (br, CHSi), 6.63 (br, CH), 6.75 (br, CH), 6.87–7.09 (m, ArH), 7.23–7.36 (m, ArH). – IR (cm^{-1}): $\tilde{\nu}$ = 3089 (w), 3067 (w), 3038 (w), 2960 (m), 2924 (w), 2901 (w), 1595 (s), 1491 (vs), 1254 (vs), 1163 (m), 1068 (m), 1023 (w), 979 (s), 951 (s), 916 (vs), 855 (m), 803 (s), 760 (s), 715 (m), 691 (s).

1,4-$C_6H_4[OSiMe_2(C_5H_5)]_2$ (**2**): To a stirred suspension of 1.1 g of 1,4-$C_6H_4(OH)_2$ (10 mmol) and 3.0 g of $(C_2H_5)_3N$ (30 mmol) in 25 ml of toluene at 0°C is added 3.5 g of $Me_2(C_5H_5)SiCl$ (22 mmol) in 10 ml of toluene. After 1 h at room temp. the hydrochloride is filtered off and washed twice with 20 ml hexane. After removal of the volatiles in vacuo a pale yellow oil remains, from which the product slowly crystallizes. After 2 d the oil is syringed off, and the crystals are recrystallized from pentane to yield 1.4 g (41%) of colorless, cube-shaped crystals, m.p. 72°C. – ^1H NMR ($CDCl_3$): δ = 0.11 (s, $SiMe_2$), 3.10 (s, CH), 3.7 (br, CH_2), 6.55 (br, CH), 6.69 (br, CH), 6.81 (s, ArH). – IR (cm^{-1}): $\tilde{\nu}$ = 3105 (w), 3087 (w), 3061 (w), 3034 (w), 1500 (vs), 1251 (s), 1238 (s), 1224 (s), 1094 (m), 974 (s), 950 (s), 928 (s), 904 (m), 848 (m), 838 (s), 800 (s), 765 (s), 729 (m), 699 (s), 662 (m).

$C_{20}H_{26}O_2Si_2$ (354.6)	Calcd.	C 67.74	H 7.39
	Found	C 67.43	H 7.37

$(HC_5Me_4)SiMe_2Cl$[40)] (**3**): To 24.4 g of tetramethylcyclopentadiene (200 mmol), dissolved in 400 ml of THF, at 0°C is added 80 ml of Butyllithium (2.5 M in hexane) with vigorous stirring. After 1 h the suspension is cooled to –78°C, and 28 g of Me_2SiCl_2 (30

[a)] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55263, the name of the author and the journal citation.

mmol) is added rapidly. The reaction mixture is slowly warmed to room temp. (ca. 1 h) and the pale yellow solution refluxed for 12 h. The volatiles are removed in vacuo, the oily residue is extracted twice with hexane, the LiCl is removed and the filtrate fractionated over a 30-cm Vigreux column (b.p. 67–71°C/5 Torr) to yield 30.6 g of $(HC_5Me_4)SiMe_2Cl$ (80%) as a pale yellow, fluorescent liquid. – ^1H NMR ($CDCl_3$): $\delta = 0.25$ (s, 6H, $SiMe_2$), 1.83 (s, 6H, CH_3), 1.98 (s, 6H, CH_3), 3.15 (s, 1H, CH). – IR (cm^{-1}): $\tilde{\nu} = 2965$ (s), 2914 (s), 2858 (s), 2741 (w), 1632 (w), 1442 (m), 1401 (m), 1381 (m), 1300 (w), 1251 (s), 1215 (m), 1120 (m), 1110 (m), 1049 (m), 1024 (m), 988 (m), 954 (m), 917 (w), 843 (vs), 812 (vs), 787 (s), 756 (w), 736 (w), 692 (m), 655 (s).

Common Procedure for the Reaction of Phenols with $(HC_5Me_4)SiMe_2Cl$: 50 mmol of the phenol and $(C_2H_5)_3N$ (1.5 equivalents per OH group) are suspended in 50 m of toluene. The reaction mixture is cooled to 0°C and $(HC_5Me_4)SiMe_2Cl$ (1.05 equivalents per OH group) added with vigorous stirring. The suspension is then allowed to warm to room temp. and subsequently heated to 80°C for 2 h. The Et_3NHCl is filtered off, washed twice with 25 ml of hexane, and the filtrate is purified by filtration over a 3-cm layer of silica gel. The volatiles are removed in vacuo, and a pale yellow oil is obtained.

$(HC_5Me_4)SiMe_2(OC_6H_5)$ (**4**): Yield 74%. – ^1H NMR ($CDCl_3$): $\delta = 0.06$ (s, $SiMe_2$), 1.81 (s, CpMe), 1.97 (s, CpMe), 3.15 (br, CpH), 6.82–6.97 (m, ArH), 7.19–7.27 (m, ArH). – (IR) (cm^{-1}): 3086 (w), 3061 (m), 3038 (m), 3024 (m), 2964 (s), 2914 (s), 2857 (s), 2739 (w), 1632 (m), 1596 (s), 1491 (s), 1444 (m), 1251 (vs), 1216 (s), 1165 (m), 1110 (m), 1069 (m), 1048 (m), 1023 (m), 986 (s), 952 (m), 913 (vst), 890 (st), 838 (st), 812 (st), 786 (st), 757 (st), 711 (m), 691 (st), 639 (m).

$C_{17}H_{24}OSi$ (272.5) Calcd. C 74.94 H 8.88
Found C 72.10 H 8.71

$1,3\text{-}C_6H_4[OSiMe_2(HC_5Me_4)]_2$ (**5**): Yield 53%. – ^1H NMR ($CDCl_3$): $\delta = 0.07$ (s, $SiMe_2$), 1.84 (s, CH_3), 2.00 (s, CH_3), 3.18 (s, CH_3), 6.42 (t, 2.6 Hz, Ph), 6.50 (d, 8.5 Hz, Ph), 7.10 (t, 8.0 Hz, Ph). – IR (cm^{-1}): $\tilde{\nu} = 3069$ (w), 3026 (w), 2962 (s), 2914 (s), 2857 (s), 2737 (w), 1593 (vs), 1488 (m), 1477 (s), 1440 (m), 1294 (m), 1256 (s), 1217 (w), 1178 (vs), 1147 (s), 1110 (m), 1048 (m), 1024 (m), 994 (s), 953 (w), 896 (m), 835 (s), 822 (vs), 786 (s), 688 (m), 640 (m).

$C_{28}H_{42}O_2Si_2$ (466.15) Calcd. C 72.04 H 9.07
Found C 69.58 H 8.84

$1,4\text{-}C_6H_4[OSiMe_2(HC_5Me_4)]_2$ (**6**): Yield 55%, m.p. 73°C. The *para*-derivative is a solid and is further purified by recrystallisation from pentane. – ^1H NMR ($CDCl_3$): $\delta = 0.04$ (s, $SiMe_2$), 1.81 (s, CH_3), 1.98 (s, CH_3), 3.14 (s, CH_3), 6.72 (s, Ph). – IR (cm^{-1}): $\tilde{\nu} =$ 3045 (w), 3731 (w), 1633 (w), 1501 (vs), 1301 (w), 1258 (s), 1249 (s), 1233 (vs), 1213 (s), 1121 (m), 1110 (m), 1097 (m), 1045 (m), 1026 (m), 986 (s), 953 (m), 910 (vs), 839 (s), 828 (s), 805 (s), 748 (w), 698 (w), 688 (w), 659 (m).

$C_{28}H_{42}O_2Si_2$ (466.15) Calcd. C 72.04 H 9.07
Found C 72.43 H 9.04

$1,3,5\text{-}C_6H_3[OSiMe_2(HC_5Me_4)]_3$ (**7**): Yield 45%. – ^1H NMR ($CDCl_3$): $\delta = 0.09$ (s, $SiMe_2$), 1.84 (s, CH_3), 2.00 (s, CH_3), 3.18 (br., CpH), 6.10 (s, Ph). – IR (cm^{-1}): $\tilde{\nu} = 2962$ (s), 2912 (s), 2856 (m), 2738 (w), 1590 (vs), 1442 (s), 1378 (w), 1298 (w), 1250 (s), 1216 (w), 1164 (vs), 1108 (m), 1028 (s), 984 (m), 952 (m), 890 (w), 822 (vs), 784 (s), 740 (w), 684 (w), 640 (m).

$C_{39}H_{61}O_3Si_3$ (662.2) Calcd. C 70.74 H 9.29
Found C 67.89 H 9.46

$C_6H_5OSiMe_2-(C_5H_4)M(CO)_3Me$ [M = Mo (**8**), W (**9**)]: To a stirred suspension of 0.046 g of NaH (20 mmol) in 25 ml of THF at 0°C are first added 0.216 g of $CpSiMe_2OPh$ (1.00 mmol), then after 30 min 0.391 g (M = W) or 0.303 g (M = Mo) of $(MeCN)_3M(CO)_3$ (1.00 mmol). The reaction mixture is warmed to room temp. and after 1 h 0.284 g of CH_3I (2.00 mmol) is added. After 1 hour the volatiles are removed in vacuo, and the residue is extracted with 25 ml of toluene. After filtration the toluene is removed in vacuo. The remaining yellow oil is purified by chromatography (hexane/toluene 2:1).

$C_6H_5OSiMe_2-(C_5H_4)Mo(CO)_3Me$ (**8**): Yield 0.283 g (69%) of yellow-green crystals, m.p. 53°C. – ^1H NMR ($CDCl_3$): $\delta = 0.39$ (s, $MoCH_3$), 0.49 (s, $SiMe_2$, $^3J_{SiH} = 6.9$ Hz), 5.24 („t", Cp, $J = 2.1$ Hz), 5.51 („t", Cp, $J = 2.1$ Hz), 6.72 (d, 2-ArH, $^3J = 7.4$ Hz), 6.90 (t, 4-ArH, $^3J = 7.4$ Hz), 7.13 („t", 3-ArH, $^3J = 7.4$ Hz). – IR (cm^{-1}): $\tilde{\nu}$(CO) = 2020, 1934.

$C_{17}H_{18}MoO_4Si$ (410.4) Calcd. C 50.76 H 4.42
Found C 50.51 H 4.68

$C_6H_5OSiMe_2-(C_5H_4)W(CO)_3Me$ (**9**): Yield 0.375 g (75%) of yellow crystals, m.p. 70°C. – ^1H NMR ($CDCl_3$): $\delta = 0.42$ (s, WCH_3, $^2J_{WH} = 3.7$ Hz), 0.50 (s, $SiMe_2$, $^2J_{SiH} = 6.8$ Hz), 5.25 („t", Cp, $J = 2.1$ Hz), 5.59 („t", Cp, $J = 2.1$ Hz), 6.82 (d, 2-ArH, $^3J =$ 8.5 Hz), 6.97 (t, 4-ArH, $^3J = 7.1$ Hz), 7.24 (m, 3,5-ArH). – IR (cm^{-1}): $\tilde{\nu}$(CO) = 2012, 1910.

$C_{17}H_{18}O_4SiW$ (498.3) Calcd. C 40.98 H 3.64
Found C 40.95 H 3.58

$1,4\text{-}C_6H_4[OSiMe_2-(C_5H_4)M(CO)_3Me]_2$ [M = Mo (**10**), W (**11**): To a stirred suspension of 0.096 g of NaH (2.00 mmol) in THF at 0°C are first added 0.177 g of $1,4\text{-}C_6H_4(OSiMe_2Cp)_2$ (0.50 mmol), then after 1 h 0.391 g (M = W) or 0.301 g (M = Mo) of $(CO)_3M(CH_3CN)_3$ (1.00 mmol). The reaction mixture is warmed to room temp. and after 1 h 0.284 g of CH_3I (2.00 mmol) is added. After another hour the volatiles are removed in vacuo, and the residue is extracted with 25 ml of toluene. After filtration the toluene is removed in vacuo. The remaining yellow oil is purified by chromatography (hexane/toluene 5:2).

$1,4\text{-}C_6H_4[OSiMe_2-(C_5H_4)Mo(CO)_3Me]_2$ (**10**): Yield 0.137 g (37%) of a pale-yellow powder, dec. > 110°C. – ^1H NMR ($CDCl_3$): $\delta = 0.35$ (s, $MoCH_3$), 0.44 (s, $SiMe_2$, $^2J_{SiH} = 6.7$ Hz), 5.18 („t", Cp, $J = 2.1$ Hz), 5.48 („t", Cp, $J = 2.1$ Hz), 6.64 (s, ArH). – IR (cm^{-1}): $\tilde{\nu}$(CO) = 2008, 1919.

$C_{28}H_{30}Mo_2O_8Si_2$ (742.6) Calcd. C 46.29 H 4.07
Found C 46.61 H 4.48

$1,4\text{-}C_6H_4[OSiMe_2-(C_5H_4)W(CO)_3Me]_2$ (**11**): Yield 0.188 g (41%), yellow crystals, m.p. 144°C. – ^1H NMR (C_6D_6): $\delta = 0.29$ (s, $SiMe_2$, $^2J_{SiH} = 6.9$ Hz), 0.46 (s, WCH_3, $^2J_{WH} = 3.8$ Hz), 4.55 („t", Cp, $J = 4.2$ Hz), 4.67 („t", Cp, $J = 4.3$ Hz), 6.66 (s, Ph). – IR (cm^{-1}): $\tilde{\nu}$(CO) = 1918, 2008.

$C_{28}H_{30}O_8Si_2W_2$ (918.4) Calcd. C 36.62 H 3.29
Found C 36.55 H 3.36

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[124/91]