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## Polycyclopentadienyls: synthesis of arylsilylcyclopentadienyl compounds and their $\eta^5$ -complexes with tungsten

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### Abstract

A general route to arylsilylcyclopentadienyl compounds starting from 1,4- $C_6H_4Br_2$ , 2,6- $C_5NH_3Br_2$  and 1,3,5- $C_6H_3Br_3$  is described. The aryl bromides were treated with  $Mg/ClSiMe_2H$  to give the aryl dimethylsilanes 1,4- $C_6H_4(SiMe_2H)_2$ , 2,6- $C_5NH_3(SiMe_2H)_2$ , and 1,3,5- $C_6H_3(SiMe_2H)_3$  which after reaction with  $Cl_2$  or  $Br_2$  yielded the aryl dimethylsilyl halides 1,4- $C_6H_4(SiMe_2Br)_2$ , 2,6- $C_5NH_3(SiMe_2Br)_2$ , 1,3,5- $C_6H_3(SiMe_2X)_3$  ( $X = Br$  or  $Cl$ ) in excellent yields. The halide can be replaced by various cyclopentadienides to give aryl dimethylsilylcyclopentadienes of the general type 1,4- $C_6H_4(SiMe_2Cp)_2$  and 1,3,5- $C_6H_3(SiMe_2Cp)_3$  ( $Cp = C_5H_5$  (**8,11**),  $C_5H_3(t-C_4H_9)_2$  (**9,12**),  $C_5HMe_4$  (**10,13**)). Compounds  $C_6H_5(SiMe_2(C_5H_5))$ , 1,4- $C_6H_4(SiMe_2(C_5H_5))_2$  (**8**) and 1,3,5- $C_6H_3(SiMe_2(C_5H_5))_3$  (**11**) were in turn treated with  $NaH$ ,  $(MeCN)_3W(CO)_3$ , and  $MeI$  to give the  $\eta^5$ -bound complexes  $C_6H_5(SiMe_2(C_5H_4)W(CO)_3Me)$  (**14**), 1,4- $C_6H_4(SiMe_2(C_5H_4)W(CO)_3Me)_2$  (**15**), 1,3,5- $C_6H_3(SiMe_2(C_5H_4)W(CO)_3Me)_3$  (**16**), which contain up to three half-sandwich units within one molecule.

### Introduction

Ever since the discovery of ferrocene [1], cyclopentadienyls [2] have been among the most important ligands in transition metal chemistry [3]. Recently more attention has been given to ligands that contain more than one cyclopentadiene unit [4]. Novel properties could be expected to result from the cooperation of several metals held in close proximity [5]. In the main three types of ligands containing two cyclopentadienyl (Cp) groups have been used, viz. fulvalene [5,6],  $CpCH_2Cp$  [7] and  $CpSiMe_2Cp$  [8]. Only a few metal complexes incorporating three cyclopentadienyl units are known [9,10]. Free ligands of this type are extremely rare [11]. In this paper I describe the synthesis of compounds containing two or

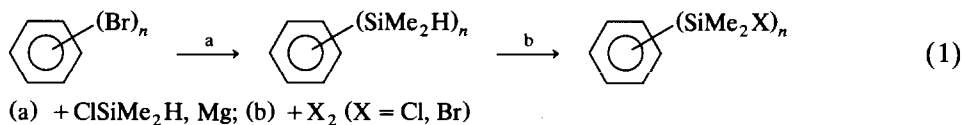
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three cyclopentadienyl moieties and their transformation into organometallic compounds with two or three half-sandwich units. Our objective is first to synthesize species containing several cyclopentadienyl units linked to a common backbone (the benzene ring) via chains of variable length [10] and then attach metal entities to the polyfunctional ligand. This approach should in principle be applicable to all metals that form stable metallocenes. An alternative approach would be to use cyclopentadienyl-centered reactivity to connect preformed metallocene units to an organic backbone. This route has been used [11] for compounds such as  $(C_5H_4Li)Mn(CO)_3$  and  $(C_5H_5)Fe(C_5H_4Li)$ , but is limited to only a few metal complexes. With cyclopentadienyl ligands other than  $C_5H_5$  the situation becomes more complicated as the reactive sites at the ring are less accessible and no longer equivalent.

## Results

For the synthesis of compounds containing several cyclopentadienyl groups linked to an aromatic backbone we chose arylsilyl halides as the connecting units. Although benzyl halides usually are well suited for nucleophilic substitution, substituted cyclopentadienes (especially those with sterically demanding substituents) form anions of high basicity and low nucleophilicity that are not well suited for C–C bond formation [13]. The reaction of  $NaC_5H_5$  with benzyl halides proceeds smoothly, but the products are rather unstable with respect to Diels–Alder dimerization [14]. The greater bulk of the  $PhSiMe_2$  group compared with  $PhCH_2$  leads to a decrease in the rate of this unwanted side reaction.

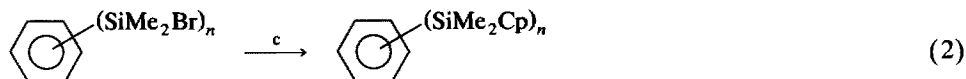
The arylsilyl halide precursors were prepared as outlined in eq. 1.



Following a general procedure by Fink [15], the aryl bromides 1,4- $C_6H_4Br_2$ , 2,6- $C_5NH_3Br_2$  and 1,3,5- $C_6H_3Br_3$  were converted into the corresponding arylsilanes 1,4- $C_6H_4(SiMe_2H)_2$ , 2,6- $C_5NH_3(SiMe_2H)_2$  and 1,3,5- $C_6H_3(SiMe_2H)_3$  by reaction with  $ClSiMe_2H/Mg$ . The compounds 2,6-bis(dimethylsilyl)pyridine and 1,3,5-tris(dimethylsilyl)benzene were obtained in yields of 85 and 75%, respectively. Arylsilanes of this type can be readily converted into the corresponding arylsilyl bromides or chlorides. For this purpose the arylsilanes were dissolved in  $CCl_4$ , cooled to  $0^\circ C$  and treated with a solution of elemental bromine in  $CCl_4$  or with chlorine gas; the reactions gave almost quantitative yields of the corresponding halosilanes, showing that no significant silicon–carbon bond cleavage had occurred. However, in the case of 2,6-bis(dimethylsilyl)pyridine it was necessary to carry out the reaction in the presence of a fivefold excess of pyridine, to prevent the precipitation of the silane as the insoluble hydrobromide. Halosilanes in amounts of 100 g or more are readily available by this route and are ideal starting materials for the synthesis of molecules containing several cyclopentadienyl groups.

In our initial attempts we treated  $NaC_5H_5$  with 1,4- $C_6H_4(SiMe_2Cl)_2$  and obtained the desired product 1,4- $C_6H_4(SiMe_2(C_5H_5))_2$  (**8**), but the yields (*ca.* 15%) were unsatisfactory. However, when silyl bromides were used instead of the

silyl chlorides and  $\text{NaC}_5\text{H}_5$  was replaced by  $\text{KC}_5\text{H}_5$ , there was a substantial increase in the yields of the silylcyclopentadienes (e.g. that of **8** was 75%). A solution of the arylbromosilane in THF was reacted with  $\text{KC}_5\text{H}_5$  at room temperature, and in 3 h the reaction was complete (eq. 2).



(c) +  $\text{KCp}$  (Cp =  $\text{C}_5\text{H}_5$ ,  $\text{C}_5\text{H}_3(\text{t-C}_4\text{H}_9)_2$ ,  $\text{C}_5\text{HMe}_4$ )

Cp =	$\text{C}_5\text{H}_5$	$\text{C}_5\text{H}_3(\text{t-C}_4\text{H}_9)_2$	$\text{C}_5\text{HMe}_4$
1,4- $\text{C}_6\text{H}_4(\text{SiMe}_2\text{Cp})_2$	<b>8</b>	<b>9</b>	<b>10</b>
1,3,5- $\text{C}_6\text{H}_3(\text{SiMe}_2\text{Cp})_3$	<b>11</b>	<b>12</b>	<b>13</b>

Compounds **8** and **11** are only moderately stable at room temperature and are best stored at  $-30^\circ\text{C}$ .

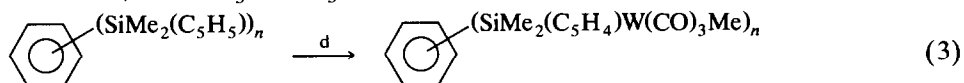
A similar procedure was used for Cp = 1,3-( $^t\text{Bu}$ ) $_2\text{C}_5\text{H}_3$ ,  $\text{HC}_5\text{Me}_4$ ; in these cases the relevant potassium salts were allowed to react overnight with the bromosilanes in refluxing THF (eq. 2). Compounds containing two or three cyclopentadienyl groups are produced in good yields in this way. The workup is very simple insofar as the volatiles are removed in vacuum and the products extracted from the residue with pentane. Evaporation of the pentane extracts gives reasonably pure products, which may be used for subsequent reactions without further purification. The residue containing the 1,3,5-substituted species usually are non-volatile, highly lipophilic, oily substances, which have a low tendency to crystallize. The *para*-disubstituted species form crystalline compounds and may be purified by recrystallization from pentane, but we did this only to obtain samples for elemental analysis because it results in a substantial loss of product. To ensure a successful conversion into the cyclopentadienyl-substituted arylsilanes it is therefore imperative to use starting materials of high purity, since only then can the extracted poly-cyclopentadienyl products be used without further purification.

It is well known that cyclopentadienylsilanes display fluxional behavior in the NMR spectrum [16]. Metallotropic (degenerate) and prototropic shifts (non-degenerate) give rise to interconversion of three different isomers (one Si-allyl, two Si-vinyl). The energy barrier for the prototropic shift is in the range (5–35 kcal/mol) appropriate for observations by temperature variable NMR spectroscopy. Coalescence leads to broadening of several resonances in the room temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the silylcyclopentadienyl compounds described here. This effect and the presence of three isomers complicate the assignment of the signals especially in the  $^{13}\text{C}$  NMR spectrum. Recording the spectra in the region of slow or fast exchange removes the problem of line broadening but is impractical for routine work. In the case of Cp =  $\text{C}_5\text{H}_5$  (**8**, **11**) the room temperature resonances ( $^1\text{H}$ , 200 MHz) of the vinylic and allylic protons are broadened ( $\nu_{1/2} = 20\text{--}25$  Hz). From the temperature variable  $^1\text{H}$  NMR spectra of **8** the coalescence temperature was found to be 340 K, corresponding to an energy barrier for the hydrogen shift in of  $72.4 \pm 2$  kJ/mol [17]. For Cp = 1,3-( $^t\text{Bu}$ ) $_2\text{C}_5\text{H}_3$  (**9**, **12**) the room temperature signals of the two protons in the 4,5-position of 1,3-di-*t*-butylcyclopentadiene are broadened beyond recognition.

Recording of the spectra of **8** and **11** at 373 K in the fast exchange region revealed two signals at  $\delta = 4.65$  ppm corresponding to the averaged “missing” 4,5-protons.

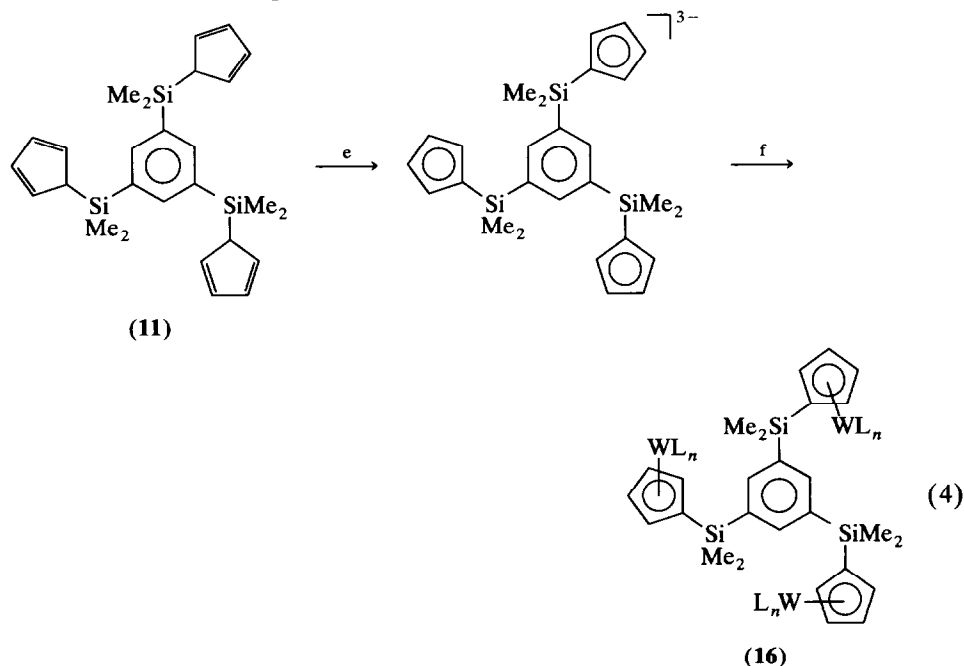
The flexibility of the use of arylsilyl bromides as starting materials is demonstrated by the fact that the cyclopentadienyl system is not limited to  $\text{Cp} = \text{C}_5\text{H}_5$ . So far we have tried the Cp-nucleophiles  $(1,3\text{-}^i\text{Bu})_2\text{C}_5\text{H}_3$  and  $\text{HC}_5(\text{CH}_3)_4$ , and in the case of **5** and **7** compounds containing two or three cyclopentadienyl groups are produced. The analogous reaction of **6** with  $\text{KC}_5\text{H}_5$  gave only minute quantities of the expected product. We expect that this type of reaction will be applicable to other cyclopentadienide systems.

After the successful synthesis of a number of polycyclopentadienyl compounds we decided to see whether these polyfunctional ligands could be used for the synthesis of species with several metals bound in a  $\eta^5$ -fashion. Thus we investigated the reactions of the mono-, bis- and tris-cyclopentadienyl compounds  $\text{C}_6\text{H}_5\text{SiMe}_2(\text{C}_5\text{H}_5)$ ,  $1,4\text{-C}_6\text{H}_4(\text{SiMe}_2(\text{C}_5\text{H}_5))_2$  and  $1,3,5\text{-C}_6\text{H}_3(\text{SiMe}_2(\text{C}_5\text{H}_5))_3$  with  $\text{NaH}$ ,  $(\text{MeCN})_3\text{W}(\text{CO})_3$  and  $\text{MeI}$  (eq. 3).



(d)  $+ 2n \text{ NaH}$ ;  $+ n (\text{MeCN})_3\text{W}(\text{CO})_3$ ;  $+ 2n \text{ MeI}$   
 ( $n = 1$ : **14**;  $n = 2$ : **15**;  $n = 3$ : **16**)

These reactions may be carried out in a one-pot manner. The pentane extracts of the arylsilylcyclopentadienes are dissolved in THF and a two-fold excess of  $\text{NaH}$  is added. After hydrogen evolution has ceased,  $(\text{MeCN})_3\text{W}(\text{CO})_3$  is added to the suspension to form the tungstate, which is then quenched with an excess of  $\text{MeI}$ . In all three cases, the reactions proceed under mild conditions to give good yields of the half-sandwich complexes.



(e)  $+ 6 \text{ NaH}$ ; (f)  $+ 3 (\text{CO})_3\text{W}(\text{CH}_3\text{CN})_3$ ,  $+ 6 \text{ MeI}$  ( $\text{WL}_n = \text{W}(\text{CO})_3\text{Me}$ )

Even compound **11** is triply deprotonated without difficulties. After triple addition of the  $W(CO)_3$  fragment and treatment with MeI, compound **16** is isolated; the 49% yield is remarkable since nine bonds are formed in the course of this one-pot reaction. Surprisingly we have never isolated metal complexes resulting from incomplete deprotonation of **11**. Compounds **14**, **15** and **16** are yellow, air-stable solids, which were purified chromatographically. Their spectroscopic data and elemental analyses are consistent with the above formulation.

Future research will be directed towards incorporating several different metals, with a view to observing metal–metal interactions and perhaps cooperative effects.

## Experimental

All reactions were carried out under argon using Schlenk techniques. Commercially available solvents and reagents were purified by standard methods [18]. Chromatography: silica MN 60. NMR: recorded at 300 K on a Bruker AC 200F ( $^1H$  NMR 200,  $^{13}C$  NMR 50 MHz) or Varian Unity 300 ( $^1H$  NMR 300,  $^{13}C$  NMR 75,  $^{29}Si$  NMR 59.6 MHz).  $^1H$  NMR spectra were recorded in  $CDCl_3$  ( $CHCl_3$  7.26 ppm),  $^{13}C$  NMR in  $CDCl_3$  (77.0 ppm) or  $C_6D_6$  (128.0 ppm) and  $^{29}Si$  NMR ( $C_6D_6$ , TMS (0.0 ppm), Cr(acac) $_3$  relaxation reagent). Elemental analysis: Mikroanalytisches Laboratorium der Chemischen Laboratorien Universität Freiburg. IR: Bruker IFS 25, Nujol mulls between NaCl plates. Starting materials:  $HC_5H_3(t-C_4H_9)_2$  [19],  $HC_5HMe_4$  [20],  $(MeCN)_3W(CO)_3$  [21], KCp (Cp =  $C_5H_5$ ,  $C_5HMe_4$ ,  $C_5H_3(t-C_4H_9)_2$ ) prepared from CpH and KH in THF.  $PhSiMe_2(C_5H_5)$  [22] was prepared from KCp and  $PhSiMe_2Br$ . The procedure described by Fink [15] for the synthesis of 1,2-bis-(dimethylsilyl)-benzene was adapted for the preparation of the silanes described here. As an example the preparation of  $1,3,5-C_6H_3(SiMe_2H)_3$  is described in detail. A similar procedure was used for  $1,4-C_6H_4(SiMe_2H)_2$  and  $2,6-C_5NH_3(SiMe_2H)_2$ .

### Synthesis of $1,3,5-C_6H_3(SiMe_2H)_3$

To a mixture of  $Me_2SiClH$  (47.3 g, 0.5 mol) and magnesium (12.2 g, 0.5 mol) in 150 ml of THF was added a solution of  $1,3,5-C_6H_3Br_3$  (31.5 g, 0.1 mol) in 100 ml of THF. The rate of addition was adjusted to maintain a gentle reflux. The mixture was subsequently heated under reflux for 3 h. The volatiles were removed under vacuum and the product extracted from the solid residue three times with 200 ml of hexane. The solvent was removed under reduced pressure and the product distilled in vacuum.

$1,4-C_6H_4(SiMe_2H)_2$  (**1**): b.p.  $95^\circ C/10$  Torr; yield: 85%.  $^1H$  NMR:  $\delta$  0.34 (d,  $SiMe_2$ ,  $^3J = 3.7$  Hz), 4.42 (hept.,  $^3J = 3.7$  Hz, SiH), 7.54 (s, ArH) ppm.

$2,6-C_5H_3N(SiMe_2H)_2$  (**2**): b.p.  $110^\circ C/10$  Torr; yield: 61%.  $^1H$  NMR:  $\delta$  0.40 (d,  $^3J = 3.7$  Hz,  $SiMe_2$ ), 4.47 (hept.,  $^3J = 3.7$  Hz,  $SiMe_2$ ), 7.46 (s, ArH) ppm.

$1,3,5-C_6H_3(SiMe_2H)_3$  (**3**): b.p.  $60^\circ C/0.1$  Torr; yield: 75%.  $^1H$  NMR:  $\delta$  0.41 (d,  $^3J = 3.7$  Hz,  $SiMe_2$ ), 4.49 (hept.,  $^3J = 3.7$  Hz, SiH), 7.78 (s, ArH);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  -3.69 ( $SiMe_2$ ), 135.97 (ArSi), 140.57 (ArH) ppm.

### General procedure for the reaction $Ar(SiMe_2H)_n \rightarrow Ar(SiMe_2Cl)_n$

Chlorine gas was bubbled through an ice-cooled stirred solution of 20 g of the silane in 100 ml of  $CCl_4$  until a yellow color persisted (ca. 1 h). Stirring was

continued for another 30 min, then  $\text{Cl}_2$ ,  $\text{HCl}$  and  $\text{CCl}_4$  were removed under vacuum. (The remaining pale yellow chlorosilanes are usually pure enough to be used without further purification, but may be distilled to give colorless materials.) The yield of the distilled products are > 90%.

1,3,5- $\text{C}_6\text{H}_3(\text{SiMe}_2\text{Cl})_3$  (**4**): b.p.  $110^\circ\text{C}/0.1$  Torr.  $^1\text{H}$  NMR:  $\delta$  0.71 (s,  $\text{SiMe}_2$ ), 7.93 (s, ArH) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.87 ( $\text{SiMe}_2$ ), 136.2 (s, ArSi), 139.7 (s, ArH) ppm.  $^{29}\text{Si}$  NMR:  $\delta$  20.8 ppm.

*General procedure for the reaction  $\text{Ar}(\text{SiMe}_2\text{H})_n \rightarrow \text{Ar}(\text{SiMe}_2\text{Br})_n$*

A 25% solution of  $\text{Br}_2$  (1.1 equiv. of  $\text{Br}_2$  per SiH group) in  $\text{CCl}_4$  was added dropwise to an ice-cooled, stirred mixture of 20 g of the silane in 100 ml  $\text{CCl}_4$ . Stirring was continued for another 30 min, then  $\text{HBr}$ ,  $\text{Br}_2$  and  $\text{CCl}_4$  were removed under vacuum. The bromosilanes were produced in almost quantitative yields. Compounds **5** and **6** were distilled; **5** is a solid, but **6** and **7** form highly viscous oils or waxy solids.

1,4- $\text{C}_6\text{H}_4(\text{SiMe}_2\text{Br})_2$  (**5**): b.p.  $130^\circ\text{C}/0.1$  Torr.  $^1\text{H}$  NMR:  $\delta$  0.83 (s,  $\text{SiMe}_2$ ), 7.67 (s, ArH) ppm.

2,6- $\text{C}_5\text{NH}_3(\text{SiMe}_2\text{Br})_2$  (**6**): b.p.  $130^\circ\text{C}/0.1$  Torr.  $^1\text{H}$  NMR:  $\delta$  0.77 (s,  $\text{SiMe}_2$ ), 7.56 (t,  $^3J = 7.5$  Hz, ArH), 7.67 (d,  $^3J = 7.5$  Hz, ArH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.27 ( $\text{SiMe}_2$ ), 128.88 (3,5-ArH), 133.04 (4-ArH), 162.97 (2,6-Ar) ppm.

1,3,5- $\text{C}_6\text{H}_3(\text{SiMe}_2\text{Br})_3$  (**7**):  $^1\text{H}$  NMR:  $\delta$  0.87 (s,  $\text{SiMe}_2$ ), 7.95 (s, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.78 ( $\text{SiMe}_2$ ), 132.68 (ArH), 138.28 (ArSi) ppm.

*General procedure for the reaction  $\text{Ar}(\text{SiMe}_2\text{Br})_n \rightarrow \text{Ar}(\text{SiMe}_2\text{Cp})_n$*

A solution of  $\text{Ar}(\text{SiMe}_2\text{Br})_n$  (50 mmol) in 200 ml of THF was added to an ice-cooled stirred suspension of  $\text{KCp}$  (1.1 equiv. per  $\text{SiMe}_2\text{Br}$  group) in 200 ml of THF. The mixture was allowed to warm to room temperature and stirred for 3 h. The volatiles were evaporated under vacuum, hexane (200 ml) was added, and the suspension was filtered through silica. After removal of the hexane under vacuum the colorless  $\text{Ar}(\text{SiMe}_2\text{Cp})_n$  compounds remained and were used without further purification.

The 1,4-substituted compounds are solids, and may be recrystallized from pentane to give samples of analytical purity. The 1,3,5-substituted compounds form highly viscous oils. (The yields given refer to the crude products)

1,4- $\text{C}_6\text{H}_4(\text{SiMe}_2(\text{C}_5\text{H}_5))_2$  (**8**): yield: 76%.  $^1\text{H}$  NMR:  $\delta$  0.20 (s,  $\text{SiMe}_2$ ), 3.64 (br,  $\nu_{1/2} = 25$  Hz, CHSi), 6.64 (br,  $\nu_{1/2} = 20$  Hz,  $\text{C}_5\text{H}_5$ ), 7.58 (s, ArH) ppm.  $^{29}\text{Si}$  NMR:  $\delta$  -3.4 ppm. Analysis Found: C, 74.20; H, 8.19.  $\text{C}_{20}\text{H}_{26}\text{Si}_2$  (322.60) calc.: C, 74.46; H, 8.12%.

1,4- $\text{C}_6\text{H}_4(\text{SiMe}_2(\text{C}_5\text{H}_3(\text{t-Bu})_2))_2$  (**9**): yield: 73%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 K):  $\delta$  0.25 (s,  $\text{SiMe}_2$ ), 1.13 (s, t- $\text{C}_4\text{H}_9$ ), 6.39 (s, CH), 7.53 (s, ArH) ppm.  $^1\text{H}$  NMR (toluene- $d_8$ , 373 K):  $\delta$  0.24 (s,  $\text{SiMe}_2$ ), 1.15 (s, t- $\text{C}_4\text{H}_9$ ), 4.64 (br,  $\nu_{1/2} = 10$  Hz,  $2 \times \text{CH}$ ), 6.43 (s, CH), 7.41 (s, ArH) ppm.  $^{29}\text{Si}$  NMR:  $\delta$  -4.9 ppm. Analysis Found: C, 78.67; H, 10.42.  $\text{C}_{36}\text{H}_{58}\text{Si}_2$  (547.03) calc.: C, 79.04; H, 10.69%.

1,4- $\text{C}_6\text{H}_4(\text{SiMe}_2(\text{HC}_5\text{Me}_4))_2$  (**10**): yield: 49%.  $^1\text{H}$  NMR:  $\delta$  0.18 (s,  $\text{SiMe}_2$ ), 1.71 (s, CpMe), 1.75 (s, CpMe), 3.07 (br, CpH), 7.42 (s, ArH) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -3.89 ( $\text{SiMe}_2$ ), 11.31 (Me), 14.66 (Me), 54.75 (CHSi), 132.86, 133.15 (ArH), 135.94, 139.80 ppm.  $^{29}\text{Si}$  NMR:  $\delta$  -2.9 ppm. Analysis Found: C, 76.45; H, 9.59.  $\text{C}_{28}\text{H}_{42}\text{Si}_2$  (434.82) calc.: C, 77.35; H, 9.74%.

1,3,5-C<sub>6</sub>H<sub>3</sub>(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>))<sub>3</sub> (**11**): yield: 65%. <sup>1</sup>H NMR: δ 0.22 (s, SiMe<sub>2</sub>), 3.1 (br, CH<sub>2</sub>), 3.8 (br, allyl-CH), 6.65 (br, vinyl-CH), 7.69 (s, ArH) ppm. <sup>29</sup>Si NMR: δ -3.0 ppm.

1,3,5-C<sub>6</sub>H<sub>3</sub>(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>(<sup>t</sup>Bu)<sub>2</sub>))<sub>3</sub> (**12**): yield: 55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K): δ 0.22 (s, SiMe<sub>2</sub>), 1.12 (s, t-C<sub>4</sub>H<sub>9</sub>), 6.39 (s, CH), 7.72 (s, ArH) ppm. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 373 K): δ 0.25 (s, SiMe<sub>2</sub>), 1.15 (s, t-C<sub>4</sub>H<sub>9</sub>), 4.65 (br, ν<sub>1/2</sub> = 10 Hz, 2 × CH), 6.45 (s, CH), 7.50 (s, ArH) ppm. <sup>29</sup>Si NMR: δ -4.0 ppm. Analysis Found: C, 75.58; H, 10.54. C<sub>36</sub>H<sub>58</sub>Si<sub>3</sub> (575.12) calc.: C, 75.18; H, 10.17%.

1,3,5-C<sub>6</sub>H<sub>3</sub>(SiMe<sub>2</sub>(HC<sub>5</sub>Me<sub>4</sub>))<sub>3</sub> (**13**): yield: 37%. <sup>1</sup>H NMR: δ 0.22 (s, SiMe<sub>2</sub>), 1.77 (s, CpMe), 3.09 (br, CpH), 7.54 (s, ArH) ppm. <sup>29</sup>Si NMR: δ -3.1 ppm.

*General procedure for the reaction Ar(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>))<sub>n</sub> → Ar(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>))W(CO)<sub>3</sub>Me<sub>n</sub>*

Ar(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>))<sub>n</sub> (1 mmol) was added to a suspension of NaH (two equiv. of NaH per SiCp unit) in THF at 0°C. After 30 min stirring (CO)<sub>3</sub>W(CH<sub>3</sub>CN)<sub>3</sub> (one equiv. of tungsten complex per SiCp unit) was added, and then after 1 h at room temperature, MeI (two equiv. per SiCp unit) was added. After 1 h the volatiles were evaporated and the solid residue extracted with toluene. The toluene was removed in vacuo and the solid remaining purified by chromatography (toluene/hexane = 2/1).

C<sub>6</sub>H<sub>5</sub>SiMe<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)W(CO)<sub>3</sub>Me (**14**): NaH (96 mg, 2 mmol), C<sub>6</sub>H<sub>5</sub>(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)) (200 mg, 1 mmol), (CO)<sub>3</sub>W(CH<sub>3</sub>CN)<sub>3</sub> (391 mg, 1 mmol), MeI (284 mg, 2 mmol). Yield: 370 mg (77%) yellow crystals. Anal. Found: C, 42.70; H, 3.90. C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>SiW (482.27) calc.: C, 42.34; H, 3.76%. <sup>1</sup>H NMR: δ 0.34 (s, WMe), 0.52 (s, SiMe<sub>2</sub>), 5.16 (‘t’, 2.1 Hz, C<sub>5</sub>H<sub>4</sub>), 5.54 (‘t’, 2.1 Hz, C<sub>5</sub>H<sub>4</sub>), 7.33–7.39 (m, ArH), 7.49–7.53 (m, ArH) ppm. IR (cm<sup>-1</sup>): ν(CO) 1910, 2011.

1,4-C<sub>6</sub>H<sub>4</sub>(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)W(CO)<sub>3</sub>Me)<sub>2</sub> (**15**): NaH (96 mg, 2 mmol), *p*-C<sub>6</sub>H<sub>4</sub>(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>))<sub>2</sub> (161 mg, 0.5 mmol), (CO)<sub>3</sub>W(CH<sub>3</sub>CN)<sub>3</sub> (391 mg, 1 mmol), MeI (284 mg, 2 mmol). Yield: 465 mg (52%) yellow crystals. Anal. Found: C, 38.57; H, 3.48. C<sub>26</sub>H<sub>30</sub>O<sub>6</sub>Si<sub>2</sub>W<sub>2</sub> (892.47) calc.: C, 37.68; H, 3.39%. <sup>1</sup>H NMR: δ 0.37 (s, WCH<sub>3</sub>), 0.54 (s, SiMe<sub>2</sub>), 5.19 (‘t’, 2.2 Hz, C<sub>5</sub>H<sub>4</sub>), 5.58 (‘t’, 2.2 Hz, C<sub>5</sub>H<sub>4</sub>), 7.55 (s, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -34.47 (WCH<sub>3</sub>), -1.94 (SiMe<sub>2</sub>), 95.82 (C<sub>5</sub>H<sub>4</sub>), 96.49 (C<sub>5</sub>H<sub>4</sub>), 96.99 (CHSi), 133.16 (ArH), 138.84 (ArSi), 216.12 (1,3-CO), 229.33 (2-CO) ppm. <sup>29</sup>Si NMR: δ -7.8 ppm. IR (cm<sup>-1</sup>): ν(CO) 1912, 2008.

1,3,5-C<sub>6</sub>H<sub>3</sub>(SiMe<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)W(CO)<sub>3</sub>Me)<sub>3</sub> (**16**): NaH (48 mg, 2 mmol), 1,3,5-C<sub>6</sub>H<sub>3</sub>(SiMe<sub>2</sub>Cp)<sub>3</sub> (156 mg, 0.35 mmol), (MeCN)<sub>3</sub>W(CO)<sub>3</sub> (411 mg, 1.05 mmol), MeI (284 mg, 2 mmol). Yield: 220 mg (49%) yellow powder. Anal. Found: C, 36.90; H, 3.19. C<sub>39</sub>H<sub>42</sub>O<sub>9</sub>Si<sub>3</sub>W<sub>3</sub> (1290.6) calc.: C, 36.30; H, 3.28%. <sup>1</sup>H NMR: δ 0.34 (s, WCH<sub>3</sub>), 0.55 (s, SiCH<sub>3</sub>), 5.15 (‘t’, 2.1 Hz, C<sub>5</sub>H<sub>4</sub>), 5.58 (‘t’, 2.1 Hz, C<sub>5</sub>H<sub>4</sub>), 7.75 (s, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -34.44 (WMe), -1.82 (SiMe<sub>2</sub>), 95.63 (C<sub>5</sub>H<sub>4</sub>), 96.63 (C<sub>5</sub>H<sub>4</sub>), 97.11 (CHSi), 135.97 (ArH), 140.18 (ArSi), 216.13 (1,3-CO), 229.29 (2-CO) ppm. <sup>29</sup>Si-NMR: δ -8.1. IR (cm<sup>-1</sup>): ν(CO) 1912, 2007.

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