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Transition-Metal-Catalyzed Bis-Silylation of Propyne by [2]Chromoarenophanes

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A crystal structure determination of the thf adduct of dilithiated bis(benzene)chromium disclosed an unsymmetrical, dimeric composition in the solid state, i.e., a formula of $[Cr(\eta^6\text{-}C_6H_5Li)_2]_2\cdot(thf)_7$, in which both subunits are connected by three bridging lithium atoms. The [2]silachromoarenophanes $[Cr(\eta^6\text{-}C_6H_5)_2Si_2Me_4]$ and $[Cr(\eta^5\text{-}C_5H_4)(\eta^7\text{-}C_7H_6)Si_2Me_4]$ were prepared in high yields by salt elimination reactions of the corresponding dimetalated sandwich complexes with $Cl_2Si_2Me_4$. Structural characterization by X-ray diffraction of $[Cr(\eta^6\text{-}C_6H_5)_2Si_2Me_4]$ revealed the presence of only weak molecular ring strain demonstrated by a tilt angle of 2.78(12)° [cf. $[Cr(\eta^5\text{-}C_5H_4)(\eta^7\text{-}C_7H_6)Si_2Me_4]$, 2.60(15)°]. These species were successfully employed as precursors for the transition-metal-catalyzed bis-silylation of propyne to yield *ansa*-bis(silyl)alkenes. The reactions were accomplished under homogeneous catalysis conditions employing 5 mol % $[Pd(PPh_3)_4]$ at 125 °C. The formation of the bis-silylated products was authenticated by a crystal structure analysis of the trochrocene derivative $[Cr(\eta^7\text{-}C_7H_6)SiMe_2C(Me){=}C(H)SiMe_2(\eta^5\text{-}C_5H_4)]$.

Introduction

The first reports of the selective dimetalation of ferrocene, $[Fe(\eta^5\text{-}C_5H_5)_2]$,[1] and bis(benzene)chromium, $[Cr(\eta^6\text{-}C_6H_6)_2]$,[2] by BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) were an early and important achievement in organometallic chemistry and disclosed access to a variety of ring-substituted metallocene derivatives, in particular to *ansa*-bridged-type systems. To date, an entire string of different bridging atoms has been realized,[3] and their application in the synthesis of metal-containing polymers via ring opening polymerization (ROP) has been described in detail and can be considered as a fundamental highlight in both organometallic chemistry and materials science.[4] The intrinsic molecular ring strain of [*n*]-metallocenophanes is also reflected by an enhanced reactivity of the strained bond between the aryl ligands and the bridging element(s)[3f,5] or between the bridging elements[6] or the M−arene bond,[7] which led to the isolation of several insertion and ring opening products. Recently, we showed that [2]borametalloarenophanes are susceptible to strain release by transition-metal-mediated insertion of alkynes into the strained B−B bond, which was achieved under stoichiometric as well as homogeneous and heterogeneous catalysis conditions.[6c] Here we report on the extension of this chemistry to the palladium-mediated insertion of propyne into the Si−Si bond of disilane-bridged derivatives of bis(benzene)chromium, $[Cr(\eta^6\text{-}C_6H_5)_2Si_2Me_4]$ (**1**), and trochrocene, $[Cr(\eta^5\text{-}C_5H_4)(\eta^7\text{-}C_7H_6)Si_2Me_4]$ (**2**). In addition, a more convenient route for the preparation of **1** as well as the solid-state structures of **1** and the dilithiated bis(benzene)-chromium precursor is presented.

Results and Discussion

The readily accessible [2]silachromoarenophanes **1** and **2** were prepared by salt elimination reactions of the dilithiated precursors, i.e., $[Cr(\eta^6\text{-}C_6H_5Li)_2]\cdot$tmeda and $[Cr(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6\text{-}Li)]\cdot$tmeda, and $Cl_2Si_2Me_4$ in aliphatic solvents, as described

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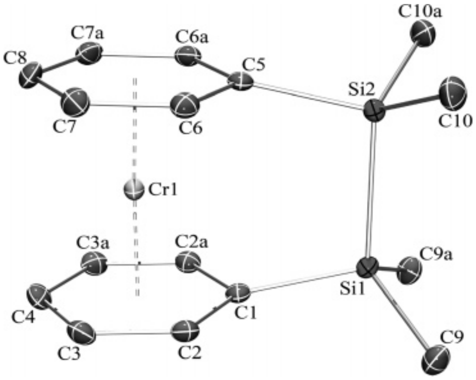
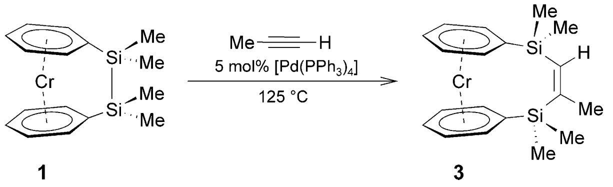


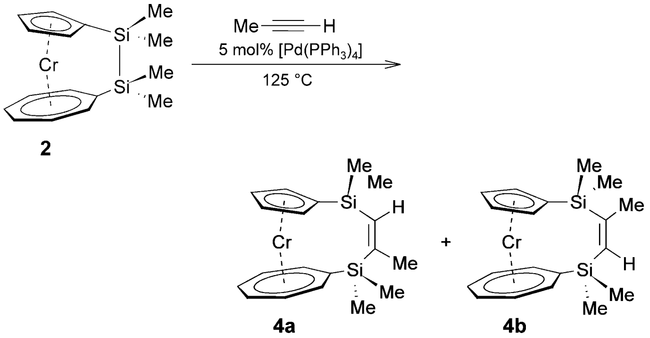
Figure 1. Molecular structure of **1**. Symmetry-related positions (x, $-y + 1/2$, z) are labeled with "a". Selected distances (Å) and angles (deg): Cr1−C1, 2.1604(21); Cr1−C2, 2.1490(15); Cr1−C3, 2.1572(15); Cr1−C4, 2.1554(22); Cr1−C5, 2.1600(21); Cr1−C6, 2.1427(15); Cr1−C7, 2.1501(15); Cr1−C8, 2.1589(23); C1−Si1, 1.8874(22); C5−Si2, 1.8924(23); Si1−Si21, 2.3394(8); Cr1−X_{Ph1}, 1.622; Cr1−X_{Ph2}, 1.616; C1−Si1−Si2, 102.79(7); C5−Si2−Si1, 102.18(7); C1−Si1−Si2−C5, 0.00; X_{Ph1}−Cr1−X_{Ph2}, 177.80 (X_{Ph1} = centroid of the C_6H_5 ring C1−C4; X_{Ph1} = centroid of the C_6H_5 ring C5−C8).

previously for the trochrocene derivative **2**.[8] Following this synthetic protocol, **1** was obtained as an orange crystalline material in high yields of 80%. The identity was confirmed by NMR spectroscopy, which afforded data consistent with those reported in the literature.[9] In contrast, the published procedure for the synthesis of **1** requires the utilization of MVS (MVS = metal vapor synthesis) techniques and a low-yield reductive coupling step with an overall yield of only 15%.[9] The formation of the disila bridge in **1** was confirmed by a single-crystal X-ray diffraction study (Figure 1). As expected, the geometry of **1** is found to be only slightly distorted in comparison to that of the parent sandwich complex[10] with a tilt angle $\alpha = 2.78(12)°$ between the planes of the six-membered rings. This value is in accordance with tilt angles found in **2** [2.60(15)°][8] or the structurally related [2]silaferrocenophanes[11] and [2]silatrovacenophanes.[12] In addition, the angle δ [177.80°], defined by the ring centroids and the metal center, indicates an almost ideal linear arrangement [cp. **2**, 177.24°]. Consequently, the molecular ring strain in these systems seems to be notedly diminished with respect to that found in the corresponding [2]bora complexes, arguably because of the longer Si−Si bond.[3i,6b] The absence of molecular ring strain is also reflected by the geometry around the bridging silicon centers that display an almost ideal tetrahedral environment, whereas the largest discrepancy is found for the *ipso*-carbon−Si−Si angles [C1−Si1−Si2, 102.79(7)°; C5−Si2−Si1, 102.18(7)°]. The two benzene rings adopt an eclipsed position, highlighted by the torsion angle C1−Si1−Si2−C5 equal to 0.00°, which is in contrast to the staggered conformation found for the previously reported [2]bora derivative [dihedral angle 11.4(5)°].[3i]

Scheme 1. Palladium-Catalyzed Insertion of Propyne To Yield 3



Scheme 2. Palladium-Mediated Syntheses of the *ansa*-Bis(silyl)alkenes 4a/b



Contrary to the facile oxidative addition of the strained B−B bond of the corresponding [2]bora congeners to the Pt center of [Pt(PEt_3)$_3$],[6c] the Si−Si bond of **1** and **2** turned out to be much more resistant. Thus, stoichiometric reaction with different transition-metal complexes such as [Pt(PEt_3)$_3$], [Pt(PCy_3)$_2$], [Pd(PPh_3)$_4$], or [Pd(^{t}BuNC)$_2$] proved to be unsuccessful even at elevated temperature, whereas either unreacted starting material or decomposition products could be detected. With this unsatisfying result in mind, we turned our attention to catalytic processes for the bis-silylation of alkynes, which was already successfully demonstrated for the palladium-catalyzed insertion of alkynes into the disilane bridge of [2]silaferrocenophane.[6a] As depicted in Schemes 1 and 2, toluene solutions of **1** and **2** were treated with excess propyne in the presence of catalytic amounts of [Pd(PPh_3)$_4$]. In a typical experiment, a sealable tube was charged with the *ansa* complex, a 10-fold excess of propyne, and 5 mol % [Pd(PPh_3)$_4$] and was heated to 125 °C. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and the gradual consumption of the starting materials and the formation of the bis-silylated products **3** and **4** were observed. The reaction proceeded quantitatively within 48 h and was not accompanied by the formation of soluble side or degradation products. **3** and **4** were isolated analytically pure after recrystallization from pentane in very high yields of 92% and 95%, respectively. During the synthesis of **4**, the crude reaction mixture revealed the presence of the two regioisomers **4a** and **4b** in a ratio of 3:1, with the methyl group of the bridging −C(Me)=C(H)− moiety pointing toward the C_7H_6 ring or toward the C_5H_4 ring, respectively (Scheme 2). The pure isomer **4a** was separated by crystallization from diluted pentane solutions. It should be noted that control experiments were carried out which confirmed that the [2]silachromoarenophanes **1** and **2** underwent no reaction with propyne in the absence of the palladium catalyst.

The ^{1}H NMR spectra of **3** and **4a/b** are consistent with time-averaged C_s symmetry in solution and display the characteristic signal pattern for the Me (doublet) and H (quartet) substituents of the bridging alkene moiety [**3**, $\delta = 2.12$ (3H), 6.65 (1H); **4a**, $\delta = 2.23$ (3H), 6.66 (1H); **4b**, $\delta = 2.11$ (3H), 6.84 (1H)]. Likewise, the silicon-bound methyl groups are observed as two well-separated resonances [**3**, $\delta = 0.33$ and 0.36; **4a**, $\delta = 0.26$

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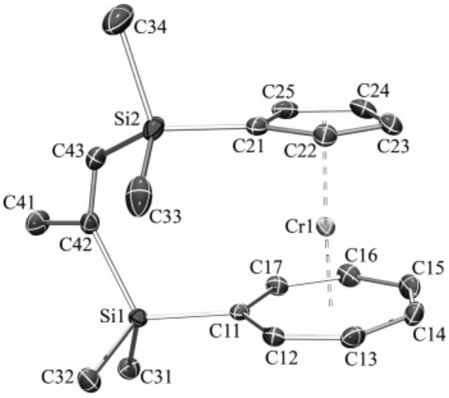

Figure 2. Molecular structure of **4a**. Selected distances (Å) and angles (deg): Cr1−C11, 2.1939(18); Cr1−C12, 2.1768(18); Cr1−C13, 2.1653(18); Cr1−C14, 2.1599(18); Cr1−C15, 2.1615(19); Cr1−C16, 2.1575(18); Cr1−C17, 2.1542(18); Cr1−C21, 2.2037(18); Cr1−C22, 2.1872(18); Cr1−C23, 2.1842(18); Cr1−C24, 2.1843(19); Cr1−C25, 2.1845(18); C11−Si1, 1.8838(18); C21−Si2, 1.8586(20); Si1−C42, 1.8928(18); Si2−C43, 1.8723(20); C41−C42, 1.5244(22); C42−C43, 1.3423(27); Cr1−X_{Cht}, 1.432; Cr1−X_{Cp}, 1.825; C11−Si1−C42, 115.55(8); C21−Si2−C43, 111.54(9); Si1−C42−C43, 126.23(14); Si2−C43−C42, 134.47(15); C41−C42−C43, 119.23(16); Si1−C42−C41, 114.40(13); Si1−C42−C43−Si2, 0.65(30); C41−C42−C43−Si2, 176.20(16); X_{Cht}−Cr1−X_{Cp}, 176.60 (X_{Cht} and X_{Cp} = centroids of the C_7H_6 and the C_5H_4 rings, respectively).

and 0.54; **4b**, $\delta = 0.23$ and 0.59]. Both complexes **3** and **4a/b** comprise two chemically nonequivalent silicon nuclei, which are detected as two distinct signals in the corresponding ^{29}Si NMR spectra [**3**, $\delta = -9.91$ and -5.56; **4a**, $\delta = -14.48$ and -2.03; **4b**, $\delta = -9.62$ and -5.66]. As expected, the chemical shifts strongly resemble those of the starting compounds **1** [$\delta = -12.67$] and **2** [$\delta = -14.8$ and 6.90].[8] The ^{13}C NMR signals of the unsaturated alkene carbon atoms [**3**, $\delta = 145.31$ and 158.42; **4a**, $\delta = 143.55$ and 157.81; **4b**, $\delta = 144.56$ and 155.38] are found in a region very similar to that reported for the related ferrocenophanes.[6a] To authenticate the formation of the bis-silylated products, a single-crystal diffraction study of **4a** was conducted (Figure 2). The bis(silyl)alkene subunit exhibits an almost planar environment, demonstrated by the torsion angles Si1−C42−C43−Si2 [0.65(30)°] and C41−C42−C43−Si2 [176.20(16)°]. Interestingly, the Si−C═C angles are perspicuously widened [126.23(14)° and 134.47(15)°] with respect to the expected value of 120° for an sp^2 carbon center, and as a consequence, the angle Si1−C42−C41 appears slightly contracted to a value of 114.40(13)°. However, the C═C bond length [1.3423(27) Å] is only marginally elongated compared to the typical value of carbon−carbon double bonds [1.317 Å].[13] The silicon−carbon bond distances lie within the expected range [between 1.8586(20) and 1.8928(18) Å], and the geometry around the silicon centers deviates only fractionally from the ideal tetrahedral arrangement. In contrast to the molecular structure of **2**,[8] the silicon atoms lie slightly above and below the planes of the C_5H_4 and C_7H_6 moieties, respectively, resulting in a complementary tilting of these carbocycles with respect to the *ansa* bridge [$\alpha = 4.27(10)°$]. This trend is also illustrated by the chromium−*ipso*-carbon bond distances that represent the longest Cr−C bond to both aromatic rings in **4a** [2.1939(18) and 2.2037(18) Å].

During the course of our studies on strained metalloarenophanes, we also became interested in the structural characterization of the dimetalated sandwich precursors, whose high reactivity eluded structural characterization by X-ray diffraction for several years, even though the structural parameters are of great interest. In fact, structural data of metalated sandwich complexes are actually rare to date, though several examples are reported in the literature, for instance, the long known dilithiated ferrocene derivatives $[Fe(\eta^5\text{-}C_5H_4Li)_2]\cdot$pmdta[14] (pmdta = *N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) and $[Fe(\eta^5\text{-}C_5H_4Li)_2]_3\cdot(tmeda)_2$.[15] Recently, we added the molecular structures of dilithiated $[Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$,[16] bis(benzene)molybdenum, $[Mo(\eta^6\text{-}C_6H_6)_2]$,[17] and trochrocene[18] to this area of research. The structural characterization of selectively mono-, di-, and tetrametalated ferrocene as well as monometalated bis(benzene)chromium by Mulvey et al. and Jäkle et al. also contributed to the understanding of the fundamentals that determine the conformation of this class of organometallic compounds.[19] However, the solid-state structure of the dilithiated bis(benzene)chromium derivative employed in the synthesis of **1** remained unknown to date, even though the synthesis was already published in 1968. Thus, recrystallization of $[Cr(\eta^6\text{-}C_6H_5Li)_2]\cdot$tmeda (**5**·tmeda) from a saturated thf solution at −70 °C yielded red crystals that were formulated as **5**·(thf)$_3$ on the basis of ^{1}H NMR spectroscopy; i.e., dissolving in thf causes the replacement of the tmeda ligand by coordinating thf molecules. As expected, the NMR spectroscopic data in [D$_8$]-thf solution are very similiar to those of the tmeda adduct (**5**·tmeda). The solid-state structure consists of two bis(benzene)-chromium fragments deprotonated in the 1,1′-positions that are connected by two bridging lithium atoms (Li2 and Li3), one semibridging lithium atom (Li1), and one terminal lithium atom (Li4) (Figure 3). The unsaturated lithium centers are stabilized by the coordination of the deprotonated *ipso*-carbon atoms of the C_6H_5 rings and the thf oxygen atoms. The thf molecules show extensive disorder, thus requiring a combination of constraints and restraints in the refinement, and as a consequence, the structural parameters within these moieties are excluded from the following discussion. Four distinct lithium environments can be distinguished: (1) The semibridging lithium atom Li1 adopts a highly distorted tetrahedral geometry. Stabilization is achieved by the coordination of two *ipso*-carbon atoms of two different C_6H_5 moieties and two thf molecules. The lithium···carbon separation distance Li1···C31 [2.457(8) Å] is significantly elongated with respect to the other Li−C bonds (vide infra), but notedly shorter than the related Li4···

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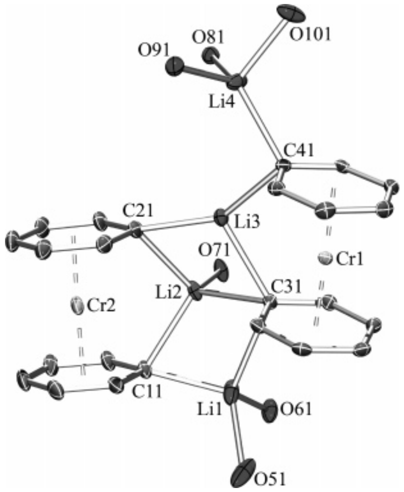

Figure 3. Molecular structure of the $[Cr(\eta^6\text{-}C_6H_5Li)_2]_2\cdot(thf)_7$ (**5**) solvate. For clarity, only the oxygen atoms of the thf molecules are shown and thf molecules incorporated in the crystal lattice are omitted. Selected bond lengths (Å) and angles (deg): Li1−Li2, 2.510(11); Li2−Li3, 2.393(9); Li3−Li4, 3.062(9); Li1−C11, 2.151(8); Li1−C31, 2.457(8); Li2−C11, 2.184(7); Li2−C21, 2.217(8); Li2−C31, 2.277(7); Li3−C21, 2.131(7); Li3−C31, 2.214(7); Li3−C41, 2.118(7); Li4−C41, 2.159(7); Cr2−C_{Ph1}, 2.130(4)−2.229(4) [av 2.157(4)]; Cr2−C_{Ph2}, 2.132(4)−2.232(4) [av 2.157(4)]; Cr1−C_{Ph3}, 2.130(3)−2.230(3) [av 2.155(3)]; Cr1−C_{Ph4}, 2.128(3)−2.226(3) [av 2.153(3)]; Cr2−X_{Ph1}, 1.621; Cr2−X_{Ph2}, 1.622; Cr1−X_{Ph3}, 1.619; Cr1−X_{Ph4}, 1.618; C11−Li1−C31, 100.90(31); C11−Li2−C21, 96.27(26); C11−Li2−C31, 105.79(29); C11−Li2−O71, 118.34(41); C21−Li2−C31, 106.29(27); C21−Li2−O71, 118.62(58); C31−Li2−O71, 109.93(36); C21−Li3−C31, 111.70(29); C21−Li3−C41, 148.56(35); C31−Li3−C41, 98.01(26); X_{Ph1}−Cr2−X_{Ph2}, 177.8; X_{Ph3}−Cr1−X_{Ph4}, 178.2 (X_{Ph1} = centroid of the C_6H_5 ring C11−C16; X_{Ph2} = centroid of the C_6H_5 ring C21−C26; X_{Ph3} = centroid of the C_6H_5 ring C31−C36; X_{Ph4} = centroid of the C_6H_5 ring C41−C46).

C21 contact [4.217 Å]. Similar stabilization effects were observed in the crystal structure of $[Fe(\eta^5\text{-}C_5H_4Li)_2]_3\cdot(tmeda)_2$; the interaction was described as the completion of the tetrahedral coordination sphere of the unsaturated lithium center via η^1-bonding to the deprotonated carbon atom or by a Li···C−H interaction.[15] Hence, there seems little doubt that the stabilizing interaction exists in **5** and consists most probably of a η^1-bonding mode to the deprotonated carbon atom C31. (2) Both bis(benzene)chromium subunits act as bidentate ligands to one of the bridging lithium atoms through the deprotonated *ipso*-carbons (Li2, C11 and C21; Li3, C31 and C41) and further stabilize the other bridging lithium atom by coordination of the inner *ipso*-carbon atom (Li2−C31 and Li3−C21). As expected for a tetracoordination, Li2 exhibits a distorted tetrahedral geometry with one additional thf molecule on the fourth coordination side. (3) In contrast, the unsaturated lithium atom Li3 remains three-coordinate and displays a distorted trigonal planar environment ($\Sigma = 358.2°$). (4) The terminal lithium atom Li4 is bound to the *ipso*-carbon of one six-membered ring and is further stabilized by the coordination of three thf oxygen atoms, thus featuring a tetrahedral geometry. Both the Li−C bond distances [2.118(7)−2.277(7) Å][14−18] and the Li−O bond lengths [1.897(8)−2.081(11) Å][20] lie within previously reported ranges. The Li···Li separation distances between the Li1, Li2, and Li3 atoms [Li1···Li2 = 2.510(11) and Li2···Li3 = 2.393(9) Å] differ significantly from that to the terminal lithium atom [Li3···Li4 = 3.062(9) Å], which is in agreement with the structural parameters found in related dilithiated sandwich complexes.[14−18] The relatively short values of the two former are very similiar to that found in cylcohexyllithium [2.397 Å][21] and might suggest a direct lithium−lithium interaction. However, according to earlier investigations on alkyllithium reagents, this type of stabilization is weak at best.[22] The structural parameters of the bis(benzene)chromium subunits are in agreement with the anticipated attributes of an unstrained 1,1′-disubstituted sandwich molecule. The chromium−CH carbon bond distances are found within the range 2.128(3)−2.158(4) Å, though the chromium−*ipso*-carbon bonds are significantly elongated for both six-membered rings [between 2.226(3) and 2.232(4) Å].

Conclusion

In conclusion, we showed that the readily available [2]-silachromoarenophanes $[Cr(\eta^6\text{-}C_6H_5)_2Si_2Me_4]$ and $[Cr(\eta^5\text{-}C_5H_4)(\eta^7\text{-}C_7H_6)Si_2Me_4]$ can be employed in the homogeneously catalyzed bis-silylation of propyne to yield *ansa*-bis(silyl)-alkenes. As a consequence of the lower molecular ring strain, these systems exhibit a diminished reactivity in comparison to the analogous [2]bora derivatives; hence, the syntheses require higher temperatures. The determination of the solid-state structure of $[Cr(\eta^6\text{-}C_6H_5Li)_2]_2\cdot(thf)_7$ revealed an unsymmetric dimeric composition and contributes to the understanding of the fundamentals that determine the conformation of this class of organometallic compounds.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox. Solvents were dried according to standard procedures, freshly distilled prior to use, degassed, and stored under argon over activated molecular sieves. Deuterated solvents were distilled from potassium over a glass bridge and subjected to several freeze−pump−thaw cycles. $[Cr(\eta^6\text{-}C_6H_5Li)_2]\cdot tmeda$[2] and $[Cr(\eta^5\text{-}C_5H_4)(\eta^7\text{-}C_7H_6)Si_2Me_4]$[8] were prepared according to known methods. $Cl_2Si_2Me_4$ was obtained from Aldrich and distilled from magnesium turnings before use. All other chemicals were obtained commercially and were used without further purification. Propyne was used as a 5.0 mol L^{-1} solution in toluene. The NMR spectra were recorded on a Bruker AV 500 (^1H, 500.13 MHz; ^7Li, 194.37 MHz, ^{13}C, 125.76 MHz; ^{29}Si, 99.26 MHz) FT-NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to external TMS via the residual protio of the solvent (^1H) or the solvent itself (^{13}C). $^7Li\{^1H\}$ NMR spectra were referenced to external LiCl and $^{29}Si\{^1H\}$ NMR spectra to external TMS. Microanalyses for C, H, and N were performed on a Leco CHNS-932 elemental analyzer.

$[Cr(\eta^6\text{-}C_6H_5)_2Si_2Me_4]$ (1). A slurry of **5**·tmeda (0.75 g, 2.23 mmol) in hexane (10 mL) was cooled to −78 °C and treated dropwise over a period of 2 h with a solution of $Cl_2Si_2Me_4$ (0.42 g, 2.23 mmol) in hexane (5 mL). After complete addition, the reaction mixture was stirred for an additional 2 h at −78 °C and subsequently allowed to reach ambient temperature. During this time, the color of the suspension turned from pale brown to red, and a white precipitate was deposited. After the solid had settled,

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the solution was filtered into another flask by a filter cannula, and the filtrate was concentrated to about 3 mL in volume. Cooling to −60 °C afforded **1** as an orange crystalline solid, which was obtained analytically pure after washing with cold pentane (3 × 3 mL, −100 °C) and drying in vacuo (0.57 g, 1.78 mmol, 80%). Crystals were grown from saturated hexane solutions at −30 °C. ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 0.36$ (s, 12H, SiMe_2), 4.37 (m, 6H, C_6H_5), 4.73 (m, 4H, C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = -0.04$ (SiMe_2), 78.62, 79.03, 82.85 (C_6H_5), 80.88 (*ipso*-C_6H_5). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 297 K): $\delta = -12.67$. Anal. Calcd for $C_{16}H_{22}CrSi_2$ (322.51): C, 59.57; H, 6.88. Found: C, 59.77; H, 7.20.

[Cr(η^6-C_6H_5)SiMe$_2$C(Me)═C(H)SiMe$_2$(η^6-C_6H_5)] (3). A resealable tube was charged with **1** (0.10 g, 0.31 mmol), [Pd(PPh_3)$_4$] (17.1 mg, 15.5 μmol, 5 mol %), propyne (620 μL, 3.10 mmol, 10 equiv), and toluene (4 mL) and heated to 125 °C over a period of 48 h. All volatiles were removed in vacuo, and the residue was extracted with pentane (2 × 2 mL). The solution was filtered into another flask by a filter cannula, and the remaining insoluble material was dried in vacuo. Hereby, analytically pure [Pd(PPh_3)$_4$] could be recovered almost quantitatively. Concentration of the filtrate to about 1.5 mL in volume and storage at −60 °C afforded **3** as an orange microcrystalline solid (0.10 g, 0.29 mmol, 92%). ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 0.33$ (s, 6H, SiMe_2), 0.36 (s, 6H, SiMe_2), 2.12 (d, 3H, $^4J_{\mathrm{HCCCH}} = 1.65$ Hz, ═CMe), 4.25 (m, 2H, C_6H_5), 4.31 (m, 8H, C_6H_5), 6.65 (q, 1H, $^4J_{\mathrm{HCCCH}} = 1.65$ Hz, ═CH). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 0.80$, 1.56 (SiMe_2), 32.79 (═CMe), 73.97, 74.43 (*ipso*-C_6H_5), 74.94, 75.16, 77.15, 77.40, 79.05, 79.50 (C_6H_5), 145.31 (═CH), 158.42 (═CMe). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 297 K): $\delta = -9.91$, −5.56. Anal. Calcd for $C_{19}H_{26}CrSi_2$ (362.58): C, 62.94; H, 7.23. Found: C, 63.11; H, 7.53.

[Cr(η^7-C_7H_6)SiMe$_2$C(R)═C(R′)SiMe$_2$(η^5-C_5H_4)] [4a (R = Me, R′ = H), 4b (R = H, R′ = Me)]. The reaction was performed analogously to that of **3**, employing **2** (0.10 g, 0.31 mmol), [Pd(PPh_3)$_4$] (17.1 mg, 15.5 μmol, 5 mol %), propyne (620 μL, 3.10 mmol, 10 equiv), and toluene (4 mL). The reaction was complete after the mixture was heated to 125 °C for 48 h. After removal of all volatiles in vacuo, the residue was extracted with pentane, yielding the pure catalyst and a turquoise solution. The filtrate was concentrated to about 1.5 mL in volume and stored at −80 °C to afford a mixture of the regioisomers **4a** and **4b** in a ratio of 3:1 as a green solid (0.11 g, 0.29 mmol, 95%). The major isomer **4a** was obtained analytically pure as a green crystalline material upon recrystallization from diluted pentane solutions at −35 °C. Crystals suitable for X-ray diffraction were grown from saturated hexane solutions at −30 °C.

Data for 4a (Isolated Pure after Recrystallization). ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 0.26$ (s, 6H, SiMe_2), 0.54 (s, 6H, SiMe_2), 2.23 (d, 3H, $^4J_{\mathrm{HCCCH}} = 4.10$ Hz, ═CMe), 3.79 (m, 2H, C_5H_4), 3.89 (m, 2H, C_5H_4), 5.56 (m, 4H, C_7H_6), 5.68 (m, 2H, C_7H_6), 6.66 (q, 1H, $^4J_{\mathrm{HCCCH}} = 4.10$ Hz, ═CH). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 0.82$, 1.59 (SiMe_2), 32.37 (═CMe), 74.11 (*ipso*-C_5H_4), 79.06, 79.95 (C_5H_4), 86.66 (*ipso*-C_7H_6), 87.66, 89.00, 90.98 (C_7H_6), 144.38 (═CH), 158.64 (═CMe). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 297 K): $\delta = -14.48$, −2.03. Anal. Calcd for $C_{19}H_{26}CrSi_2$ (362.58): C, 62.94; H, 7.23. Found: C, 63.29; H, 7.17.

Data for 4b (Crude Mixture with 4a). ^{1}H NMR (500 MHz, C_6D_6, 297 K): $\delta = 0.23$ (s, 6H, SiMe_2), 0.59 (s, 6H, SiMe_2), 2.11 (d, 3H, $^4J_{\mathrm{HCCCH}} = 4.10$ Hz, ═CMe), 3.74 (m, 2H, C_5H_4), 3.87 (m, 2H, C_5H_4), 5.54 (m, 4H, C_7H_6), 5.69 (m, 2H, C_7H_6), 6.84 (q, 1H, $^4J_{\mathrm{HCCCH}} = 4.10$ Hz, ═CH). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K): $\delta = 0.85$, 1.61 (SiMe_2), 32.50 (═CMe), 74.61 (*ipso*-C_5H_4), 78.93, 79.72 (C_5H_4), 87.01 (*ipso*-C_7H_6), 88.12, 89.07, 91.39 (C_7H_6), 145.38 (═CH), 157.31 (═CMe). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 297 K): $\delta = -9.62$, −5.66.

[Cr(η^6-C_6H_5Li)$_2$]·(thf)$_3$ [5·(thf)$_3$]. Recrystallization of the dilithiated complex [Cr(η^6-C_6H_5Li)$_2$]·tmeda (**5**·tmeda) (0.10 g, 0.30 mmol) from a saturated thf solution (1 mL) afforded **5**·(thf)$_3$ as red crystals that were washed with cold pentane (2 × 1 mL) and dried in vacuo (0.09 g, 0.24 mmol, 75%). ^{1}H NMR (500 MHz, [D$_8$]thf, 297 K): $\delta = 1.77$ (m, 6H, CH_2), 3.62 (m, 6H, OCH_2), 3.86 (m, 4H, C_6H_5), 4.02 (m, 2H, C_6H_5), 4.25 (m, 4H, C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]thf, 297 K): $\delta = 26.36$ (CH$_2$), 68.21 (OCH$_2$), 72.75, 76.14, 85.38 (C_6H_5), 103.99 (*ipso*-C_6H_5). ^{7}Li{^{1}H} NMR (194 MHz, [D$_8$]thf, 297 K): $\delta = 2.56$. X-ray-quality crystals of the thf solvate [Cr(η^6-C_6H_5Li)$_2$]$_2$·(thf)$_7$ showed additional thf molecules incorporated into the crystal lattice and were obtained during the recrystallization procedure described above.

Crystal Structure Determinations. The crystal data of **1**, **4a**, and **5** were collected with a Bruker X8Apex diffractometer with a CCD area detector and multilayer mirror monochromated Mo K_α radiation. The structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen, 1997), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in the structure factor calculations.

Crystal data for **1**: $C_{16}H_{22}CrSi_2$, $M_r = 322.52$, orange needles, 0.45 × 0.075 × 0.05 mm^3, orthorhombic space group *Pnma*, $a = 13.2196(4)$ Å, $b = 11.8440(4)$ Å, $c = 9.7441(3)$ Å, $V = 1525.66(8)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.404$ g·cm^{-3}, $\mu = 0.891$ mm^{-1}, $F(000) = 680$, $T = 100(2)$ K, $R_1 = 0.0237$, $wR_2 = 0.0681$, 1580 independent reflections [$2\theta \le 52.1°$], and 97 parameters.

Crystal data for **4a**: $C_{19}H_{26}CrSi_2$, $M_r = 362.58$, green blocks, 0.16 × 0.10 × 0.05 mm^3, orthorhombic space group *Pbca*, $a = 9.4352(3)$ Å, $b = 12.5514(4)$ Å, $c = 31.2216(10)$ Å, $V = 3697.4(2)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.303$ g·cm^{-3}, $\mu = 0.743$ mm^{-1}, $F(000) = 1536$, $T = 100(2)$ K, $R_1 = 0.0308$, $wR_2 = 0.0735$, 3647 independent reflections [$2\theta \le 52.08°$], and 200 parameters.

Crystal data for **5**: $C_{52}H_{76}Cr_2Li_4O_7$, $M_r = 944.89$, red blocks, 0.20 × 0.14 × 0.09 mm^3, triclinic space group $P\bar{1}$, $a = 10.1815(4)$ Å, $b = 12.3894(5)$ Å, $c = 19.2910(7)$ Å, $\alpha = 93.776(2)°$, $\beta = 90.841(2)°$, $\gamma = 93.436(2)°$, $V = 2423.35(16)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.295$ g·cm^{-3}, $\mu = 0.499$ mm^{-1}, $F(000) = 1008$, $T = 95(2)$ K, $R_1 = 0.0727$, $wR_2 = 0.1796$, 13290 independent reflections [$2\theta \le 59.28°$], and 690 parameters. Due to high disorder of the thf solvent molecules, the bond distances were fixed within these groups during the refinement.

Crystallographic data are also deposited with the Cambridge Crystallographic Data Centre. Copies of the data [**1**, **4a**, and **5**, CCDC 646679−646681] can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB 1EZ, U.K., fax +44 1223 336033.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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