

Group 4 Metallocene Complexes of Tris(trimethylsilyl)silylacetylene and Related Alkynes

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Oligosilyl-substituted alkyne complexes of group 4 metallocenes have been prepared by reaction of group 4 metallocene dichlorides with magnesium in the presence of the respective alkyne. Depending on the alkyne substitution pattern, either metallacyclopentadienes or metallocene alkyne complexes were formed. In order to suppress the oxidative coupling process, PMe_3 was added to obtain the metallocene alkyne complex base adducts. The reaction of 1,4-bis[tris(trimethylsilyl)silyl]butadiyne with zirconocene caused the formation of a 1,4-bis[tris(trimethylsilyl)silyl]-substituted zirconacyclocumulene. Reactions of zirconacyclopentadienes with iodine proceeded to the expected 1,4-diiodobuta-1,3-dienes.

Introduction

Over the last years the chemistry of group 4 metallocenes has experienced tremendous progress.¹ Much of this advancement was stimulated by studies related to novel Ziegler–Natta catalysts.² Besides the development of polymerization chemistry also much fundamental metallocene alkyne complex chemistry has been explored during this time. By the reaction of zirconocene dichloride with 2 equiv of butyl lithium Negishi established the reagent that now bears his name.³ The weakly coordinating butene ligand allowed the development of the rich chemistry of the zirconocene fragment. With the introduction of bis(trimethylsilyl)acetylene (BTMSA) group 4 metallocenes recently Rosenthal has also advanced to a leading position in this area. With these compounds many exciting stoichiometric and catalytic reactions of titano- and zirconocene chemistry have been studied.⁴

Our interest in Rosenthal's chemistry has been raised by a report about Zr–Si–H interaction in zirconocene complexes of hydrosilyl-substituted alkynes.⁵ While most of the bis(trimethylsilyl)acetylene group 4 metallocene chemistry was described for titanium and zirconium, recently the field was

extended also to hafnium complexes.⁶ In this connection an exciting Si–C activation process has been found that points to some differences in the chemical behavior of zirconium and hafnium.⁷

During the past few years we have prepared several examples of oligosilylalkynes, mainly with the intention to utilize them for the synthesis of different silyl anions.⁸ In a recent paper we have reported first results on the coordination behavior of these oligosilylalkynes to dicobalt hexacarbonyl clusters.⁹ The most interesting property of the obtained compounds was a strongly enhanced reactivity of Si–Si bonds in the coordination sphere of the dicobalt unit.

Encouraged by this study and the above-mentioned interaction of zirconocene with the Si–H moiety attached to an alkyne⁵ as well as by the recent example of hafnium Si–C activation⁷ we decided to extend our research to the chemistry of group 4 metallocene complexes of oligosilylalkynes.

Results and Discussion

Tris(trimethylsilyl)silylalkyne Complexes. As has been pointed out, group 4 metallocenes show a rich chemistry with different alkynes. However, while numerous examples of alkynes with different functional groups have been complexed to titanocene and zirconocene, almost no examples containing Si–Si bonds are known.¹⁰ Initial attempts to react bis[tris(trimethylsilyl)silyl]acetylene⁸ with Cp_2MCl_2 (M = Ti, Zr) in the presence of magnesium did not show any sign of the expected

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(1) For an excellent compilation of recent group 4 metallocene chemistry see: *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002.

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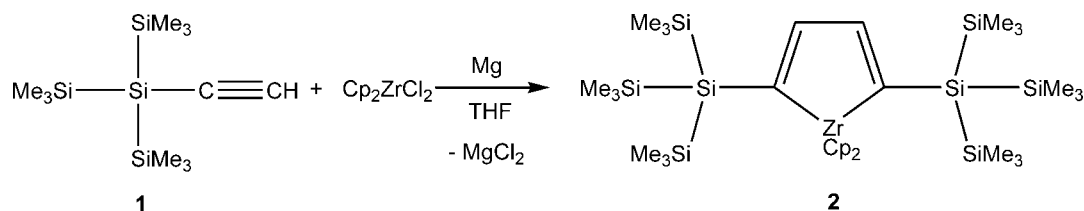
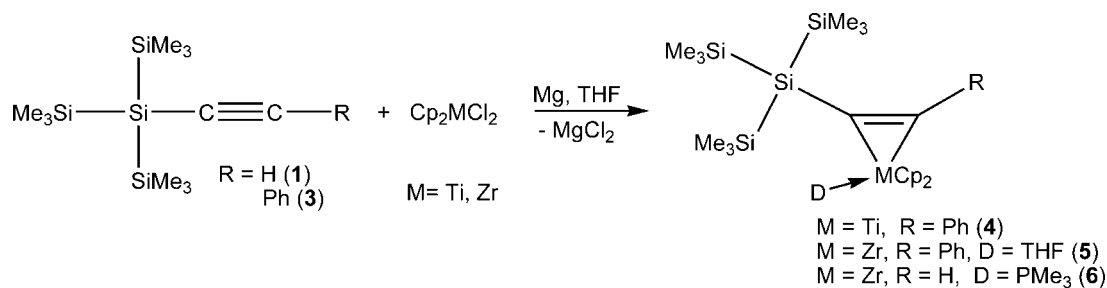
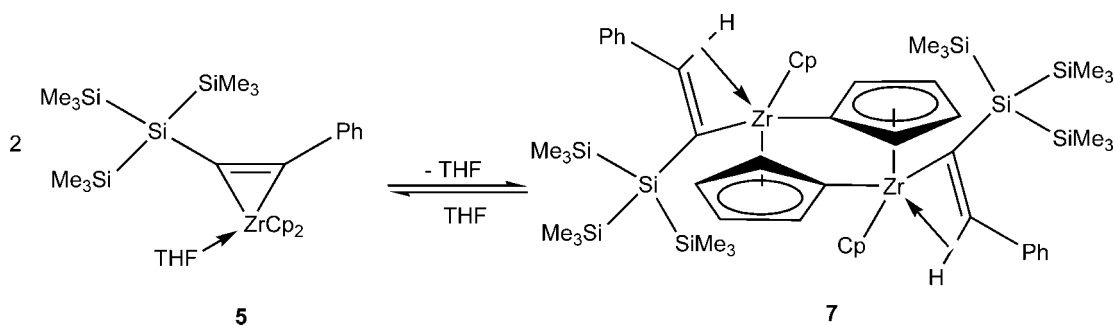
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Scheme 1. Reaction of Tris(trimethylsilyl)silylalkyne 1 with Zirconocene Dichloride and Magnesium**Scheme 2. Formation of Group 4 Metallocene Tris(trimethylsilyl)silylalkynyl Complexes****Scheme 3. Reversible Loss of THF Leading to a Dinuclear Zirconocene Vinyl Complex**

adduct. Also efforts to react $\text{Cp}_2\text{Ti}(\text{BTMSA})^{11}$ or $\text{Cp}_2\text{Zr}(\text{BTMSA}) \cdot \text{THF}^{12}$ with $(\text{Me}_3\text{Si})_3\text{SiCCSi}(\text{SiMe}_3)_3$ did not lead to the desired alkyne exchange. Similarly to the situation with the dicobalt complexes,⁹ the reason for this failure was thought to be the high steric demand of the two bulky tris(trimethylsilyl)silyl groups. In order to determine the spatial requirements of the system, we next investigated the reactivity of the tris(trimethylsilyl)silyl-monosubstituted alkyne (**1**). Reaction of **1** with Cp_2TiCl_2 and magnesium could indeed be observed but gave a mixture of two compounds, which we could not separate. On the basis of NMR spectroscopic analysis it can be assumed that the mixture consists of the alkyne complex and the respective metallacyclopentadiene. Also the possibility of formation of a vinylidene complex cannot be ruled out completely, while formation of compounds containing the structural unit $\text{TiCCSi}(\text{SiMe}_3)_3$ ¹³ can be ruled out on the basis of the spectroscopic analysis and independent synthesis. Repeating the experiment with the analogous zirconocene system led to formation of the respective zirconacyclopentadiene (**2**) exclusively (Scheme 1). The reason for the preference for the

coupling product **2** even with only one stoichiometric equivalent of alkyne present seems to be the higher reactivity of the intermediately formed alkyne complex toward the alkyne compared to the rate of reduction of the metallocene dichloride.

In order to avoid formation of the coupling product and to obtain the zirconocene alkyne complex of **1**, the reaction was carried out in the presence of trimethylphosphane. Blocking the coordination site thus led to the selective formation of the PMe_3 adduct¹⁴ of the desired complex (**6**) (Scheme 2).

The formation of complexes of alkynes with tris(trimethylsilyl)silyl and phenyl substituents proceeded with both systems to the expected complexes **4** and **5** (Scheme 2). In accordance with Rosenthal's results¹² on BTMSA the zirconocene compound **5** was obtained as the THF adduct.

Base adducts of zirconocene alkyne complexes can undergo the reversible loss of the Lewis base. In order to avoid coordinative unsaturation, oxidative addition into a neighboring Cp-H takes place. This way a dinuclear compound is formed.¹² Addition of a base leads to the reversal of the reaction. For the case of **5** we encountered this reactivity pattern. This was somewhat surprising, as we expected that oxidative addition of the relatively weak Si-Si bond would be a possible alternative to C-H activation. Nevertheless, the dinuclear C-H addition product **7** was observed exclusively (Scheme 3).

In order to check also for the formation of related germylalkynyl complexes, the reaction of the tris(trimethylsilyl)germyl

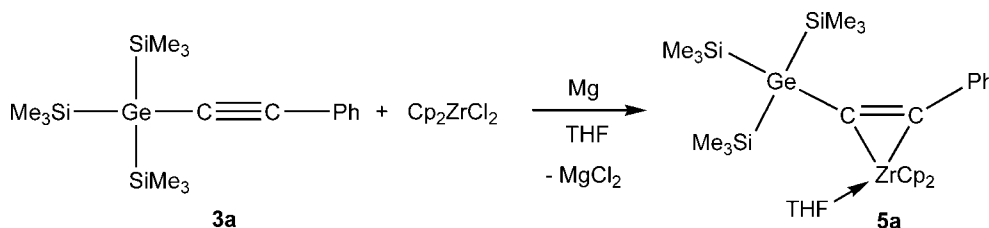
(11) (a) Burlakov, V. V.; Rosenthal, U.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *Metalloorg. Khim.* **1988**, *1*, 953-954. (b) Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Shur, V. B.; Vol'pin, M. E.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1994**, *476*, 197-206.

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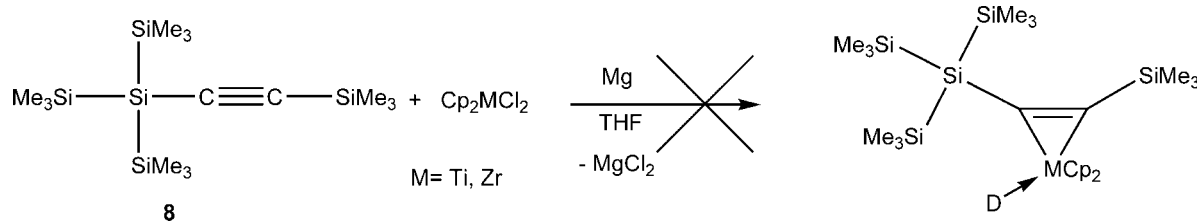
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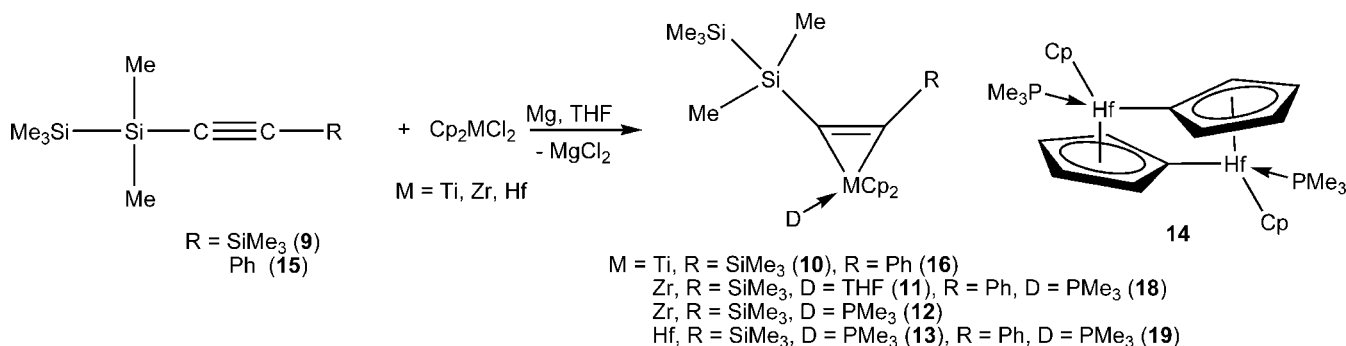
Scheme 4. Formation of a Tris(trimethylsilyl)germylalkyne Zirconocene Complex



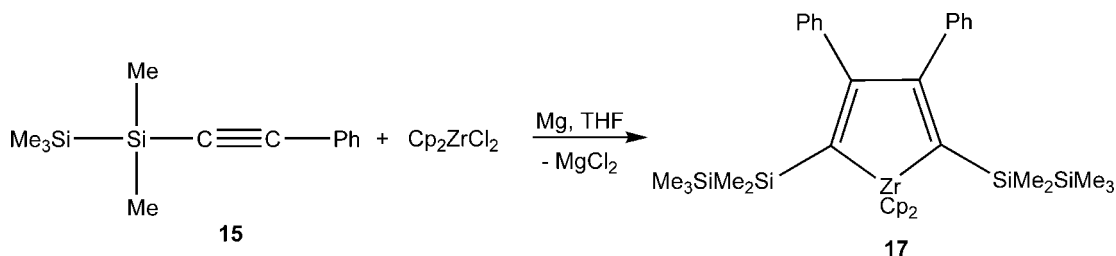
Scheme 5. No Complex Formation was Observed with Tris(trimethylsilyl)silyl(trimethylsilyl)acetylene (8)



Scheme 6. Complex Formation with Pentamethyldisilanyl-Substituted Alkynes 9 and 15



Scheme 7. Formation of Zirconacyclopentadiene 17



analogue (**3a**) of **3** was carried out with zirconocene dichloride/magnesium. The expected product **5a** was also obtained as the THF adduct (Scheme 4).

Exchange of the phenyl group of **3** for a trimethylsilyl group (**8**) did not lead to the formation of the expected complexes. Apparently this change imposes too much steric demand onto the system (Scheme 5).

Pentamethyldisilanylalkyne Complexes. As 1-[tris(trimethylsilyl)silyl]-2-trimethylsilyl-ethyne (**8**) seems to be too bulky for complex formation, we settled for only one Si–Si bond and employed 1-pentamethyldisilanyl-2-trimethylsilyl-ethyne (**9**). Reactions of **9** with titanocene and zirconocene dichlorides with magnesium proceeded smoothly in both cases (**10**, **11**) (Scheme 6). For the zirconium case again the THF adduct **11** was formed. Loss of the donor during workup can lead to the same reversible behavior as described above for **5**. Also the trimethylphosphane adduct (**12**) of the zirconocene was prepared (Scheme 6). As it is known that hafnocene complexes are not easily formed without an additional strong donor, we attempted the formation of the hafnocene complex of **9** in the presence of trimethylphosphane.⁶ While the expected product **13** was obtained, we also

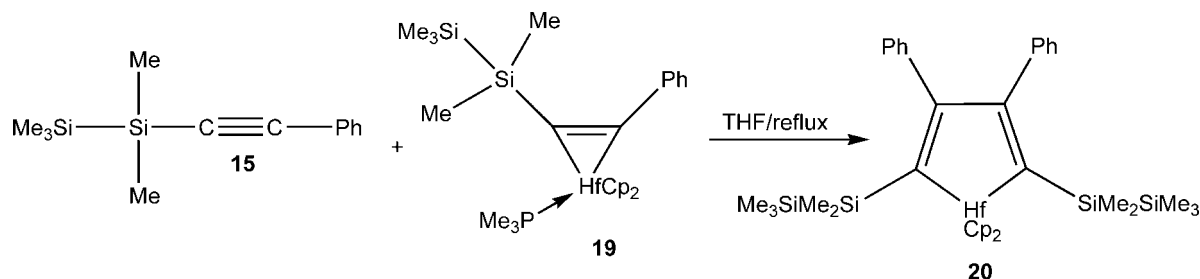
observed formation of a substantial amount of a side-product **14**, which turned out to be the known reduction product of hafnocene dichloride in the presence of trimethylphosphane.¹⁵

Exchange of the trimethylsilyl group of **9** on one side of the alkyne for phenyl (**15**) brought about the expected behavior. Reaction of **15** with titanocene gave the alkyne complex **16** (Scheme 6). while, similar to the situation above, the reaction with the zirconocene analogue gave the coupling product **17** exclusively (Scheme 7).

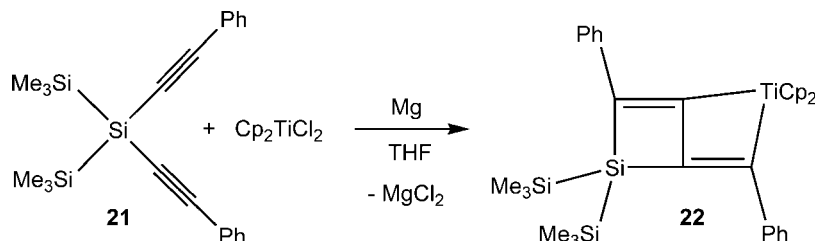
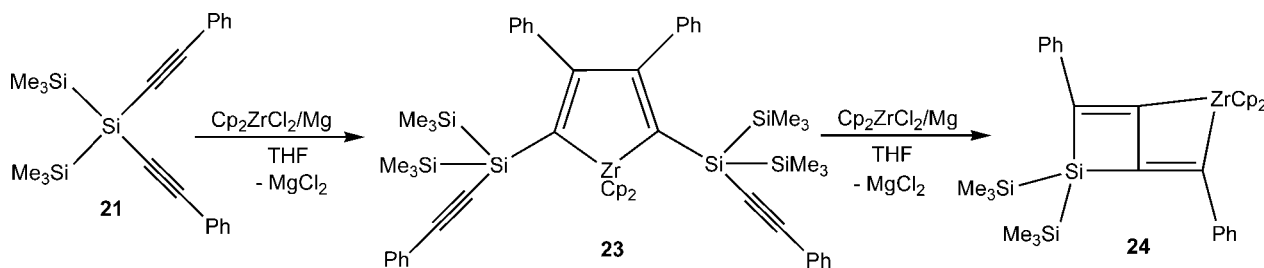
Repetition of the reaction in the presence of trimethylphosphane gave the base adduct of the zirconocene complex (**18**). In contrast to the situation with **9** the reaction of **15** in the presence of trimethylphosphane proceeded cleanly with hafnocene dichloride (**19**) (Scheme 6).

In order to examine the reactivity of **19**, its reaction with another equivalent of **15** was investigated. While no conversion could be observed at ambient conditions, raising the temperature

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Scheme 8. Formation of Hafnacyclopentadiene **20** from Phosphane Adduct **19**

Scheme 9. Formation of Fused Silacyclobutene Titanacyclobutene

Scheme 10. Formation of Oxidative Coupling Product **23** Followed by Reductive Cleavage and Rearrangement to **24**

to 65 °C brought about complete formation of the hafnacyclopentadiene **20** (Scheme 8).

Complexes with Other Oligosilylalkynes. The reactions of 1,1-bis(alkynyl)silanes with titanocene¹⁶ and zirconocene^{16b,17} fragments have been studied for several cases. The outcome of the reaction of **21** with titanocene is characterized by the formation of the silacyclobutene-annelated titanacyclobutene complex **22** (Scheme 9). Related chemistry with zirconium was discussed to involve either a zirconium vinylidene complex, which would be formed via silyl migration, or a dialkyne coupling product with a silapropane moiety.^{16a,17b} The fact that the trisilyl unit of **21** is still intact after the rearrangement seems to support the silapropane pathway in our case.

In contrast to the formation of titanacycle **22** the reaction of **21** with the zirconocene dichloride/magnesium system gave the nonrearranged coupling product **23** (Scheme 10). An attempt to react **23** further with additional zirconocene dichloride/magnesium gave a clean product (**24**). As **23** still contains two phenylalkynyl units, it was initially assumed that a macrocycle

would be obtained.¹⁸ However, the addition excess of the zirconocene fragment seems to facilitate the intermediate formation of a zirconocene alkyne complex, which subsequently undergoes the same rearrangement process as described above for the titanium species to give the rearranged product **24** in analogy to the above-described formation of **22**.

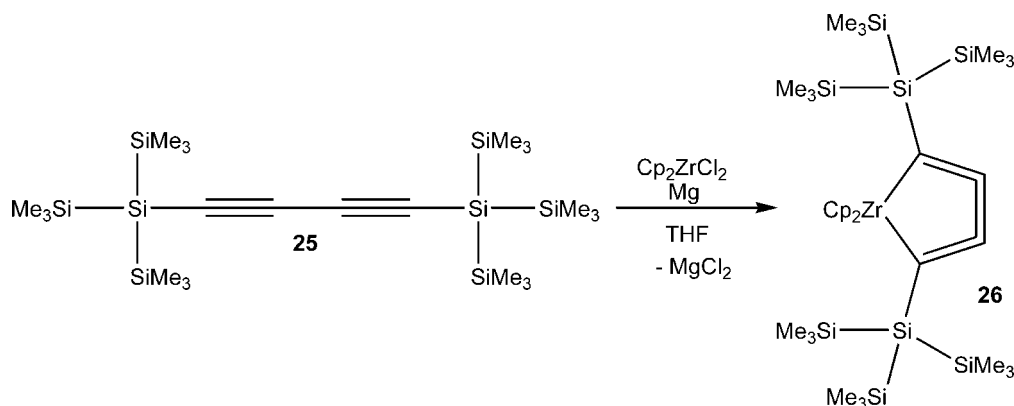
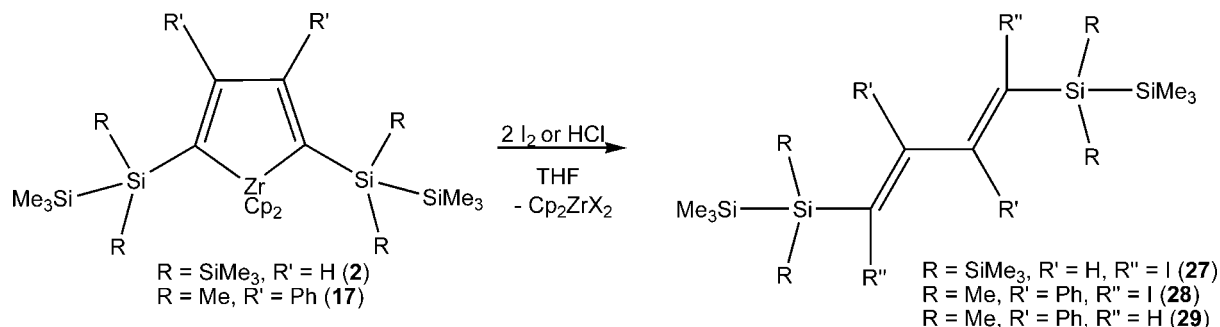
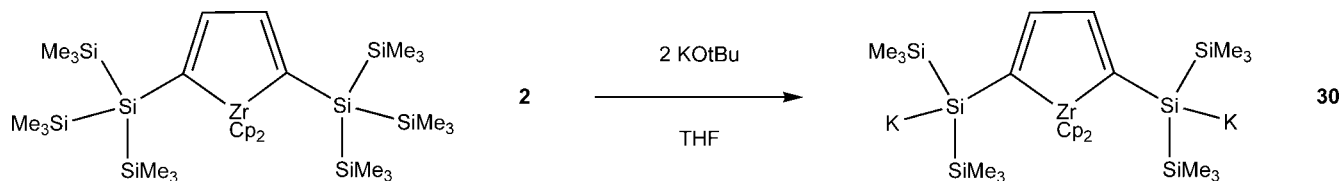
Reactions of diynes with group 4 metallocenes can lead to several different structural motifs.¹ One of those, namely, the metallacyclocumulene structure¹⁹ (**26**) was observed in the reaction of the 1,4-bis[tris(trimethylsilyl)silyl]butadiyne (**25**) with zirconocene dichloride/magnesium (Scheme 11). Interestingly, Rosenthal's similar reaction of bis(trimethylsilyl)butadiyne with zirconocene did not give the related metallacyclocumulene, but its insertion product with bis(trimethylsilyl)butadiyne.^{19a} However, the change to the Cp* ligand facilitated the formation

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Scheme 11. Formation of a 2,5-Bis[tris(trimethylsilyl)silyl]zirconacyclopenta-2,3,4-triene (**26**)Scheme 12. Decomplexation of **2** and **17** with Either I_2 or HCl , Yielding the Respective Buta-1,3-dienes **27**, **28**, and **29**Scheme 13. Reaction of **2** with Potassium *tert*-Butoxide to the Dipotassium Compound **30**Table 1. Selected Distances and Angles of Metallacyclopentadienes **2**, **17**, **20**, and **23**

compound	M–C	C–Si	Si–Si	C–Zr–C
2 (M = Zr)	2.241(8)/2.247(8)	1.893(8)/1.886(9)	2.347(3) – 2.363(3)	89.0(3)
17 (M = Zr)	2.248(6)	1.869(6)	2.365(3)	84.2(3)
20 (M = Hf)	2.2350(19)	1.879(2)	2.3547(8)	82.14(10)
23 (M = Zr)	2.275(4)/2.271(4)	1.884(4)/1.873(4)	2.363(2) – 2.3840(18)	79.26(14)

of the structure.^{19b} This seems to indicate that the steric interaction (which prevents a successive insertion reaction) between the Cp ligands and the tris(trimethylsilyl)silyl groups is similar to that between the Cp^* ligands and the trimethylsilyl groups.

Derivatization Reactions. Reactions of the obtained zirconacyclopentadienes **2** and **17** with iodine proceeded cleanly to the respective 1,4-diiodobuta-1,3-dienes (Scheme 12).²⁰ Compound **17** was also converted to butadiene **29** by reaction with hydrogen chloride.

The tris(trimethylsilyl)silyl groups attached to compounds such as **2** raised the question whether it is possible to convert them into silyl anions.²¹ Therefore, we reacted **2** with 2 equiv of potassium *tert*-butoxide. Clean conversion to the respective dianion **30** was observed (Scheme 13).

Crystal Structures. A substantial number of the compounds described in this paper could be subjected to single-crystal

structure analysis. Table 1 comprises selected structural data for the metallacyclopentadienes **2**, **17**, **20**, and **23** (Figures 1, 8, 9, 11). Comparison with related structures in the Cambridge Crystallographic Data Base²² revealed no unusual structural properties. Si–Si bond lengths of all investigated compounds are around 2.36 Å, which is typical for oligosilanes.

Table 2 contains a compilation of selected data of the metallocene alkyne complexes **4**, **6**, **12**, and **13** (Figures 2, 3, 5, 6) from this study. Again the structural features of the investigated compounds are consistently within the ranges of what was found for related compounds.²² It is interesting to note how much the phosphane ligand influences the M–C bond. In all cases the phosphane resides on the side of the metallocene, where the smaller substituent of the alkyne resides. For compound **6** (Figure 3) we do not observe an elongation of the M–C bond next to the phosphane. In contrast the same bond is significantly elongated for compounds **12** and **13**. The reason

(20) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874.

(21) (a) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221–226. (b) Marschner, C. *Organometallics* **2006**, *25*, 2110–2125.

(22) Related crystal structures from the Cambridge Crystallographic Data Base were extracted using the Conquest V1.9 program.

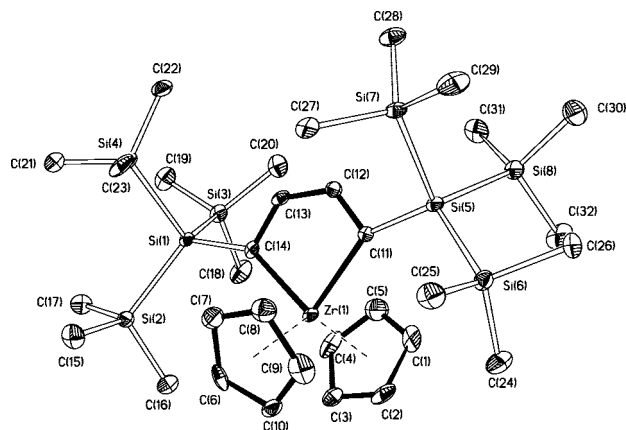


Figure 1. Molecular structure and numbering of **2**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(14) 2.241(8), Zr(1)–C(11) 2.247(8), Si(1)–C(14) 1.893(8), Si(1)–Si(2) 2.356(3), Si(1)–Si(3) 2.358(3), Si(5)–C(11) 1.886(9), Si(5)–Si(6) 2.347(3), C(11)–C(12) 1.364(12), C(12)–C(13) 1.484(12), C(13)–C(14) 1.364(12), C(14)–Zr(1)–C(11) 89.0(3), C(14)–Si(1)–Si(2) 116.0(3), Si(2)–Si(1)–Si(3) 108.30(13), Si(2)–Si(1)–Si(4) 107.79(12), C(12)–C(11)–Si(5) 115.2(6), C(12)–C(11)–Zr(1) 97.8(6), Si(5)–C(11)–Zr(1) 147.0(4), C(11)–C(12)–C(13) 127.6(8), C(11)–C(12)–Zr(1) 53.2(5), C(13)–C(12)–Zr(1) 74.4(5), C(14)–C(13)–C(12) 127.6(8), C(13)–C(14)–Si(1) 114.6(6), C(13)–C(14)–Zr(1) 97.9(6), Si(1)–C(14)–Zr(1) 147.4(5).

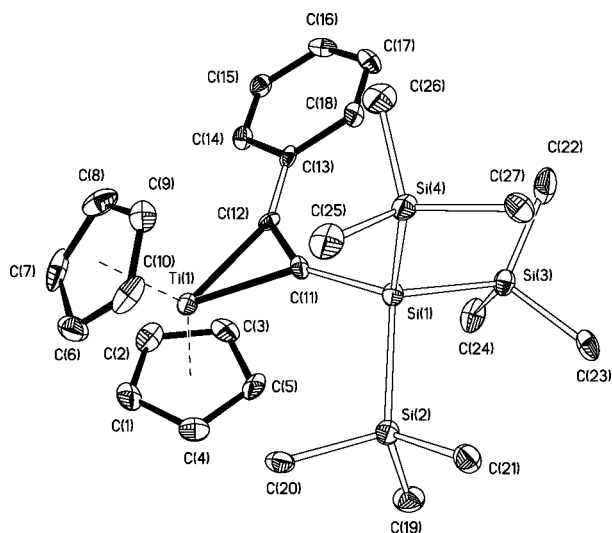


Figure 2. Molecular structure and numbering of **4**. Selected bond lengths [Å] and bond angles [deg] with SDs: Ti(1)–C(12) 2.059(6), Ti(1)–C(11) 2.108(6), Si(1)–C(11) 1.882(6), Si(1)–Si(2) 2.353(3), C(11)–C(12) 1.297(7), C(12)–C(13) 1.457(8), C(12)–Ti(1)–C(11) 36.3(2), Si(2)–Si(1)–Si(4) 107.41(9), C(11)–Si(1)–Si(3) 113.5(2), C(12)–C(11)–Si(1) 146.1(5), C(12)–C(11)–Ti(1) 69.8(4), Si(1)–C(11)–Ti(1) 143.9(4), C(11)–C(12)–C(13) 140.4(6), C(11)–C(12)–Ti(1) 73.9(4).

for this is possibly a steric interaction of the PMe_3 ligand with the trimethylsilyl group.

For the dinuclear compound **7** (Figure 4) the structure is very similar to the analogous compound derived from the THF adduct of the bis(trimethylsilyl)acetylene zirconocene complex.^{12a} The vinylic hydrogen atom of **7** could be located. The dihafnium compound **14** (Figure 7) is similar to the analogous dititanium compound, which has been structurally characterized previously.¹⁵ The bicyclic compounds **22** and **24** (Figures 10 and 12) are structurally similar to what was found previously. The

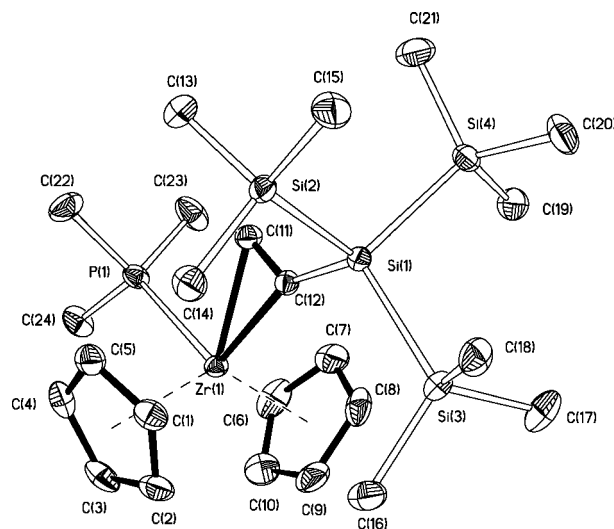


Figure 3. Molecular structure and numbering of **6**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(11) 2.243(4), Zr(1)–C(12) 2.249(4), P(1)–C(23) 1.829(5), Si(1)–C(12) 1.867(5), Si(1)–Si(4) 2.3629(18), Si(2)–C(15) 1.872(5), C(11)–C(12) 1.307(6), C(11)–Zr(1)–C(12) 33.82(16), C(23)–P(1)–Zr(1) 116.6(2), C(12)–Si(1)–Si(4) 109.40(15), Si(4)–Si(1)–Si(2) 109.64(7), C(12)–Si(1)–Si(3) 116.77(14), Si(4)–Si(1)–Si(3) 106.92(7), Si(2)–Si(1)–Si(3) 108.21(7), C(12)–C(11)–Zr(1) 73.4(3), C(11)–C(12)–Si(1) 134.1(4), C(11)–C(12)–Zr(1) 72.8(3), Si(1)–C(12)–Zr(1) 152.9(2).

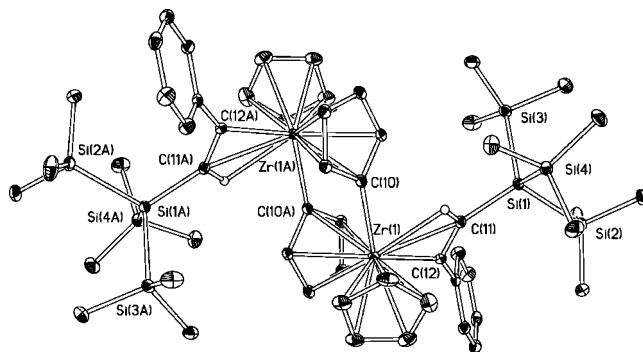


Figure 4. Molecular structure and numbering of **7**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(12) 2.238(3), Si(1)–C(11) 1.904(3), Si(1)–Si(4) 2.3606(13), Si(1)–Si(3) 2.3618(12), Si(1)–Si(2) 2.3703(13), C(11)–C(12) 1.338(4), C(12)–C(13) 1.462(4), Si(4)–Si(1)–Si(3) 109.17(5), C(11)–Si(1)–Si(2) 113.55(10), C(12)–C(11)–Si(1) 137.4(2), C(12)–C(11)–Zr(1) 58.29(17), Si(1)–C(11)–Zr(1) 164.19(16), C(11)–C(12)–C(13) 128.7(3), C(11)–C(12)–Zr(1) 91.1(2), C(13)–C(12)–Zr(1) 139.0(2).

bond between the metal and the nonbridging carbon is slightly longer compared to the bridging one. However, the difference for the titanocene **22** (Figure 10) is not as pronounced as found for a related Cp^*_2Ti system.^{16a} The analogous zirconocene **24** (Figure 12) is structurally close to the compounds obtained from tetraalkynylsilanes.^{16b} The identity of zirconacyclocumulene **26** (Figure 13) could be established unambiguously, but unfortunately, the poor quality of the structure solution does not allow much further discussion. Only two 1,4-diiodo-buta-1,3-dienes²³

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(24) Erker, G.; Zwettler, R.; Krüger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524–530.

(25) Jones, S. B.; Petersen, J. L. *Organometallics* **1985**, *4*, 966–971.

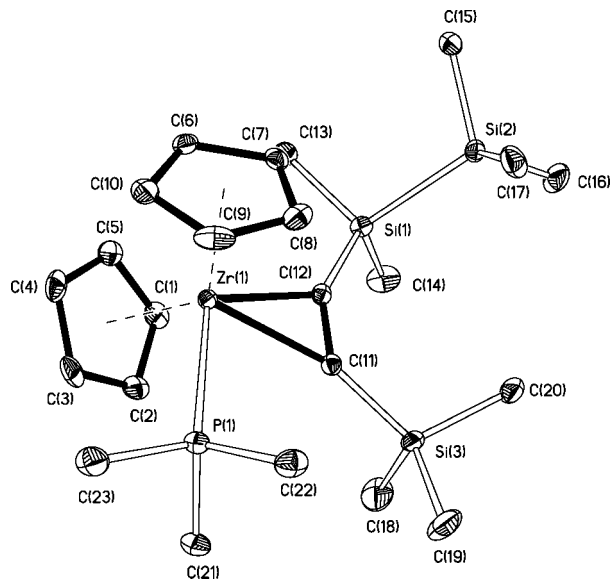


Figure 5. Molecular structure and numbering of **12**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(12) 2.2268(18), Zr(1)–C(11) 2.3140(18), P(1)–C(22) 1.822(2), Si(1)–C(12) 1.8532(18), Si(1)–Si(2) 2.3637(9), C(11)–C(12) 1.310(3), C(12)–Zr(1)–C(11) 33.46(6), C(12)–Si(1)–Si(2) 113.90(6), C(12)–C(11)–Si(3) 125.85(14), C(12)–C(11)–Zr(1) 69.61(10), Si(3)–C(11)–Zr(1) 163.61(10), C(11)–C(12)–Si(1) 146.36(14), C(11)–C(12)–Zr(1) 76.92(11), Si(1)–C(12)–Zr(1) 136.71(9).

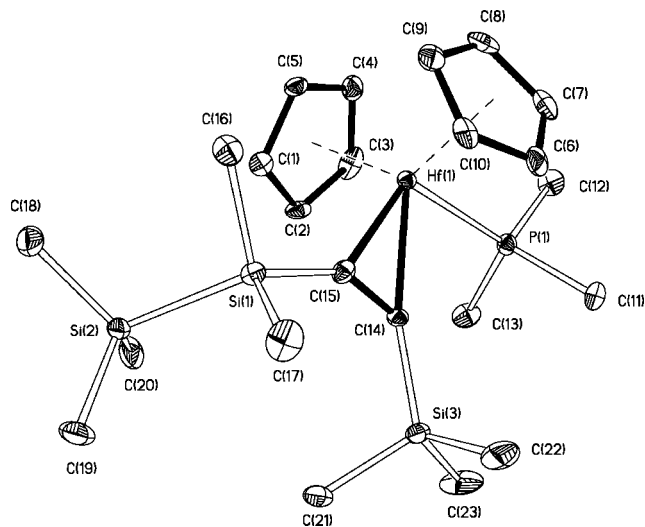


Figure 6. Molecular structure and numbering of **13**. Selected bond lengths [Å] and bond angles [deg] with SDs: Hf(1)–C(15) 2.211(9), Hf(1)–C(14) 2.281(9), P(1)–C(13) 1.819(10), Si(1)–C(15) 1.847(9), Si(1)–Si(2) 2.367(4), Si(3)–C(14) 1.856(9), C(14)–C(15) 1.331(12), C(15)–Hf(1)–C(14) 34.4(3), C(15)–Si(1)–Si(2) 114.8(3), C(14)–Si(3)–C(21) 112.5(4), C(15)–C(14)–Si(3) 124.3(7), C(15)–C(14)–Hf(1) 69.9(5), Si(3)–C(14)–Hf(1) 164.8(5), C(14)–C(15)–Si(1) 146.1(8), C(14)–C(15)–Hf(1) 75.7(6), Si(1)–C(15)–Hf(1) 138.1(5).

have been structurally characterized so far. However, **27** (Figure 14) is different from the known examples, as it allows free rotation around the bond C(2)–C(2A). The molecule adopts a planar conformation with an *anti*-parallel arrangement of the two C–I bonds.

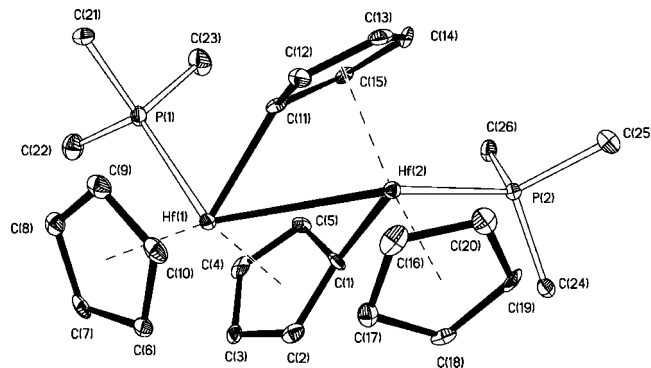


Figure 7. Molecular structure and numbering of **14**. Selected bond lengths [Å] and bond angles [deg] with SDs: Hf(1)–C(11) 2.283(9), Hf(1)–C(1) 2.358(9), Hf(1)–P(1) 2.652(3), Hf(2)–C(1) 2.294(9), Hf(2)–C(11) 2.359(9), Hf(2)–P(2) 2.664(3), P(1)–C(23) 1.819(10), P(2)–C(26) 1.810(10), C(11)–Hf(1)–C(1) 81.7(3), C(11)–Hf(1)–P(1) 79.2(2), C(1)–Hf(2)–C(11) 81.4(3), C(11)–Hf(2)–P(2) 120.4(2), Hf(2)–C(1)–Hf(1) 87.9(3), Hf(1)–C(11)–Hf(2) 88.1(3).

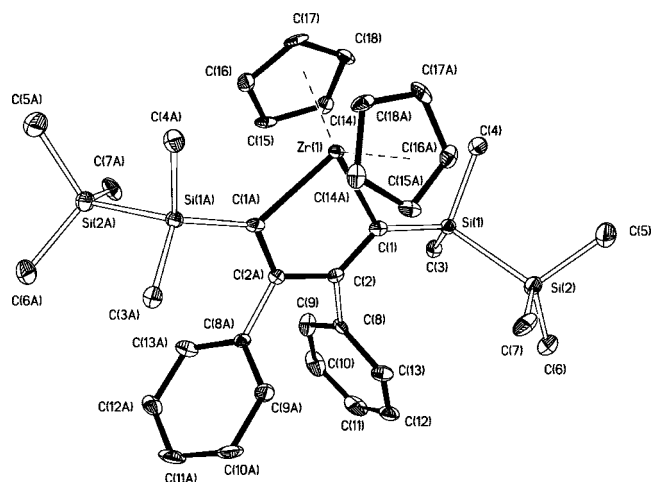


Figure 8. Molecular structure and numbering of **17** (a molecule of benzene was found to cocrystallize and is not shown). Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(1) 2.248(6), Si(1)–C(1) 1.869(6), Si(1)–C(14) 1.880(6), Si(1)–Si(2) 2.365(3), Si(2)–C(18) 1.886(8), C(1)–C(2) 1.360(8), C(2)–C(8) 1.506(8), C(2)–C(2A) 1.510(11), C(1A)–Zr(1)–C(1) 84.2(3), C(1)–Si(1)–C(15) 109.9(3), C(1)–Si(1)–Si(2) 113.9(2), C(2)–C(1)–Si(1) 126.0(5), C(2)–C(1)–Zr(1) 104.3(4), Si(1)–C(1)–Zr(1) 129.6(3), C(1)–C(2)–C(8) 120.8(5), C(1)–C(2)–C(2A) 123.5(3), C(8)–C(2)–C(2A) 115.5(3).

NMR Spectroscopy. For the characterization of metallocene alkyne complexes and also metallacyclopentadienes ^{13}C NMR spectra are most useful. For the case of oligosilanes also ^{29}Si NMR spectroscopy provides some insight, as the ^{29}Si NMR shifts are quite sensitive to the hybridization state of an attached carbon atom. Tables 3 and 4 contain compilations of some relevant ^{13}C and ^{29}Si NMR resonances of compounds discussed in this study as well as of some related compounds. For the metallacyclopentadienes the ^{13}C NMR shifts of the ring carbons are within the range of related compounds. The metal connected carbons resonate around 200 ppm, while C_β shifts are around 150 ppm. Compound **2**, which is derived from a monosubstituted alkyne is different, as the resonances for C_α (175 ppm) and C_β (128 ppm)²⁵ are both shifted some 25 ppm to higher field. For the metallacyclocumulenes derived from bis(trimethylsilyl)-butadiyne and Cp^*_2M fragments ^{13}C NMR resonances at 188.0 ppm (Zr) and 189.3 ppm (Hf) for the C_α and 144.5 ppm (Zr)

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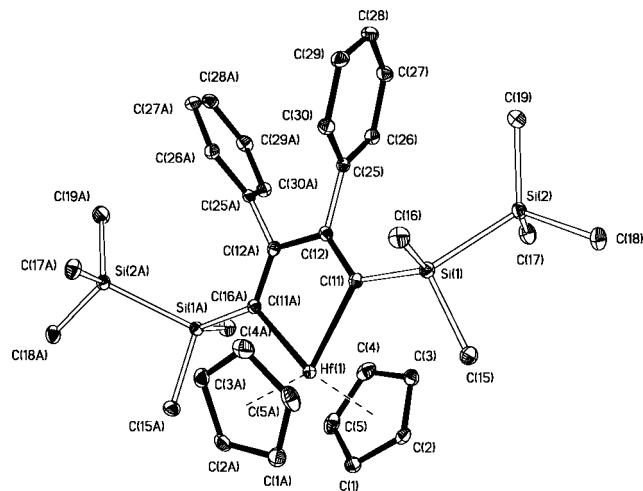


Figure 9. Molecular structure and numbering of **20**. Selected bond lengths [Å] and bond angles [deg] with SDs: Hf(1)–C(11) 2.2350(19), Si(1)–C(11) 1.879(2), Si(1)–Si(2) 2.3547(8), C(11)–C(12) 1.363(3), C(12)–C(12A) 1.518(4), C(11)–Hf(1)–C(11A) 82.14(10), C(11)–Si(1)–C(16) 111.84(9), C(11)–Si(1)–Si(2) 118.92(6), C(16)–Si(1)–Si(2) 110.47(8), C(12)–C(11)–Si(1) 126.21(14), C(12)–C(11)–Hf(1) 107.57(13), Si(1)–C(11)–Hf(1) 126.21(10), C(11)–C(12)–C(12A) 121.36(11).

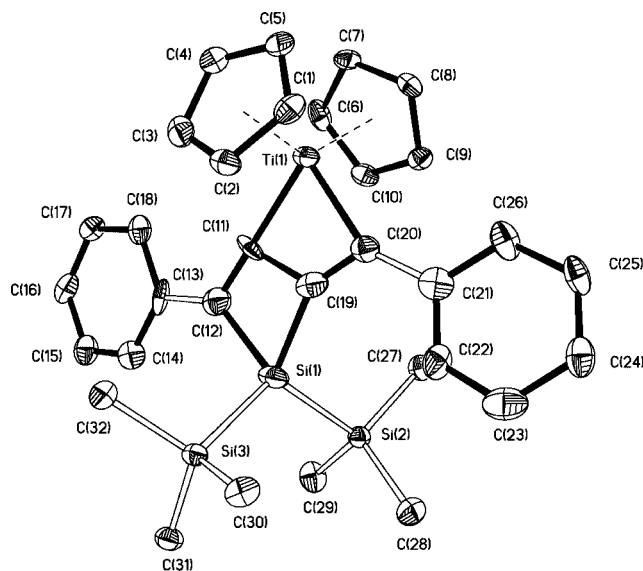


Figure 10. Molecular structure and numbering of **22**. Selected bond lengths [Å] and bond angles [deg] with SDs: Ti(1)–C(11) 2.030(7), Ti(1)–C(20) 2.081(7), Ti(1)–C(19) 2.261(7), Si(1)–C(12) 1.939(8), Si(1)–Si(2) 2.346(3), Si(1)–C(11) 2.377(7), C(11)–C(12) 1.317(9), C(11)–C(19) 1.579(10), C(12)–C(13) 1.461(10), C(19)–C(20) 1.282(10), C(20)–C(21) 1.524(10), C(11)–Ti(1)–C(20) 76.8(3), C(11)–Ti(1)–C(19) 42.8(3), C(20)–Ti(1)–C(19) 34.0(3), C(19)–Si(1)–C(12) 75.1(3), C(19)–Si(1)–Si(2) 112.0(2), C(12)–Si(1)–Si(2) 117.4(2), C(19)–Si(1)–Si(3) 117.5(2), C(12)–Si(1)–Si(3) 111.1(2), C(19)–Si(1)–C(11) 41.5(3), C(12)–Si(1)–C(11) 33.6(3), Si(3)–Si(1)–C(11) 119.75(18), C(12)–C(11)–C(19) 107.0(7), C(12)–C(11)–Ti(1) 174.3(6), C(19)–C(11)–Ti(1) 76.4(4), C(12)–C(11)–Si(1) 54.6(4), C(19)–C(11)–Si(1) 52.4(4), Ti(1)–C(11)–Si(1) 128.8(4), C(20)–C(19)–C(11) 126.0(7), C(20)–C(19)–Si(1) 147.6(6), C(11)–C(19)–Si(1) 86.1(5), C(20)–C(19)–Ti(1) 65.3(4), C(11)–C(19)–Ti(1) 60.8(3), Si(1)–C(19)–Ti(1) 146.8(5), C(19)–C(20)–C(21) 128.0(7), C(19)–C(20)–Ti(1) 80.7(5).

and 144.9 ppm (Hf) for C_β have been reported.^{19a,h} Compared to this, the respective resonances for the tris(trimethylsilyl)si-

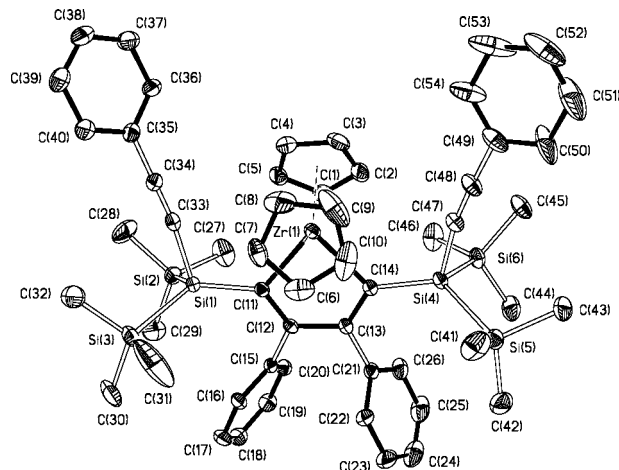


Figure 11. Molecular structure and numbering of **23**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(14) 2.271(4), Zr(1)–C(11) 2.275(4), Si(1)–C(33) 1.877(5), Si(1)–C(11) 1.884(4), Si(1)–Si(2) 2.3753(19), Si(1)–Si(3) 2.3840(18), C(9)–C(10) 1.331(11), C(11)–C(12) 1.355(5), C(12)–C(13) 1.504(5), C(13)–C(14) 1.359(5), C(13)–C(21) 1.496(6), C(14)–Zr(1)–C(11) 79.26(14), Si(2)–Si(1)–Si(3) 110.24(7), Si(1)–C(11)–Zr(1) 125.8(2), Si(4)–C(14)–Zr(1) 124.8(2).

lylated cyclooctatetraene (176.2/131.4 ppm) **26** are again shifted about 12 ppm to higher field. The similarity of the ^{13}C NMR resonances of **2** and **26** even for C_β is somewhat surprising.

The ^{13}C NMR resonances of alkyne complexes listed in Table 4 are in accordance with what has been found for other group 4 metallocene alkyne complexes. As found previously, the shifts of the coordinated alkynes to lower field are strongest for titanocene complexes. Accordingly the resonances of the coordinated carbon atoms of compound **10** are as expected very close to the shift of the analogous bis(trimethylsilyl)acetylene complex. Also the zirconocene THF complex **11** resembles very much the related THF BTMSA complex. The same is true for the PMe_3 complexes **12**, **13**, **18**, and **19**, which correspond to the BTMSA and trimethylsilylphenylacetylene complexes. The comparison of the zirconocene complexes **12** and **18** to the analogous hafnocenes **13** and **19** shows that the latter exhibits a downfield shift for both alkyne carbons of about 7 ppm. Finally the disilanylphenylacetylene titanocene complex **16** resembles the analogous trimethylsilylphenylacetylene complex.

The complexes containing tris(trimethylsilyl)silylalkynes (**4**, **5**, **6**) exhibit a similar behavior to the trimethylsilyl alkyne complexes. However, the influence of the tris(trimethylsilyl)silyl substituent on the shift of C_α of the alkyne was found to be weaker and that on C_β to be stronger than that of the trimethylsilyl group.^{8b} Given for example the ^{13}C NMR resonances of **4**, a comparison to **16** and the analogous titanocene trimethylsilylphenylacetylene complex shows that a similar effect of about the same size is also present for the observed complexes.

The rearrangement products derived from 1,1-bis(phenylethynyl)silanes give a distinct pattern for the former alkynyl carbons of resonances around 265, 210, 155, and 80 ppm for the Cp_2Ti fragment¹⁶ and 255, 210, 160, and 100 ppm for Cp_2Zr .¹⁷ Compounds **22** (Ti) and **24** (Zr) of this study also fall into these ranges.

Conclusion

The first examples of oligosilyl-substituted alkyne complexes of group 4 metallocenes have been prepared by reaction of group

Table 2. Selected Distances and Angles of Metallocene Alkyne Complexes **4**, **6**, **12**, and **13**

compound	M–C(Si/C)	C–Si	Si–Si	C–Zr–C
4 (M = Ti)	2.108(6)/2.059(6)	1.882(6)	2.353(3) – 2.361(3)	36.3(2)
6 (M = Zr)	2.249(4)/2.243(4)	1.867(5)	2.3629(18) – 2.3685(19)	33.82(16)
12 (M = Zr)	2.2268(18)/2.3140(18)	1.8532(18)/1.8484(18)	2.3637(9)	33.46(6)
13 (M = Hf)	2.211(9)/2.281(9)	1.847(9)/1.856(9)	2.367(4)	34.4(3)

4 metallocene dichlorides with magnesium in the presence of the respective alkyne. Depending on the alkyne substitution pattern, either metallacyclopentadienes or metallocene alkyne complexes were formed. In order to suppress the oxidative coupling process, PMe_3 was added to obtain the metallocene alkyne complex base adducts. Despite some precedence indicating interaction of the metal with Si–H groups attached to the alkyne, no Si–Si bond activation was observed during the study. This was surprising, as intermolecular C–H activation was observed in the cases of base loss of THF-stabilized zirconocene complexes without any participation of Si–Si bonds. The reaction of a 2,2-bis(alkynyl)trisilane led to a rearrangement process, which again did not involve the polysilane moiety. The reaction of 1,4-bis[tris(trimethylsilyl)silyl]butadiyne with zirconocene caused the formation of a 1,4-bis[tris(trimethylsilyl)silyl]-substituted zirconacyclocumulene. Reactions of two examples of zirconacyclopentadienes with iodine proceeded to the expected 1,4-diiodobuta-1,3-dienes.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or

argon using either Schlenk techniques or a glovebox. Solvents were dried using a column solvent purification system.²⁸ Potassium *tert*-butanolate was purchased from Merck. All other chemicals were bought from different suppliers and were used without further purification.

¹H (300 MHz), ¹³C (75.4 MHz), ²⁹Si (59.3 MHz), and ³¹P (124.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise for all samples, C_6D_6 was used as solvent. To compensate for the low isotopic abundance of ²⁹Si, the INEPT pulse sequence was used for the amplification of the signal.²⁹ Completeness of conversion of the reactions was checked by ²⁹Si NMR spectroscopy using aliquots of the reactions mixture

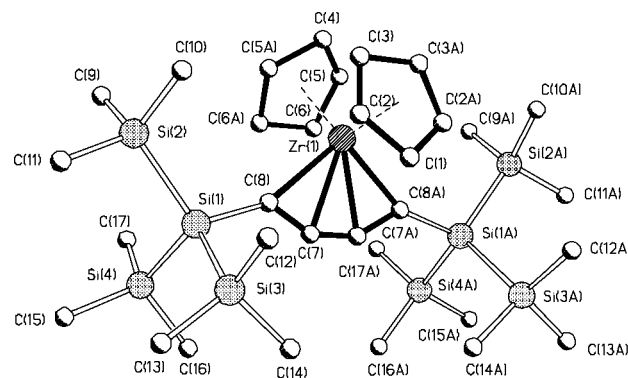


Figure 13. Molecular structure and numbering of **26**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(7) 2.270(15), Zr(1)–C(8) 2.353(15), Si(1)–C(8) 1.880(15), Si(1)–Si(4) 2.358(6), C(7)–C(7A) 1.27(3), C(7)–C(8) 1.32(2), C(7A)–Zr(1)–C(7) 32.5(7), C(7A)–Zr(1)–C(8A) 33.1(5), C(7)–Zr(1)–C(8A) 65.6(5), C(7A)–Zr(1)–C(8) 65.6(5), C(7)–Zr(1)–C(8) 33.1(5), C(8A)–Zr(1)–C(8) 98.7(8), Si(4)–Si(1)–Si(2) 110.4(2), Si(4)–Si(1)–Si(3) 109.1(3), Si(2)–Si(1)–Si(3) 112.3(2), C(7A)–C(7)–C(8) 150.6(9), C(7A)–C(7)–Zr(1) 73.7(4), C(8)–C(7)–Zr(1) 76.9(9), C(7)–C(8)–Si(1) 134.2(12), C(7)–C(8)–Zr(1) 70.0(9), Si(1)–C(8)–Zr(1) 155.7(8).

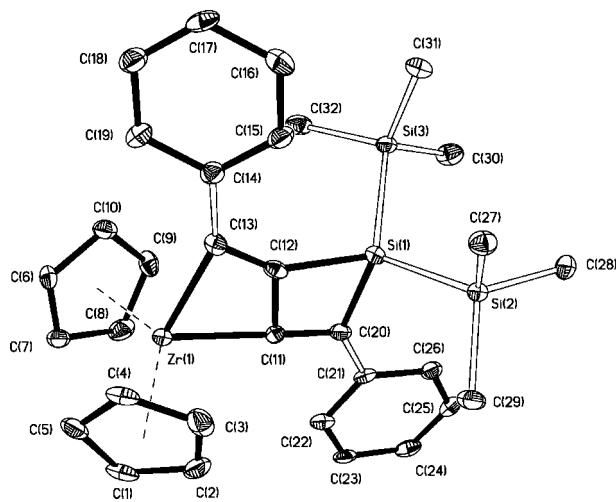


Figure 12. Molecular structure and numbering of **24**. Selected bond lengths [Å] and bond angles [deg] with SDs: Zr(1)–C(11) 2.150(7), Zr(1)–C(13) 2.184(7), Zr(1)–C(12) 2.393(7), Si(1)–C(20) 1.876(7), Si(1)–C(12) 1.910(7), Si(1)–Si(3) 2.346(3), Si(1)–C(11) 2.381(7), C(11)–C(20) 1.354(9), C(11)–C(12) 1.583(10), C(12)–C(13) 1.328(9), C(13)–C(14) 1.480(9), C(11)–Zr(1)–C(13) 73.7(3), C(11)–Zr(1)–C(12) 40.3(2), C(13)–Zr(1)–C(12) 33.3(2), C(20)–Si(1)–C(12) 76.1(3), C(20)–Si(1)–Si(3) 117.9(2), C(12)–Si(1)–Si(3) 111.3(2), C(20)–Si(1)–Si(2) 112.0(2), C(12)–Si(1)–Si(2) 116.8(2), Si(3)–Si(1)–Si(2) 116.58(11), C(20)–Si(1)–C(11) 34.6(3), C(12)–Si(1)–C(11) 41.5(3), Si(3)–Si(1)–C(11) 122.87(19), Si(2)–Si(1)–C(11) 120.51(18), C(20)–C(11)–C(12) 105.0(6), C(20)–C(11)–Zr(1) 174.6(6), C(12)–C(11)–Zr(1) 78.1(4), C(20)–C(11)–Si(1) 51.9(4), C(12)–C(11)–Si(1) 53.1(3), Zr(1)–C(11)–Si(1) 131.2(3), C(13)–C(12)–C(11) 126.1(6), C(13)–C(12)–Si(1) 148.1(6), C(11)–C(12)–Si(1) 85.4(4), C(13)–C(12)–Zr(1) 64.7(4), C(11)–C(12)–Zr(1) 61.5(3), Si(1)–C(12)–Zr(1) 146.8(4), C(12)–C(13)–Zr(1) 82.0(4).

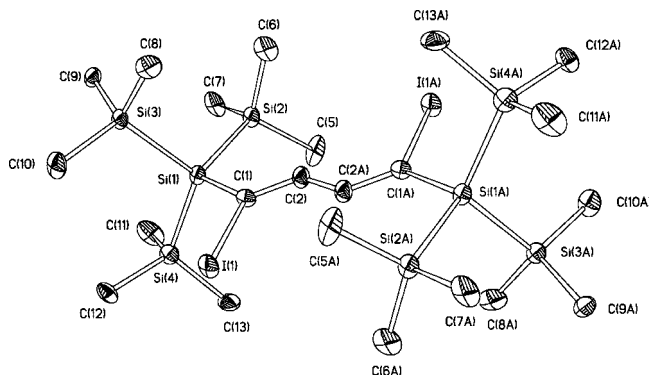


Figure 14. Molecular structure and numbering of **27**. Selected bond lengths [Å] and bond angles [deg] with SDs: Si(1)–C(1) 1.887(12), Si(1)–Si(4) 2.350(6), Si(1)–Si(3) 2.355(5), Si(1)–Si(2) 2.368(4), I(1)–C(1) 2.135(10), C(1)–C(2) 1.343(17), C(2)–C(2A) 1.41(2), Si(4)–Si(1)–Si(3) 114.82(19), C(1)–Si(1)–Si(2) 106.9(4), Si(4)–Si(1)–Si(2) 111.18(19), Si(3)–Si(1)–Si(2) 107.98(17), C(2)–C(1)–Si(1) 126.9(9), C(2)–C(1)–I(1) 118.1(8), Si(1)–C(1)–I(1) 115.0(6), C(1)–C(2)–C(2A) 130.2(15).

Table 3. Selected NMR Data of Metallacyclopentadienes $\text{Cp}_2\text{M(RCCR')}_2$

compound (M, R, R') ^a	¹³ C M–C (δ, ppm)	¹³ C Cp (δ, ppm)	²⁹ Si C–Si–Si (δ, ppm)
2 (Zr, Si ₄ , H)	175.7/128.1	110.2	–76.9/–14.0
17 (Zr, Si ₂ , Ph)	203.2/149.0	111.6	–33.7/–18.9
20 (Hf, Si ₂ , Ph)	202.0/149.1	111.0	–31.8/–18.4
23 (Zr, Si ₃ CC, Ph)	195.9/157.0	113.5	–76.0/–15.1
26 (Zr, Si ₄ , cumulene))	176.2/131.4	104.7	–82.4/–12.4
(Zr, Si, Ph) ²⁴	204.6/150.1		
(Zr, Ph, Ph) ^{25,b}	194.5/143.4		
(Zr, Ph, H) ^{25,c}	190.8/118.8		
(Zr, SiMe ₂ CC, Ph) ^{17d}	201.1/157.0	112.6	
(Zr, Si, cumulene) ^{19b}	188.0/144.5		

^a Si₄ = Si(SiMe₃)₃, Si₃CC = Si(SiMe₃)₂C≡CPh, Si₂ = SiMe₂SiMe₃, Si = SiMe₃. ^b Cp' instead of Cp compounds listed. ^c Cp* instead of Cp compound listed.

Table 4. Selected NMR Data of Metallocene Alkyne Complexes $\text{Cp}_2\text{M(RCCR')D}$

compound (M, R, R', D) ^a	¹³ C M–C (δ, ppm)	¹³ C Cp (δ, ppm)	²⁹ Si C–Si–Si (δ, ppm)	²⁹ Si C–SiMe ₃ (δ, ppm)
4 (Ti, Si ₄ , Ph)	199.0/221.1	116.6	–84.2/–13.5	
5 (Zr, Si ₄ , Ph, THF)	185.4/195.9	107.7	–85.6/–14.1	
6 (Zr, Si ₄ , H, PMe ₃)	172.7/170.6	103.0	–85.2/–14.1	
10 (Ti, Si ₂ , Si)	243.8/241.9	118.0	–33.2/–19.9	–15.0
11 (Zr, Si ₂ , Si, THF)	214.3/208.8	106.6	–28.5/–20.0	–11.5
12 (Zr, Si ₂ , Si, PMe ₃)	202.0/175.5	102.6	–27.9/–20.1	–8.5
13 (Hf, Si ₂ , Si, PMe ₃)	210.4/182.5	101.7	–25.9/–19.3	–6.6
16 (Ti, Si ₂ , Ph)	212.0/219.8	116.6	–32.9/–19.0	
18 (Zr, Si ₂ , Ph, PMe ₃)	180.2/176.4	103.0	–26.9/–20.4	
19 (Hf, Si ₂ , Ph, PMe ₃)	187.0/181.7	102.2	–25.2/–20.1	
(Ti, Si, Ph) ²⁶	213.0/219.6	116.6		
(Ti, Si, Si) ²⁶	248.5	121.9		
(Zr, Si, Si, THF) ¹²	212.9	107.0		
(Zr, Si, Si, PMe ₃) ^{14a}	205.7/177.3	103.1		
(Zr, Si, Ph, PMe ₃) ¹⁴	181.0/177.4 ^{14c} 182.5/177.6 ^{14a}	103.1 ^{14c} 103.6 ^{14a}		
(Ti, Ph, Ph) ²⁷	196.0	115.9		

^a Si₄ = Si(SiMe₃)₃, Si₂ = SiMe₂SiMe₃, Si = SiMe₃.

Table 5. Crystallographic Data for Compounds **2**, **4**, **6**, **7**, and **12**

	2	4	6	7	12
empirical formula	ZrSi ₈ C ₃₂ H ₆₆	TiSi ₄ C ₂₇ H ₄₂	ZrPSi ₄ C ₂₄ H ₄₇	Zr ₂ Si ₈ C ₃₄ H ₈₄	ZrPSi ₃ C ₂₃ H ₄₃
<i>M</i> _w	766.79	526.87	570.17	1140.37	526.03
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.33 × 0.26 × 0.18	0.35 × 0.22 × 0.18	0.28 × 0.22 × 0.20	0.36 × 0.28 × 0.24	0.33 × 0.28 × 0.22
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/c	P2(1)	P2(1)/c	P2(1)/n	P2(1)/c
<i>a</i> [Å]	38.848(9)	11.335(4)	17.927(4)	16.088(3)	18.106(4)
<i>b</i> [Å]	9.374(2)	10.597(3)	11.581(2)	10.731(2)	10.444(2)
<i>c</i> [Å]	29.955(2)	12.796(4)	17.288(3)	17.823(4)	15.295(3)
α [deg]	90	90	90	90	90
β [deg]	123.61(2)	94.356(5)	118.57(3)	105.34(3)	98.92(3)
γ [deg]	90	90	90	90	90
<i>V</i> [Å ³]	9058(4)	1532.6(8)	3152(2)	2967(2)	2857(2)
<i>Z</i>	8	2	4	2	6
ρ _{calc} [g cm ^{−3}]	1.121	1.142	1.201	1.276	1.223
absorp coeff [mm ^{−1}]	0.472	0.448	0.562	0.545	0.574
<i>F</i> (000)	3280	564	1208	1200	1112
θ range	1.63 < θ < 23.50	1.80 < θ < 25.00	2.18 < θ < 24.50	1.52 < θ < 26.37	2.26 < θ < 26.37
no. of reflns collected/unique	27 802/6727	10 876/5284	19 904/5235	23 040/6050	22 190/5831
completeness to θ [%]	99.9	99.7	99.8	99.9	99.8
no. of data/restraints/params	6727/18/388	5284/1/299	5235/0/283	6050/0/302	5831/0/264
goodness of fit on <i>F</i> ²	1.04	0.83	1.01	1.23	1.04
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.104, <i>wR</i> 2 = 0.251	<i>R</i> 1 = 0.068, <i>wR</i> 2 = 0.084	<i>R</i> 1 = 0.061, <i>wR</i> 2 = 0.135	<i>R</i> 1 = 0.050, <i>wR</i> 2 = 0.107	<i>R</i> 1 = 0.027, <i>wR</i> 2 = 0.067
<i>R</i> indices (all data)	<i>R</i> 1 = 0.133, <i>wR</i> 2 = 0.277	<i>R</i> 1 = 0.119, <i>wR</i> 2 = 0.095	<i>R</i> 1 = 0.079, <i>wR</i> 2 = 0.146	<i>R</i> 1 = 0.054, <i>wR</i> 2 = 0.109	<i>R</i> 1 = 0.031, <i>wR</i> 2 = 0.068
largest diff peak/hole [e [−] /Å ³]	4.74/−1.24	0.43/−0.49	0.79/−0.89	0.85/−0.49	0.57/−0.24

and D₂O capillaries. Elementary analyses were carried out using a Heraeus Vario Elementar with the addition of WO₃ to suppress SiC formation.

X-Ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to *F*_o² and

corrected for absorption effects with SAINT³⁰ and SADABS,³¹ respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).³² If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted

Table 6. Crystallographic Data for Compounds 13, 14, 17, 20, and 22

	13	14	17	20	22
empirical formula	HfPSi ₃ C ₂₃ H ₄₃	Hf ₂ P ₂ C ₂₆ H ₃₆	ZrSi ₄ C ₄₂ H ₅₆	HfSi ₄ C ₃₆ H ₅₀	TiSi ₃ C ₃₂ H ₃₈
<i>M_w</i>	613.30	767.47	764.45	773.61	554.79
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.34 × 0.28 × 0.22	0.38 × 0.30 × 0.22	0.34 × 0.22 × 0.18	0.34 × 0.26 × 0.22	0.34 × 0.26 × 0.22
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>Pccn</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> [Å]	18.106(4)	17.472(4)	19.608(4)	20.769(4)	9.301(2)
<i>b</i> [Å]	10.445(2)	22.229(4)	11.116(2)	11.323(2)	31.000(6)
<i>c</i> [Å]	15.257(3)	12.832(3)	19.047(4)	15.923(3)	11.056(2)
α [deg]	90	90	90	90	90
β [deg]	99.06(3)	90	97.32(3)	103.04(3)	108.86(3)
γ [deg]	90	90	90	90	90
<i>V</i> [Å ³]	2849(2)	7679(2)	4118(2)	3648(2)	3017(2)
<i>Z</i>	4	8	4	4	4
ρ _{calc} [g cm ^{−3}]	1.430	2.046	1.233	1.409	1.222
absorp coeff [mm ^{−1}]	3.851	8.466	0.411	3.014	0.422
<i>F</i> (000)	1240	2928	1616	1576	1176
θ range	1.14 < θ < 25.00	1.48 < θ < 25.00	2.09 < θ < 24.99	2.01 < θ < 26.35	2.05 < θ < 25.00
no. of reflns collected/unique	19 751/5009	34 163/4394	14 493/3624	14 125/3699	21 572/5295
completeness to θ [%]	99.9	100	99.8	99.6	99.9
no. of data/restraints/params	5009/0/264	4394/0/277	3624/2/218	3699/0/202	5295/0/332
goodness of fit on <i>F</i> ²	1.26	1.13	1.29	1.05	1.01
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.062, <i>wR</i> 2 = 0.111	<i>R</i> 1 = 0.047, <i>wR</i> 2 = 0.083	<i>R</i> 1 = 0.091, <i>wR</i> 2 = 0.171	<i>R</i> 1 = 0.017, <i>wR</i> 2 = 0.042	<i>R</i> 1 = 0.085, <i>wR</i> 2 = 0.153
<i>R</i> indices (all data)	<i>R</i> 1 = 0.072, <i>wR</i> 2 = 0.114	<i>R</i> 1 = 0.063, <i>wR</i> 2 = 0.089	<i>R</i> 1 = 0.108, <i>wR</i> 2 = 0.178	<i>R</i> 1 = 0.018, <i>wR</i> 2 = 0.042	<i>R</i> 1 = 0.186, <i>wR</i> 2 = 0.193
largest diff peak/hole [e [−] /Å ³]	1.71/−4.05	1.91/−1.17	0.86/−1.62	0.71/−0.42	1.13/−0.61

Table 7. Crystallographic Data for Compounds 23, 24, 26, and 27

	23	24	26	27
empirical formula	ZrSi ₆ C ₅₄ H ₆₆	ZrSi ₃ C ₃₂ H ₃₈	ZrSi ₈ C ₃₂ H ₆₄	Si ₈ I ₂ C ₂₂ H ₅₆
<i>M_w</i>	974.83	598.11	764.77	799.19
temperature [K]	100(2)	100(2)	100(2)	200(2)
size [mm]	0.30 × 0.25 × 0.20	0.33 × 0.26 × 0.18	0.36 × 0.22 × 0.18	0.30 × 0.20 × 0.15
cryst syst	monoclinic	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>A</i> ma2	<i>P</i> $\bar{1}$
<i>a</i> [Å]	19.039(4)	9.2332(2)	28.738(6)	8.7389(2)
<i>b</i> [Å]	9.6121(2)	31.118(6)	16.791(6)	9.4834(2)
<i>c</i> [Å]	30.102(6)	11.252(2)	9.5167(2)	13.512(3)
α [deg]	90	90	90	97.87(3)
β [deg]	93.73(3)	109.38(3)	90	92.04(3)
γ [deg]	90	90	90	117.03(3)
<i>V</i> [Å ³]	5497(2)	3050(2)	4592(2)	982(4)
<i>Z</i>	4	4	4	1
ρ _{calc} [g cm ^{−3}]	1.178	1.303	1.106	1.351
absorp coeff [mm ^{−1}]	0.363	0.497	0.467	1.856
<i>F</i> (000)	2056	1248	1632	406
θ range	1.67 < θ < 25.38	2.03 < θ < 26.31	2.43 < θ < 23.00	2.45 < θ < 24.49
no. of reflns collected/unique	39 551/10 032	18 254/5910	13 467/3271	5945/3184
completeness to θ [%]	99.2	95.4	99.9	97.5
no. of data/restraints/params	10 032/0/562	5910/0/331	3271/37/200	3184/0/145
goodness of fit on <i>F</i> ²	0.96	0.98	1.20	1.00
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.061, <i>wR</i> 2 = 0.126	<i>R</i> 1 = 0.082, <i>wR</i> 2 = 0.146	<i>R</i> 1 = 0.135, <i>wR</i> 2 = 0.285	<i>R</i> 1 = 0.085, <i>wR</i> 2 = 0.201
<i>R</i> indices (all data)	<i>R</i> 1 = 0.121, <i>wR</i> 2 = 0.149	<i>R</i> 1 = 0.162, <i>wR</i> 2 = 0.173	<i>R</i> 1 = 0.144, <i>wR</i> 2 = 0.291	<i>R</i> 1 = 0.135, <i>wR</i> 2 = 0.226
largest diff peak/hole [e [−] /Å ³]	0.40/−0.33	0.84/−1.15	1.13/−1.97	2.27/−2.09

for clarity. Unfortunately the obtained crystal quality of some substances was poor. This fact is reflected by quite high *R* and low θ values.

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **4**, **6**, **7**, **12**, **13**, **14**, **17**, **20**, **22**, **23**, **24**, **26**, and **27** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-664708 (**2**), 668145 (**4**), 664709 (**6**), 664710 (**7**), 664714 (**12**), 664712 (**13**), 664713 (**14**), 664706 (**17**), 666457 (**20**), 664711 (**22**), 664707 (**23**), 670068 (**24**), 670067 (**26**), and 664715 (**27**). Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/products/csd/request.

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Pentamethyl(trimethylsilyl)ethynyl)disilane (**9**),³³ pentamethyl(phenylethynyl)disilane (**15**),³⁴ tris(trimethylsilyl)silylthyne (**1**),³⁵

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tris(trimethylsilyl)silylphenylacetylene (**3**),^{8b} and 2,2-bis(phenylalkynyl)hexamethyltrisilane (**21**)^{8b} were prepared according to published procedures.

Preparation of Starting Materials. Tris(trimethylsilyl)germylphenylacetylene (3a). At $-70\text{ }^{\circ}\text{C}$ methyl lithium (5% in Et_2O , 59 mg, 2.702 mmol) was added to a solution of phenylacetylene (276 mg, 2.702 mmol) in Et_2O (15 mL). After complete addition the reaction was stirred at rt for 18 h, and a precipitate was formed. The formed suspension was added dropwise at $-70\text{ }^{\circ}\text{C}$ to a solution of tris(trimethylsilyl)germyl chloride (843 mg, 2.573 mmol) in Et_2O (30 mL). Stirring was continued for 2 days at rt before the reaction was complete. The mixture was poured onto degassed ice-cold 0.5 M H_2SO_4 for workup. After drying with sodium sulfate and evaporation of the solvent **3a** (907 mg, 90%) was afforded as a light yellow oil. ^{29}Si NMR (δ ppm): -4.9 . ^1H NMR (δ ppm): 7.45 (m, 2H); 7.30 (m, 3H); 0.37 (s, 27H, $3\times\text{SiMe}_3$). ^{13}C NMR (δ ppm): 132.0; 128.3; 127.4; 125.5; 106.8; 89.6; 1.4. Anal. Calcd for $\text{C}_{17}\text{H}_{32}\text{GeSi}_3$ (393.30): C 51.91, H 8.20. Found: C 51.33, H 8.18.

1,4-Bis[tris(trimethylsilyl)silyl]butadiyne (25). To a solution of 1,4-bis(trimethylsilyl)butadiyne (833 mg, 4.28 mmol) in THF (10 mL) was added at once potassium *tert*-butoxide (1.00 g, 8.91 mmol). After 30 min the reaction mixture was cooled to $-50\text{ }^{\circ}\text{C}$ and chlorotris(trimethylsilyl)silane (2.42 g, 8.54 mmol) in THF (10 mL) was added dropwise. Stirring was continued for 12 h at $0\text{ }^{\circ}\text{C}$ and a further 48 h at rt. The solvent was removed and the residue extracted with toluene (30 mL). After evaporation of the solvent and flash chromatography with heptane **25** (1.68 g, 73%) was obtained as a slight yellow solid (mp: $148-150\text{ }^{\circ}\text{C}$). ^{29}Si NMR (δ ppm): -11.5 ; -100.5 . ^1H NMR (δ ppm): 0.16 (s, 54H). ^{13}C NMR (δ ppm): 93.4; 79.2; 0.4. Anal. Calcd for $\text{C}_{22}\text{H}_{54}\text{Si}_8$ (543.35): C 48.63, H 10.02. Found: C 48.27, H 9.89.

Metallocene Complexes. Reaction of Tris(trimethylsilyl)silylethyne with Cp_2ZrCl_2 (2). To a solution of tris(trimethylsilyl)silylethyne (**1**) (200 mg, 0.733 mmol) and Cp_2ZrCl_2 (214 mg, 0.733 mmol) in THF (4 mL) were added Mg turnings (18 mg, 0.740 mmol). The reaction mixture was stirred for 18 h, after which the precipitate was removed by centrifugation. After evaporation of the solvent the residue was treated with heptane, and again the precipitate was removed by centrifugation. Cooling to $-70\text{ }^{\circ}\text{C}$ afforded yellow-green crystals of **2** (298 mg, 53%; mp: $151-155\text{ }^{\circ}\text{C}$). ^{29}Si NMR (δ ppm): -14.0 (SiMe_3); -76.9 . ^1H NMR (δ ppm): 5.98 (s, 10H, Cp); 5.87 (s, 2H); 0.34 (s, 54H, SiMe_3). ^{13}C NMR (δ ppm): 175.7; 128.1; 110.2 (Cp); 2.0 (SiMe_3). Anal. Calcd for $\text{C}_{32}\text{H}_{66}\text{Si}_8\text{Zr}$ (766.77): C 50.12, H 8.68. Found: C 49.73, H 8.81.

Reaction of Tris(trimethylsilyl)silylphenylacetylene with Cp_2TiCl_2 (4). Reaction was done analogously to the preparation of **2** using tris(trimethylsilyl)silylphenylacetylene (**3**) (100 mg, 0.287 mmol), Cp_2TiCl_2 (71 mg, 0.287 mmol), and Mg turnings (7 mg, 0.288 mmol), and stirring was continued for 3 days. Orange crystals of **4** (43 mg, 28%) were obtained (using pentane instead of heptane). ^{29}Si NMR (δ ppm): -13.5 (SiMe_3); -84.2 . ^1H NMR (δ ppm): 7.03 (m, 2H); 6.83 (m, 1H); 6.48 (m, 2H); 6.33 (s, 10H, Cp); 0.12 (s, 27H, SiMe_3). ^{13}C NMR (δ ppm): 222.1; 199.0; 143.8; 127.8; 125.0; 125.4; 116.6 (Cp); 1.8 (SiMe_3). Anal. Calcd for $\text{C}_{27}\text{H}_{42}\text{Si}_4\text{Ti}$ (526.86): C 61.55, H 8.04. Found: C 60.82, H 8.15.

Reaction of Tris(trimethylsilyl)silylphenylacetylene with Cp_2ZrCl_2 (5, 7). Reaction was done analogously to the preparation of **2** using tris(trimethylsilyl)silylphenylacetylene (**3**) (200 mg, 0.573 mmol), Cp_2ZrCl_2 (152 mg, 0.521 mmol), and Mg turnings (13 mg, 0.535 mmol). Yellow crystals of **5** (274 mg, 82%) were obtained from benzene. ^{29}Si NMR (δ ppm): -14.1 (SiMe_3); -85.6 . ^1H NMR (δ ppm): 7.20 (m, 2H); 6.93 (m, 3H); 5.77 (s, 10H, Cp); 3.12 (m, 4H, THF); 0.95 (m, 4H, THF); 0.35 (s, 27H, SiMe_3). ^{13}C NMR (δ ppm):

195.9; 185.4; 156.9; 127.6; 123.3; 122.2; 107.7 (Cp); 75.3 (THF); 25.7 (THF); 2.5 (SiMe_3). Anal. Calcd for $\text{C}_{31}\text{H}_{50}\text{OSi}_4\text{Zr}$ (642.29): C 57.97, H 7.85. Found: C 57.92, H 7.83.

As a result of THF dissociation in the NMR solution, colorless crystals of compound **7** precipitated. If the removal of THF was forced by subjecting a vacuum to a solution of **5**, the dimerization product **7** was formed quantitatively. Addition of THF caused regeneration of **5**.

Due to the very poor solubility of **7** in noncoordinating solvents, only proton NMR data could be obtained. **7**: ^{29}Si NMR (δ ppm): -14.3 (SiMe_3); -88.6 . ^1H NMR (δ ppm): 7.20–6.90 (m, 12H, $2\times\text{Ph}$ and $=\text{CH}$); 6.24 (s, 10H, Cp); 6.00–5.70 (m, 8H, C_5H_4); 0.26 (s, 54H, SiMe_3). Anal. Calcd for $\text{C}_{54}\text{H}_{84}\text{Si}_8\text{Zr}_2$ (1140.38): C 56.87, H 7.42. Found: C 56.67, H 7.31.

Reaction of Tris(trimethylsilyl)germylphenylacetylene with Cp_2ZrCl_2 (5a): Reaction was done analogously to the preparation of **2** using tris(trimethylsilyl)germylphenylacetylene (**3a**) (100 mg, 0.254 mmol), Cp_2ZrCl_2 (74 mg, 0.254 mmol), and Mg turnings (7 mg, 0.288 mmol). **5a** (81 mg, 47%) was obtained as a red solid (using pentane instead of heptane). ^{29}Si NMR (δ ppm): -8.1 (SiMe_3). ^1H NMR (δ ppm): 7.20 (m, 2H); 6.94 (m, 3H); 5.76 (s, 10H, Cp); 3.21 (m, 4H, THF); 1.08 (m, 4H, THF); 0.39 (s, 27H, SiMe_3). Anal. Calcd for $\text{C}_{31}\text{H}_{50}\text{GeOSi}_3\text{Zr}$ (686.82): C 54.21, H 7.34. Found: C 53.69, H 7.41. The removal of the solvent under vacuum from a solution of **5a** also caused formation of the dimerization product **7a**.

Reaction of Tris(trimethylsilyl)silylethyne with Cp_2ZrCl_2 and PMe_3 (6). Reaction was done analogously to the preparation of **2** using tris(trimethylsilyl)silylethyne (**1**) (150 mg, 0.550 mmol), Cp_2ZrCl_2 (161 mg, 0.550 mmol), PMe_3 (42 mg, 0.550 mmol), and Mg turnings (14 mg, 0.576 mmol). Green crystals of **6** (163 mg, 52%) were obtained. ^{29}Si NMR (δ ppm): -14.1 ; -85.2 (d, $J = 5.6\text{ Hz}$). ^1H NMR (δ ppm): 8.76 (d, $J = 3.4\text{ Hz}$, 1H); 5.24 (d, $J = 1.8\text{ Hz}$, 10H, Cp); 0.93 (d, $J = 5.9\text{ Hz}$, 9H, PMe_3); 0.41 (s, 27H, SiMe_3). ^{13}C NMR (δ ppm): 172.7 (d, $J = 8.9\text{ Hz}$); 170.6 (d, $J = 27.4\text{ Hz}$); 103.0 (Cp); 16.6 (d, $J = 17.9\text{ Hz}$, PMe_3); 1.7 (SiMe_3). ^{31}P NMR (δ ppm): 4.8. Anal. Calcd for $\text{C}_{24}\text{H}_{47}\text{PSi}_4\text{Zr}$ (570.17): C 50.56, H 8.31. Found: C 50.62, H 8.57.

Reaction of Pentamethyl(trimethylsilylethynyl)disilane with Cp_2TiCl_2 (10). Reaction was done analogously to the preparation of **2** using pentamethyl(trimethylsilylethynyl)disilane (**9**) (150 mg, 0.656 mmol), Cp_2TiCl_2 (163 mg, 0.656 mmol), and Mg turnings (16 mg, 0.658 mmol). **10** (157 mg, 59%) was obtained as a red oil. ^{29}Si NMR (δ ppm): -15.0 (C– SiMe_3); -19.9 ($\text{Me}_3\text{SiSiMe}_2$); -33.2 (SiMe_2). ^1H NMR (δ ppm): 6.44 (s, 10H, Cp); 0.09 (s, 9H, SiMe_3); -0.36 (s, 9H, C– SiMe_3); -0.44 (s, 6H, SiMe_2). ^{13}C NMR (δ ppm): 243.8; 241.9; 118.0; 0.6; -1.6 ; -1.7 . Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{Si}_3\text{Ti}$ (406.61): C 59.08, H 8.43. Found: C 58.47, H 8.42.

Reaction of Pentamethyl(trimethylsilylethynyl)disilane with Cp_2ZrCl_2 (11). Reaction was done analogously to the preparation of **2** using pentamethyl(trimethylsilylethynyl)disilane (**9**) (100 mg, 0.875 mmol), Cp_2ZrCl_2 (256 mg, 0.875 mmol), and Mg turnings (22 mg, 0.905 mmol). A turquoise oil of **11** (68%, 312 mg) was obtained. ^{29}Si NMR (THF/ D_2O , δ ppm): -11.5 (SiMe_3); -20.0 (SiMe_3); -28.5 (SiMe_2). ^1H NMR (δ ppm): 5.69 (s, 10H, Cp); 3.78 (m, THF); 1.90 (m, THF); 0.32 (s, 6H, SiMe_2); 0.25 (s, 9H, SiMe_3); 0.19 (s, 9H, SiMe_3). ^{13}C NMR (δ ppm): 214.3; 208.8; 106.6; 67.8; 25.8; 2.0; 0.3; -1.1 . Anal. Calcd for $\text{C}_{24}\text{H}_{42}\text{OSi}_3\text{Zr}$ (522.07): C 55.21, H 8.11. Found: C 54.50, H 8.17.

Reaction of Pentamethyl(trimethylsilylethynyl)disilane with Cp_2ZrCl_2 and PMe_3 (12). Reaction was done analogously to the preparation of **2** using pentamethyl(trimethylsilylethynyl)disilane (**9**) (100 mg, 0.438 mmol), Cp_2ZrCl_2 (128 mg, 0.438 mmol), PMe_3 (33 mg, 0.438 mmol), and Mg turnings (11 mg, 0.453 mmol). Orange crystals of **12** (163 mg, 71%) were obtained (using pentane instead of heptane). ^{29}Si NMR (δ ppm): -8.5 ($\equiv\text{C}-\text{SiMe}_3$); -20.1 (SiMe_3); -27.9 (d, $J = 3.8\text{ Hz}$, $-\text{SiMe}_2$). ^1H NMR (δ ppm):

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5.14 (d, $J = 1.2$ Hz, 10H, Cp); 1.05 (d, $J = 5.5$ Hz, 9H, PMe_3); 0.59 (s, 6H, $SiMe_2$); 0.29 (s, 9H, $SiMe_3$); 0.28 (s, 9H, $SiMe_3$). ^{13}C NMR (δ ppm): 202.0 (d, $J = 4.0$ Hz); 175.5 (d, $J = 11.2$ Hz); 102.6 (Cp); 18.7 (d, $J = 15.6$ Hz, PMe_3); 3.2; 1.3; -0.5 . ^{31}P NMR (δ ppm): 2.1. Anal. Calcd for $C_{23}H_{43}PSi_3Zr$ (526.05): C 52.51, H 8.24. Found: C 52.01, H 8.14.

Reaction of Pentamethyl(trimethylsilyl)ethynyl)disilane with Cp_2HfCl_2 and PMe_3 (13 and Hf complex 14). Reaction was done analogously to the preparation of **2** using pentamethyl(trimethylsilyl)ethynyl)disilane (**9**) (150 mg, 0.656 mmol), Cp_2HfCl_2 (249 mg, 0.656 mmol), PMe_3 (50 mg, 0.656 mmol), and Mg turnings (16 mg, 0.658 mmol). Yellow crystals of **13** (84 mg, 21%) were obtained together with red crystals of **14**. **13**: ^{29}Si NMR (δ ppm): -6.6 (d, $J = 2.8$ Hz, $SiMe_3$); -19.3 ($SiMe_3$); -25.9 (d, $J = 4.0$ Hz, $SiMe_2$). 1H NMR (δ ppm): 5.05 (d, $J = 1.6$ Hz, 10H, Cp); 1.12 (d, $J = 5.8$ Hz, PMe_3); 0.60 (s, 6H); 0.28 (s, 9H); 0.26 (s, 9H). ^{13}C NMR (δ ppm): 210.4 (d, $J = 5.2$ Hz); 182.5 (d, $J = 8.2$ Hz); 101.7 (Cp); 19.6 (d, $J = 18.6$ Hz, PMe_3); 3.4; 1.6; -0.4 . ^{31}P NMR (δ ppm): -8.9 . Anal. Calcd for $C_{23}H_{43}HfPSi_3$ (613.31): C 45.04, H 7.07. Found: C 44.49, H 7.13.

Reaction of Pentamethyl(phenylethynyl)disilane with Cp_2TiCl_2 (16). Reaction was done analogously to the preparation of **2** using pentamethyl(phenylethynyl)disilane (**15**) (100 mg, 0.430 mmol), Cp_2TiCl_2 (107 mg, 0.430 mmol), and Mg turnings (11 mg, 0.452 mmol). **16** (83 mg, 47%) was obtained as a red oil. ^{29}Si NMR (δ ppm): -19.0 ($SiMe_3$); -32.9 ($SiMe_2$). 1H NMR (δ ppm): 7.00 (m, 2H); 6.87 (m, 1H); 6.32 (s, 10H, Cp); 6.18 (m, 2H); 0.11 (s, 9H, $SiMe_3$); -0.21 (s, 6H, $SiMe_2$). ^{13}C NMR (δ ppm): 219.8; 212.0; 142.5; 128.7; 126.6; 126.0; 116.6 (Cp); -1.4 ($SiMe_3$); -1.8 ($SiMe_2$). Anal. Calcd for $C_{23}H_{30}Si_2Ti$ (410.52): C 67.29, H 7.37. Found: C 66.90, H 7.44.

Reaction of Pentamethyl(phenylethynyl)disilane with Cp_2ZrCl_2 (17). Reaction was done analogously to the preparation of **2** using pentamethyl(phenylethynyl)disilane (**15**) (200 mg, 0.860 mmol), Cp_2ZrCl_2 (229 mg, 0.782 mmol), and Mg turnings (21 mg, 0.864 mmol). Orange crystals of **17** were obtained (224 mg, 76%) (using pentane instead of heptane). ^{29}Si NMR (δ ppm): -18.9 ($SiMe_3$); -33.7 . 1H NMR (δ ppm): 6.82 (m, 4H); 6.71 (m, 2H); 6.62 (m, 4H); 6.18 (s, 10H, Cp); 0.08 (s, 18H, $SiMe_3$); -0.09 (s, 12H, $SiMe_2$). ^{13}C NMR (δ ppm): 203.2; 149.0; 146.4; 129.7; 127.1; 125.1; 111.6 (Cp); 1.4 ($SiMe_2$); -0.6 ($SiMe_3$). Anal. Calcd for $C_{36}H_{50}Si_4Zr$ (686.35): C 63.00, H 7.34. Found: C 62.58, H 7.57.

Reaction of Pentamethyl(phenylethynyl)disilane with Cp_2ZrCl_2 and PMe_3 (18). Reaction was done analogously to the preparation of **2** using pentamethyl(phenylethynyl)disilane (**15**) (100 mg, 0.430 mmol), Cp_2ZrCl_2 (126 mg, 0.430 mmol), PMe_3 (33 mg, 0.430 mmol), and Mg turnings (11 mg, 0.453 mmol). Orange crystals of **18** (155 mg, 68% yield) were obtained. ^{29}Si NMR (δ ppm): -20.4 ($SiMe_3$); -26.6 (d, $J = 3.2$ Hz, $SiMe_2$). 1H NMR (δ ppm): 7.15 (t, 2H); 6.92 (t, 1H); 6.67 (d, 2H); 5.33 (d, $J = 1.7$ Hz, 10H, Cp); 0.77 (d, $J = 6.0$ Hz, 9H, PMe_3); 0.45 (s, 6H, $SiMe_2$); 0.08 (s, 9H, $SiMe_3$). ^{13}C NMR (δ ppm): 180.2 (d, $J = 18.2$ Hz); 176.4 (d, $J = 7.3$ Hz); 157.8; 127.5; 123.3; 122.0; 103.0 (Cp); 17.2 (d, $J = 16.1$ Hz, PMe_3); -0.5 ($SiMe_2$); -1.6 ($SiMe_3$). ^{31}P NMR (δ ppm): -0.2 . Anal. Calcd for $C_{26}H_{39}PSi_2Zr$ (529.96): C 58.93, H 7.42. Found: C 59.07, H 7.36.

Reaction of Pentamethyl(phenylethynyl)disilane with Cp_2HfCl_2 and PMe_3 (19, 20): Reaction was done at 40 °C analogously to the preparation of **2** using pentamethyl(phenylethynyl)disilane (**15**) (100 mg, 0.430 mmol), Cp_2HfCl_2 (163 mg, 0.430 mmol), PMe_3 (33 mg, 0.430 mmol), and Mg turnings (11 mg, 0.453 mmol). An orange oil of **19** (125 mg, 47%) was obtained. ^{29}Si NMR (δ ppm): -20.1 ($SiMe_3$); -25.2 (d, $J = 3.3$ Hz, $SiMe_2$). 1H NMR (δ ppm): 7.15 (m, 2H); 6.91 (m, 2H); 6.63 (m, 1H); 5.26 (dd, $J = 0.4$ Hz; $J = 2.3$ Hz, 10H, Cp); 0.82 (d, $J = 6.2$ Hz, 9H, PMe_3); 0.44 (s, 6H, $SiMe_2$); 0.07 (s, 9H, $SiMe_3$). ^{13}C NMR (δ ppm): 187.0 (d, $J = 15.3$ Hz); 181.7 (d, $J = 7.7$ Hz); 159.9 (d, $J = 1.6$ Hz); 127.4;

123.4; 122.0; 102.2 (Cp); 17.5 (d, $J = 18.3$ Hz, PMe_3); -0.3 ($SiMe_2$); -1.5 ($SiMe_3$). ^{31}P NMR (δ ppm): -8.7 . Anal. Calcd for $C_{26}H_{39}HfPSi_2$ (617.22): C 50.59, H 6.37. Found: C 50.55, H 6.28. Repeating the experiment at rt after 3 days the solution contained a mixture of complex **19** and pentamethyl(phenylethynyl)disilane in a 1:1 ratio, and also some **14** could be observed. The solution was then heated to reflux for 14 h and cooled to rt, and the solvent was removed. The residue was twice treated with pentane and the precipitate removed by centrifugation. Slight yellow crystals of **20** (65 mg, 39%) were obtained from the pentane solution at rt. ^{29}Si NMR (δ ppm): -18.4 ($SiMe_3$); -31.8 ($SiMe_2$). 1H NMR (δ ppm): 6.82 (m, 4H); 6.72 (m, 2H); 6.64 (m, 2H); 6.11 (s, 10H, Cp); 0.09 (s, 18H, $SiMe_3$); -0.07 (s, 12H, $SiMe_2$). ^{13}C NMR (δ ppm): 202.0; 149.1; 147.0; 132.1; 129.9; 127.1; 111.0 (Cp); 1.6 ($SiMe_2$); -0.5 ($SiMe_3$). Anal. Calcd for $C_{36}H_{50}HfSi_4$ (773.61): C 55.89, H 6.51. Found: C 55.60, H 6.52.

Reaction of 2,2-Bis(phenylalkynyl)hexamethyltrisilane with Cp_2TiCl_2 (22). Reaction was done analogously to the preparation of **2** using 2,2-bis(phenylalkynyl)hexamethyltrisilane (**21**) (150 mg, 0.398 mmol), Cp_2TiCl_2 (99 mg, 0.398 mmol), and Mg turnings (10 mg, 0.411 mmol). Orange crystals of **22** (117 mg, 53%) were obtained. ^{29}Si NMR (δ ppm): -15.7 ($SiMe_3$); -58.3 . 1H NMR (δ ppm): 7.93 (m, 24H); 7.67 (m, 28H); 7.43 (m, 3H); 7.36 (m, 3H); 5.38 (s, 10H, Cp); 0.21 (s, 36H, $SiMe_3$). ^{13}C NMR (δ ppm): 256.3; 212.0; 146.0; 141.5; 140.9; 129.3; 128.9; 128.6; 127.8; 126.8; 126.7; 105.8; 72.0; -0.1 . Anal. Calcd for $C_{32}H_{38}Si_3Ti$ (554.77): C 69.28, H 6.90. Found: C 68.81, H 6.82.

Reaction of 2,2-Bis(phenylalkynyl)hexamethyltrisilane with Cp_2ZrCl_2 (23). Reaction was done analogously to the preparation of **2** using 2,2-bis(phenylalkynyl)hexamethyltrisilane (**21**) (150 mg, 0.398 mmol), Cp_2ZrCl_2 (58 mg, 0.199 mmol), and Mg turnings (5 mg, 0.205 mmol). Yellow crystals of **23** (120 mg, 62%) were obtained. ^{29}Si NMR (δ ppm): -15.1 ($SiMe_3$); -76.0 . 1H NMR (δ ppm): 7.48 (m, 4H); 7.04 (m, 8H); 6.78 (m, 8H); 6.61 (s, 10H, Cp); 0.29 (s, 36H, $SiMe_3$). ^{13}C NMR (δ ppm): 195.9; 157.0; 147.9; 131.7; 128.9; 128.8; 127.8; 125.5; 124.9; 113.5 (Cp); 110.1; 100.2; 0.8 ($SiMe_3$). Anal. Calcd for $C_{54}H_{66}Si_6Zr$ (974.84): C 66.53, H 6.82. Found: C 65.94, H 6.88.

Reaction of 2,2-Bis(phenylalkynyl)hexamethyltrisilane with 3 equiv of Cp_2ZrCl_2 (24). Reaction was done analogously to the preparation of **2** using 2,2-bis(phenylalkynyl)hexamethyltrisilane (200 mg, 0.531 mmol), Cp_2ZrCl_2 (466 mg, 1.593 mmol), and Mg turnings (39 mg, 1.605 mmol). A red crystalline solid of **24** (165 mg, 52%) was obtained. ^{29}Si NMR (δ ppm): -16.1 ($SiMe_3$); -48.3 . 1H NMR (δ ppm): 7.98 (m, 2H); 7.62 (m, 2H); 7.39 (m, 4H); 7.20 (m, 2H); 5.64 (s, 10H, Cp); 0.21 (s, 18H, $SiMe_3$). ^{13}C NMR (δ ppm): 246.9; 203.5; 154.5; 143.0; 141.7; 129.4; 128.7; 128.4; 127.1; 127.9; 126.7; 106.4 (Cp); 91.9; -0.3 ($SiMe_3$). Anal. Calcd for $C_{32}H_{38}Si_3Zr$ (598.12): C 64.26, H 6.40. Found: C 64.29, H 6.21.

Reaction of 1,4-Bis[tris(trimethylsilyl)silyl]butadiyne (25) with Cp_2ZrCl_2 (26). Reaction was done analogously to the preparation of **2** using 1,4-bis[tris(trimethylsilyl)silyl]butadiyne (**25**) (50 mg, 0.092 mmol), Cp_2ZrCl_2 (27 mg, 0.092 mmol), and Mg turnings (3 mg, 0.123 mmol). A red crystalline solid of **26** (34 mg, 48%) was obtained. ^{29}Si NMR (δ ppm): -12.4 ($SiMe_3$); -82.4 . 1H NMR (δ ppm): 5.24 (s, 10H, Cp); 0.40 (s, 54H, $SiMe_3$). ^{13}C NMR (δ ppm): 176.2; 131.4; 104.7 (Cp); 1.0 ($SiMe_3$). Anal. Calcd for $C_{32}H_{64}Si_8Zr$ (764.76): C 50.26, H 8.44. Found: C 50.63, H 8.66.

Derivatization Reactions. Reaction of 2 with I_2 : 1,4-Diiodo-1,4-bis[bis(trimethylsilyl)silyl]butadiene (27). In a J-Young tube **2** (42 mg, 0.055 mmol) and I_2 (28 mg, 0.110 mmol) were dissolved in 3 mL of THF. After 1 h the orange suspension was diluted with 5 mL of pentane and then poured onto an aqueous $Na_2S_2O_3$ solution. The layers were separated and the organic layer treated once again with brine. After drying with $NaSO_4$ **27** (14 mg, 32%) was obtained

as a semicrystalline solid. ^{29}Si NMR (δ ppm): -11.2 ; -53.0 . ^1H NMR (δ ppm): 7.34 (s, 2H); 0.34 (s, 54H). Anal. Calcd for $\text{C}_{22}\text{H}_{56}\text{I}_2\text{Si}_8$ (799.17): C 33.06, H 7.06. Found: C 32.73, H 7.12.

Reaction of 17 with I_2 : 1,4-Diiodo-1,4-pentamethyldisilanyl-2,3-diphenyl-butadiene (28). Reaction was carried out analogously to the preparation of **27** with **17** (100 mg, 0.146 mmol) and I_2 (74 mg, 0.291 mmol). **28** (54 mg, 37%) was obtained as a yellow oil. ^{29}Si NMR (δ ppm): -10.4 ; -17.5 . ^1H NMR (δ ppm): 7.44 (m, 4H); 6.92 (m, 6H); 0.41 (s, 12H); 0.25 (s, 18H). Anal. Calcd for $\text{C}_{26}\text{H}_{40}\text{I}_2\text{Si}_4$ (718.75): C 43.45, H 5.61. Found: C 42.91, H 5.59.

Reaction of 17 with HCl: 1,4-Pentamethyldisilanyl-2,3-diphenylbutadiene (29). A solution of **17** (300 mg, 0.437 mmol) in pentane (2 mL) was added dropwise to a stirred 6 M solution of aqueous HCl (3 mL) at 0°C . After 1 h the organic layer was separated and washed with saturated NaHCO_3 . **29** (140 mg, 68%) was obtained as a colorless oil after drying with NaSO_4 and evaporation of the solvent. ^{29}Si NMR (δ ppm): -18.6 ; -26.7 . ^1H NMR (δ ppm): 7.35 (m, 6H); 7.05 (m, 4H); 5.62 (s, 2H); -0.01 (s, 18H); -0.24 (s, 12H). ^{13}C NMR (δ ppm): 159.3 ; 142.6 ; 133.2 ;

129.8 ; 128.6 ; 128.5 ; -1.7 ; -3.1 . Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{Si}_4$ (466.95): C 66.88, H 9.07. Found: C 66.11, H 8.89.

Reaction of 2 with KO^tBu (30). Compound **2** (70 mg, 0.09 mmol) was solved in 3 mL of THF, and KO^tBu (21 mg, 0.183 mmol) was added. After stirring for 4 h the reaction was complete and the solvent was removed, yielding **30** as an oily residue (46 mg, 73%). ^{29}Si NMR (δ ppm): -16.1 ; -89.4 . ^1H NMR (δ ppm): 6.26 (s, 2H); 5.87 (s, 10H, Cp); 0.37 (s, 36H, SiMe_3).

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Supporting Information Available: X-ray crystallographic information for compounds **2**, **4**, **6**, **7**, **12**, **13**, **14**, **17**, **20**, **22**, **23**, **24**, **26**, and **27** in CIF format are available free of charge via the Internet at <http://pubs.acs.org>.

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