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Transition-Metal Complexes Containing Alkynylsilyl Functionalized η^6-Arene Ligands

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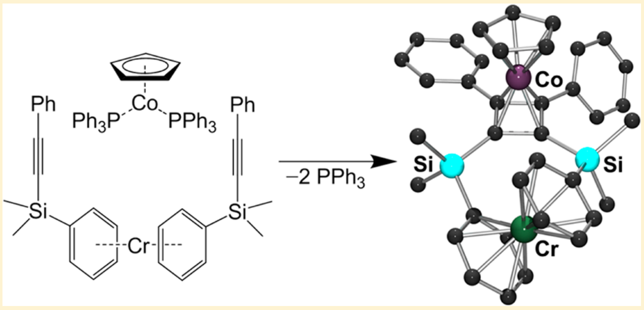
Ⓢ *Supporting Information*

ABSTRACT: Six transition-metal arene complexes containing alkynylsilyl groups have been synthesized. Direct complexation of the corresponding arenes yielded the alkynylsilylarene complexes $PhC{\equiv}CMe_2SiPhCr(CO)_3$ (**1**), *n*-$PrC{\equiv}CMe_2SiPhCr(CO)_3$ (**2**), *n*-$PrC{\equiv}CMe_2Si{-}SiMe_2{-}SiMe_2PhCr(CO)_3$ (**4**), and $PhC{\equiv}CMe_2SiPhMo(CO)_3$ (**6**), while $PhC{\equiv}CMe_2Si{-}SiMe_2PhCr(CO)_3$ (**3**) and $(PhC{\equiv}CMe_2SiPh)_2Cr$ (**7**) were synthesized by modification of precomplexed arenes. The reactivity of the C≡C triple bonds of the synthesized alkynylsilyl compounds toward complexation and carbon−carbon bond-forming reactions was studied. The alkynyl groups of **1** and **6** underwent intermolecular complexation to yield the trinuclear compounds $\mathbf{1}\cdot Ni_2Cp_2$ (**8**) and $\mathbf{6}\cdot Cp_2Mo_2(CO)_4$ (**9**), respectively, while reaction of **7** with $CpCo(PPh_3)_2$ led to intramolecular [2 + 2] cycloaddition of its two alkynyl groups with formation of the dinuclear cyclobutadiene complex $CpCo(PhCCSiMe_2Ph)_2Cr$ (**10**). All of these complexes were characterized by NMR, IR, and mostly also UV/vis (**1**, **2**, **6**−**10**) spectroscopy. The molecular and crystal structures of compounds **1**, **2**, and **6**−**10** were determined by single-crystal X-ray diffraction.



INTRODUCTION

The alkynyl group is a useful building block for metal-organic synthesis, e.g. for preparing multinuclear complexes with conjugated metal centers,[1] because of its various coordination modes, its ability to participate in delocalized systems, and its versatile reactivity.[2] Recently we reported the synthesis of some transition-metal alkynylsilyl complexes with a metal−silicon bond as well as mild subsequent reactions preserving this reactive bond.[3a] As an alternative approach toward alkynylsilyl-functionalized complexes, which circumvents the sensitivity issue associated with a direct metal−silicon bond, we successfully inserted a cyclopentadienyl spacer unit between metal and silicon.[3b] The metal−carbon and carbon−silicon bonds are more robust than a direct metal−silicon bond, while the silyl group prevents side reactions which could occur if the alkynyl residue were bound directly to the aromatic ring (conjugated π system) or via one carbon atom (activation of propargylic C−H bonds). Thus, an aromatic hydrocarbon spacer unit should also allow the complexes to resist less mild conditions when they are employed as starting materials in further reactions.

To our surprise, a literature search revealed that transition-metal complexes bearing alkynylsilyl-functionalized η^6-arene ligands are hitherto completely unknown. Of course, complexes with alkynylalkyl groups (such as propargyl) are known and have found application in organic synthesis.[4] Furthermore, there are some related alkynylsilylalkylsilylarene,[5] alkynylalkoxyalkylarene,[6] alkenylsilylarene (including silaphenanthrene),[5,7] and alkenylalkylarene complexes.[8] Alkenylsilylarene complexes have been used to synthesize metal-containing dendrimers and polymers by hydrosilylation.[7g,h] Alkynylalkoxyalkylarenes[6] as well as alkenylalkylarenes[8] acted as chelating ligands and corresponding chromium complexes have been prepared. Finally, two highly interesting chromium−iron−silicon cluster compounds can be regarded as related (ferrasilaalkenyl)silylarene chelate complexes of chromium.[9]

Herein we present the first transition-metal alkynylsilylarene complexes as well as reactions of their alkyne triple bonds which finally lead to multinuclear complexes and carbon−carbon bond coupling reactions.[10]

RESULTS AND DISCUSSION

Transition-Metal η^6-Arene Complexes with Alkynylsilylbenzenes. Similarly to the analogous alkynylsilylcyclopentadienyl compounds,[3b] the number of synthetic pathways to arene complexes bearing alkynylsilyl groups is larger than that for silyl complexes with a direct metal−silicon bond, because the Si−C bond is kinetically inert and the arene metal complex moieties are quite robust. Thus, the alkynyl group, the silyl group, and the arene metal complex fragment can be connected in several sequences depending on the reactivity of the intermediate and final complexes. In contrast, transition-metal silyl compounds are relatively sensitive to

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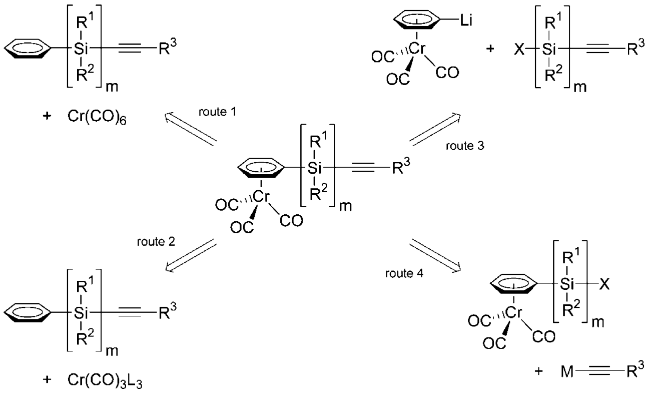
metal−silicon bond scission and their synthetic access is largely limited to nucleophilic substitution of halosilanes with metalate ions or oxidative addition of hydrosilanes to suitable metal complexes.[11]

For the synthesis of arenetricarbonylchromium complexes, the methods comprise complexation of alkynylsilylarenes with hexacarbonylchromium ($Cr(CO)_6$; Scheme 1, route 1), or presubstituted tricarbonylchromium complexes $Cr(CO)_3L_3$ (route 2) as well as introduction of alkynylsilyl groups (route 3) or protected silyl groups (route 4) into benzenetricarbonylchromium ($(C_6H_6)Cr(CO)_3$).

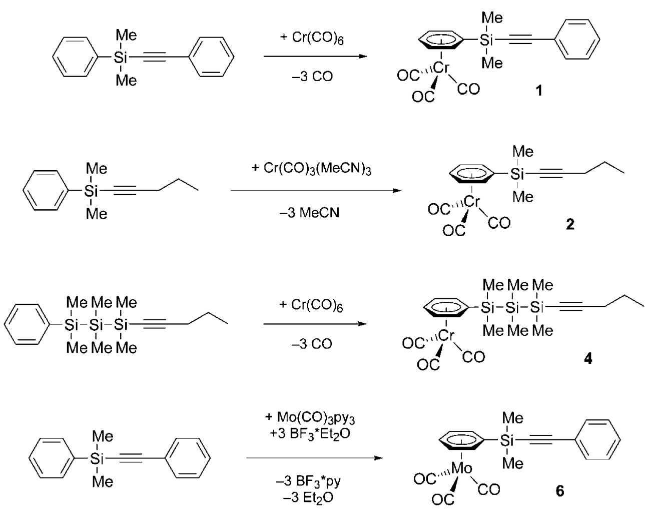
Scheme 1. Retrosynthetic Pathways to (Alkynylsilylarene)tricarbonylchromium Complexes



The first attempt to synthesize tricarbonyl[dimethyl(η^6-phenyl)phenylethynylsilane]chromium(0) ($PhC{\equiv}CMe_2SiPhCr(CO)_3$, **1**) via the reaction of lithiated $(C_6H_6)Cr(CO)_3$ (−78 °C, exclusion of light)[12] with chlorodimethyl(phenylethynyl)silane ($PhC{\equiv}CMe_2SiCl$; route 3) resulted only in a mixture of compounds, showing this route to be inefficient.

Complex **1** was finally synthesized along route 1, starting from $Cr(CO)_6$ and dimethylphenyl(phenylethynyl)silane ($PhC{\equiv}CMe_2SiPh$; Scheme 2).[13] The reaction was rather slow; a conversion of 73% was achieved only after 93 h, as judged by ^{29}Si NMR. Because of increasing byproduct formation (complexation of the alkyne-bound phenyl group) the reaction was stopped at this stage and workup gave yellow crystals of **1** in 42% yield.[14] They were air-stable for at least some days and well soluble in all common organic solvents, forming air-sensitive yellow solutions. The NMR and IR spectroscopic data were consistent with the molecular structure of **1**.

Scheme 2. Synthesis of Complexes 1, 2, 4, and 6



Apart from a CH···π contact between an ortho phenyl hydrogen and the silicon-bound carbon atom of the C≡C triple bond, the molecule does not exhibit any striking bonding parameters (Figure 1). Neighboring molecules arrange in a structural motif that was observed also in compounds **2**, **6**, and two related rhodium alkynylsilyl[3a] and titanium alkynylsilylcyclopentadienyl[3b] complexes (Figure S8; Supporting Information). This indicates CH···π interactions between the methyl hydrogens and neighboring C≡C triple bonds, but the distances are near or somewhat above the sum of the van der Waals radii. Nevertheless, this mutual arrangement of molecules appears to be especially favorable, thus representing a noteworthy feature of complexes containing a dimethyl(phenylethynyl)silyl group.

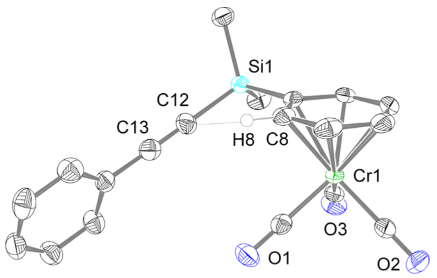


Figure 1. Molecular structure of **1** with an intramolecular CH···π interaction (hydrogen atoms except H8 omitted for clarity). Bond lengths and angles can be found in the Supporting Information. $H_{Ph}\cdots C_{C\equiv C}$ ($C_{Ph}\cdots C_{C\equiv C}$) distances (pm): H8−C12 = 283 (C8−C12 = 323), H8−C13 = 330 (C8−C13 = 394). Sum of the van der Waals radii: 300 (370) pm.[15]

In order to evaluate the influence of the organic substituent at the C≡C triple bond, tricarbonyl[dimethyl(pent-1-yn-1-yl)(η^6-phenyl)silane]chromium(0) (n-$PrC{\equiv}CMe_2SiPhCr(CO)_3$, **2**) was synthesized from dimethyl(pent-1-yn-1-yl)phenylsilane (n-$PrC{\equiv}CMe_2SiPh$) and *fac*-tris(acetonitrile)tricarbonylchromium(0) ($Cr(CO)_3(MeCN)_3$) (Scheme 1 (route 2) and Scheme 2).[14] With 1 equiv of $Cr(CO)_3(MeCN)_3$ in cyclohexane, silane conversion stopped at 67% after 16 h under reflux conditions because of thermal decomposition of the starting complex. Workup gave low-melting yellow crystals in 55% yield. In order to reduce the loss of silane, the synthesis was repeated with 2 equiv of $Cr(CO)_3(MeCN)_3$ and complete silane conversion was achieved after 24 h reflux in heptane. Compound **2** was then isolated in 80% yield referenced to n-$PrC{\equiv}CMe_2SiPh$. It is quite soluble in all common organic solvents. The solutions were more sensitive than those of **1**; e.g., **2** decomposed in chloroform (under argon) while **1** did not. The NMR and IR data were in agreement with the molecular structure of **2**.

The molecular conformation of **2** is similar to that of **1**, including the CH···π contact between an ortho phenyl hydrogen and the silicon-bound carbon atom of the C≡C triple bond (Figure 2). The propyl group is disordered with two different conformations in a ratio of about 2:1.

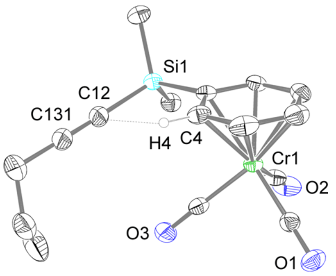
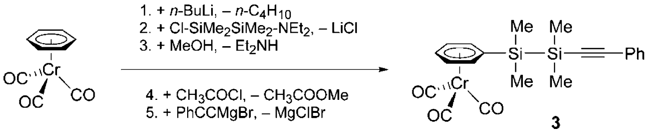


Figure 2. Molecular structure of **2** with an intramolecular CH···π interaction (30% probability thermal ellipsoids; only the more predominant of the two propyl conformations shown, hydrogen atoms except H4 omitted for clarity). Bond lengths and angles can be found in the Supporting Information. $H_{Ph}\cdots C_{C\equiv C}$ ($C_{Ph}\cdots C_{C\equiv C}$) distances (pm): H4−C12 = 277 (C4−C12 = 323), H4−C131 = 320 (C4−C131 = 389). Sum of the van der Waals radii: 300 (370) pm.[15]

The disilane compound tricarbonyl[tetramethyl-1-(η^6-phenyl)-2-phenylethynyldisilane]chromium(0) ($PhC{\equiv}CMe_2Si{-}SiMe_2PhCr(CO)_3$, **3**) was synthesized via consecutive introduction of the disilyl and alkynyl groups into the metal complex fragment (Scheme 1 (route 4) and Scheme 3). The multistep reaction consisted of initial lithiation of $(C_6H_6)Cr(CO)_3$, which was then reacted with 1-chloro-2-*N,N*-diethylaminotetramethyldisilane ($Et_2NMe_2Si{-}SiMe_2Cl$) to introduce the disilane chain. Subsequently, the amino protecting group was transformed into a methoxy and then a chloro substituent by methanol and acetyl chloride, respectively.[16] Final addition of phenylethynylmagnesium bromide ($PhC{\equiv}CMgBr$) gave **3** as a viscous brown oil in 57% total crude yield. Details about the assumed intermediates, which were not isolated, can be found in the Supporting Information. Admittedly, the NMR spectra of the product indicated a "purity" of only ~75%.[17] Unfortunately, attempts at recrystallization did not afford a pure or solid product, probably because of the flexible disilane chain, which prevented crystallization. Therefore, satisfying elemental analyses could not be obtained. Nevertheless, the identity was verified by the ^1H, ^{13}C, and ^{29}Si NMR as well as the IR spectroscopic data, which were in good agreement with the proposed structure concerning position, number, intensity, and coupling patterns of the signals.

Scheme 3. Synthesis of 3



Although it appeared unlikely to obtain a crystalline compound (cf. **3**), the trisilane complex tricarbonyl[hexamethyl-1-(pent-1-yn-1-yl)-3-(η^6-phenyl)trisilane]chromium(0) ($n\text{-}PrC{\equiv}CMe_2Si{-}SiMe_2{-}SiMe_2PhCr(CO)_3$, **4**) was synthesized from hexamethyl-1-(pent-1-yn-1-yl)-3-phenyltrisilane ($n\text{-}PrC{\equiv}CMe_2Si{-}SiMe_2{-}SiMe_2Ph$) and $Cr(CO)_6$ (Scheme 1 (route 1) and Scheme 2). As in the case of the synthesis of **1** the reaction was very slow, the conversion being 93% only after 150 h. Unexpectedly, workup yielded at first a small amount of yellow crystals. However, their NMR spectra suggested them to be [μ-octamethyl-1,4-bis(η^6-phenyl)tetrasilane]bis[tricarbonylchromium(0)] ($(OC)_3CrPh{-}(SiMe_2)_4{-}PhCr(CO)_3$, **5**).[18] This was confirmed by single-crystal X-ray structure analysis. The molecule possesses inversion symmetry with the central Si−Si bond being located on a crystallographic center of inversion (Figure 3). The tetrasilane chain is disordered with two conformations in the approximate ratio 4:1. Unfortunately, the amount of crystalline product was too small for further spectroscopic and elemental analyses.

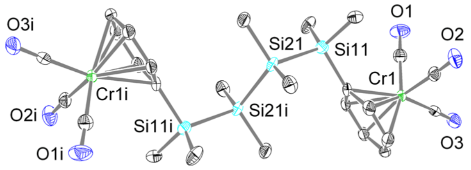


Figure 3. Molecular structure of **5** (only the more predominant of the two tetrasilane conformations shown, hydrogen atoms omitted for clarity). Bond lengths and angles can be found in the Supporting Information.

Further workup of the reaction mixture finally gave a brown oil in 65% yield with acceptable analytical data. As in the case of **3**, attempts at "recrystallization" did not lead to a pure or solid product. The IR spectroscopic data indicated the presence of minor amounts of uncomplexed trisilane ligand but were consistent with the proposed structure of **4**. However, its identity was finally confirmed by the ^1H, ^{13}C, and ^{29}Si NMR spectra, which indicated the presence of impurities, as well (purity ~90%).

Arenetricarbonylmolybdenum complexes are less stable than the analogous chromium compounds. Consequently, generally applicable synthetic routes toward these types of compounds are very limited. The recommended route comprises the substitution of the pyridine ligands in tricarbonyltris(pyridine)molybdenum ($Mo(CO)_3(py)_3$) by the arene in the presence of boron trifluoride−diethyl ether ($BF_3{\cdot}Et_2O$).[19]

Thus, $BF_3{\cdot}Et_2O$ was added to a mixture of $Mo(CO)_3py_3$ and $PhC{\equiv}CMe_2SiPh$ in diethyl ether at room temperature to synthesize tricarbonyl[dimethyl(η^6-phenyl)-phenylethynylsilane]molybdenum(0) ($PhC{\equiv}CMe_2SiPhMo(CO)_3$, **6**) (Scheme 2). Workup afforded yellow-brown crystals (light yellow under the microscope) in 46% yield. They were air-stable for at least a few days. The ^1H, ^{13}C, and ^{29}Si NMR as well as the IR spectra were consistent with the molecular structure of **6**. A special feature was the observation of ^{95}Mo satellites at the carbonyl ^{13}C NMR signal ($^1J_{MoC}$ = 95 Hz, lit.[20] 60−208 Hz). The ^{95}Mo NMR signal appeared at δ −2079 ppm with a very narrow line width ($\Delta\nu_{1/2}$ = 4 Hz), which is typical for arenetricarbonylmolybdenum derivatives.[21] Complex **6** crystallizes with four molecules of nearly identical conformation in the asymmetric unit (Figure 4). In contrast to the related chromium complex **1**, compound **6** does not establish intramolecular CH···π contacts in the crystal.

Unlike mono(arene)tricarbonylchromium complexes, bis(arene)chromium compounds are very sensitive toward oxidation.[22a,b] There are three entries into this class of complexes: (1) co-condensation of arene and chromium vapor, (2) Fischer−Hafner synthesis, and (3) modification of the arene ligands in a bis(arene)chromium complex.[22c−e] While the co-condensation requires expensive equipment, the harsh conditions of the Fischer−Hafner synthesis would lead to rearrangement or decomposition of the alkynylphenylsilanes used. The only promising pathway to alkynylsilyl derivatives of

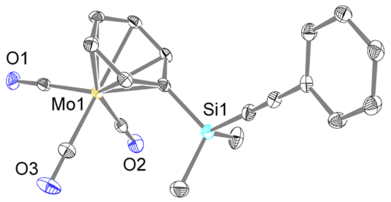


Figure 4. Molecular structure of **6** (only one of the four molecules with nearly identical conformations in the asymmetric unit shown, hydrogen atoms omitted for clarity). Bond lengths and angles can be found in the Supporting Information.

bis(benzene)chromium ($(C_6H_6)_2Cr$) seemed to be its lithiation and subsequent reaction with an alkynylchlorosilane. This sequence should result in 1,1′-disubstituted compounds since 1,1′-dilithiation is preferred (like in ferrocene).[23]

Thus, in order to synthesize bis[dimethyl(η^6-phenyl)-phenylethynylsilane]chromium(0) ($(PhC{\equiv}CMe_2SiPh)_2Cr$, **7**), $(C_6H_6)_2Cr$ was dilithiated with *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (*n*-BuLi/TMEDA) in cyclohexane under reflux (Scheme 4).[24] Subsequent addition of $PhC{\equiv}CMe_2SiCl$ furnished **7** in a slow but clean reaction in 79% yield after workup as very air-sensitive, dark red crystals. The oxidation product was supposed to be the bis(arene)chromium monocation.[22c,d] However, when we attempted to synthesize it on a preparative scale by aerobic oxidation under either acidic or basic conditions and precipitation with aqueous sodium tetraphenylborate ($NaBPh_4$) solution, complete desilylation occurred and the bis(benzene)chromium salt $(C_6H_6)_2Cr^+BPh_4^-$ was obtained.[25] Only upon oxidation in a neutral aqueous medium (phosphate buffer) could a mixture of silylated cations and $(C_6H_6)_2Cr^+$ be detected by IR spectroscopy and elemental analysis.[26]

Scheme 4. Synthesis of 7

The spectroscopic characterization of **7** was complicated by its air sensitivity. While the organosilyl groups furnished the expected signals in the ^1H, ^{13}C, and ^{29}Si NMR spectra, the peaks of the chromium-bound phenyl groups were severely broadened in benzene-d_6 (C_6D_6). This is quite common for bis(arene)chromium complexes and is caused by exchange processes with traces of their oxidation products.[27] Nevertheless, in cyclohexane these exchange processes were suppressed due to the insolubility of the cationic oxidation products and the missing signals could be observed. The stretch of the C≡C triple bond was detected by IR spectroscopy in solution at 2157 cm^{-1}. A solid-state IR spectrum of **7** could not be measured because of decomposition.

In the solid state the chromium atom of **7** is situated on a crystallographic inversion center. The phenylethynyl groups are oriented in opposite directions, leading to an elongated shape of the molecule (Figure 5). As in **1** and **2** there is a CH···π contact between an ortho phenyl hydrogen and the silicon-bound carbon atom of the C≡C triple bond.

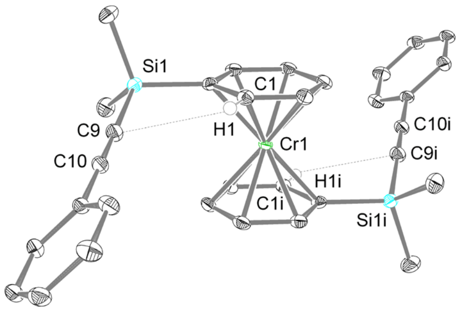
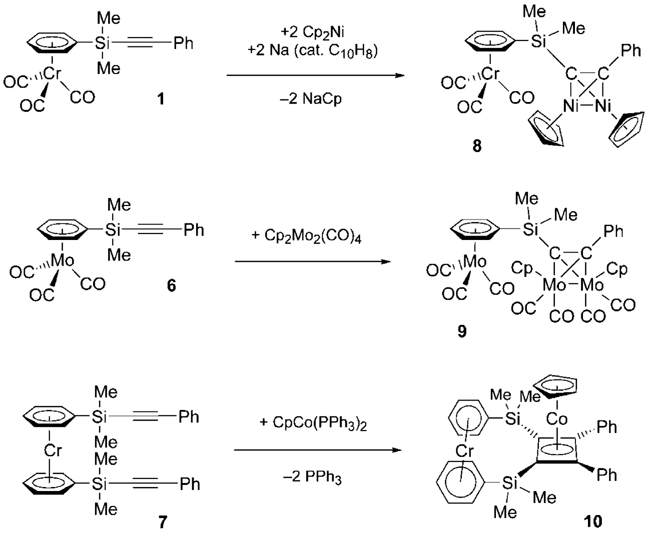


Figure 5. Molecular structure of **7** with an intramolecular CH···π interaction (hydrogen atoms except H1 and H1i omitted for clarity). Bond lengths and angles can be found in the Supporting Information. $H_{Ph}\cdots C_{C\equiv C}$ ($C_{Ph}\cdots C_{C\equiv C}$) distances (pm): H1−C9 = 280 (C1−C9 = 324), H1−C10 = 329 (C1−C10 = 395). Sum of the van der Waals radii: 300 (370) pm.[15]

Reactivity of the C≡C Triple Bond. In order to examine the synthetic potential of the alkynylsilyl complexes in further reactions, especially the synthesis of multinuclear compounds, we explored their reactivity toward complexation (inter- and intramolecular) and bond-forming reactions of the C≡C triple bond.

In an attempt to circumvent the harsh reaction conditions hitherto applied in the synthesis of complexes of the type $Cp_2Ni_2{\cdot}RC{\equiv}CR$,[28] a new synthetic procedure starting from alkyne, nickelocene (Cp_2Ni), sodium, and a small amount of naphthalene (as electron-transfer catalyst) at room temperature was developed. Tests with diphenylethyne (tolane, $PhC{\equiv}CPh$) gave good results (80−90% crude yield of $Cp_2Ni_2{\cdot}PhC{\equiv}CPh$, 40−50% after recrystallization); therefore, this reaction was used to synthesize the complex tricarbonyl-1κ^3*C*-dicyclopentadienyl-2(η^5),3(η^5)-{μ_3-dimethyl[phenyl-1(η^6)]-(phenylethynyl-2κ^2*C*,*C*′:3κ^2*C*,*C*′)silane}-1-chromium(0)-2,3-bis[nickel(I)](*Ni*−*Ni*) ($(OC)_3CrPhSiMe_2C{\equiv}CPh{\cdot}Ni_2Cp_2$, **8**) from compound **1** (Scheme 5). The reaction product was obtained after four tedious recrystallizations in 24% yield as a dark green microcrystalline solid, which showed no signs of decomposition in contact with air for at least 1 day. X-ray crystal structure analysis revealed the presence of 0.25 mol of naphthalene per 1 mol of **8** ($\mathbf{8}{\cdot}0.25C_{10}H_8$). In addition to the high solubility of **8** in organic solvents this may be an

Scheme 5. Synthesis of Di- and Trinuclear Complexes 8−10



explanation for the low yield: the amount of naphthalene used for catalysis was too small for complete crystallization of **8** as **8**·$0.25C_{10}H_8$. The IR and NMR data were consistent with the proposed molecular structure.

The asymmetric unit of **8**·$0.25C_{10}H_8$ contains two molecules of **8** (with very similar conformations) and a half molecule of naphthalene, which is situated on a crystallographic inversion center (Figure 6). The former triple bond (C12−C13) has a length of 134 pm, corresponding to a double-bond character in this complex. The crystal packing contains voids along the *a* axis between the silicon-bound methyl groups and the noncomplexed phenyl substituents of the former triple bonds which accommodate the naphthalene molecules.[29]

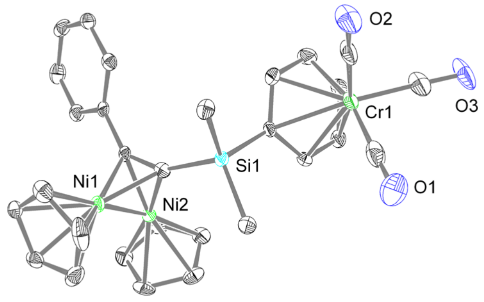


Figure 6. Molecular structure of **8**·$0.25C_{10}H_8$ (only one of the two complex molecules with nearly identical conformations in the asymmetric unit shown, hydrogen and naphthalene carbon atoms omitted for clarity). Bond lengths and angles can be found in the Supporting Information.

Compound **6** reacted with tetracarbonyldi(η^5-cyclopentadienyl)dimolybdenum ($Cp_2Mo_2(CO)_4$), resulting in the homotrinuclear complex heptacarbonyl-1κ^3C,2κ^2C,3κ^2C-dicyclopentadienyl-2(η^5),3(η^5)-{μ_3-dimethyl-[phenyl-1(η^6)](phenylethynyl-2κ^2C,C':3κ^2C,C')silane}-1-molybdenum(0)-2,3-bis[molybdenum(I)](Mo^2−Mo^3) ($(OC)_3MoPhSiMe_2C{\equiv}CPh\cdot Cp_2Mo_2(CO)_4$, **9**) in 23% yield as a dark reddish brown microcrystalline solid which could be handled in air (Scheme 5).

The IR and NMR spectral features were consistent with the molecular structure of **9**. The ^{95}Mo NMR spectrum showed two signals at δ −2071 ppm ($\Delta\nu_{1/2}$ = 6 Hz) and δ −1870 ppm ($\Delta\nu_{1/2}$ = 1200 Hz), which were assigned to the arene and the alkyne complex moiety, respectively, on the basis of literature data[21] and comparative measurements of the analogous tolane complex.[30] However, the ^{1}H and ^{29}Si NMR spectra indicated the presence of ∼5% tetracarbonyl-1κ^2C,2κ^2C-dicyclopentadienyl-1(η^5),2(η^5)-[μ-dimethyl(phenyl)(phenylethynyl-1κ^2C,C':2κ^2C,C')silane]-1,2-bis[molybdenum(I)](*Mo*−*Mo*) ($PhSiMe_2C{\equiv}CPh\cdot Cp_2Mo_2(CO)_4$) (^{29}Si NMR ($C_6D_6$): δ +0.6 ppm), formed by demetalation of the phenyl group.

The bond length of the former alkyne triple bond (138 pm) is comparable to that of an aromatic C−C bond (Figure 7). While three of the carbonyl ligands of the $Cp_2Mo_2(CO)_4$ moiety form nearly linear Mo−C−O axes, the carbon atom of the fourth ligand (C25−O4) is markedly displaced toward the opposite molybdenum atom (Mo3), their distance being below the sum of the corresponding van der Waals radii. This can be regarded as a partially bridging carbonyl ligand, as already described in the literature for other alkyne complexes of $Cp_2Mo_2(CO)_4$.[31]

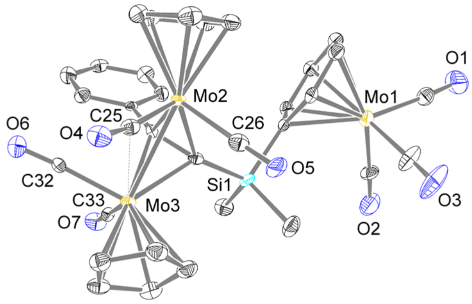


Figure 7. Molecular structure of **9** (hydrogen atoms omitted for clarity). Bond lengths and angles can be found in the Supporting Information. Mo···CO distances (pm): Mo3−C25 = 286, Mo3−C26 = 346, Mo2−C32 = 348, Mo2−C33 = 441. Sum of the van der Waals radii: 360 pm (310 pm based on the metallic radius of molybdenum).[15,32]

With appropriate transition-metal moieties, e.g. bis(triphenylphosphane)(η^5-cyclopentadienyl)cobalt(I) ($CpCo(PPh_3)_2$), the reaction does not stop at the alkyne complex stage and carbon−carbon bond coupling reactions occur.[33] Reaction of the bis(arene)chromium complex **7** with $CpCo(PPh_3)_2$ at room temperature afforded an unprecedented dinuclear bis(arene)chromium−cyclobutadienecobalt complex instead of the expected cobaltacyclopentadiene compound (Scheme 5).[34] It was isolated in 8% yield and identified by X-ray crystallography. Considering the harsh conditions hitherto reported for the formation of cyclobutadiene cobalt complexes, the mild reaction temperature is remarkable.[35] The product, 2(η^5)-cyclopentadienyl-{μ-3,4-diphenyl-1,2-bis{dimethyl-[phenyl-1(η^6)]silyl}-cyclobutadiene-2(η^4)}-1-chromium(0)-2-cobalt(I) ($CpCo[PhCCSiMe_2Ph]_2Cr$, **10**), formed large dark brown crystals which were air stable for at least a few hours. In contrast, solutions were very air sensitive. Thus, as with **7**, the NMR spectroscopic characterization was hampered by exchange processes with oxidation products (line broadening). However, analytical and spectral data were consistent with the anticipated molecular structure.

The molecular structure shows that the fixation of the alkynyl groups by the bis(arene)chromium unit apparently hampers the formation of a cobaltacyclopentadiene moiety and favors the formation of a cyclobutadiene cobalt moiety instead by forcing the phosphane out of the complex (Figure 8).[36] The former alkyne triple bonds are elongated to 147−148 pm. The compound features helical chirality with the chirality axis along the 6-fold symmetry axis of the bis(arene)chromium unit.

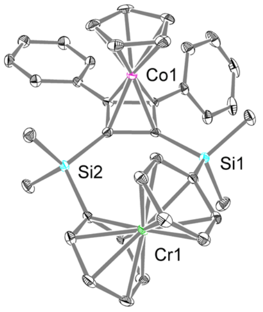


Figure 8. Molecular structure of **10** (*M* isomer, hydrogen atoms omitted for clarity). Bond lengths and angles can be found in the Supporting Information.

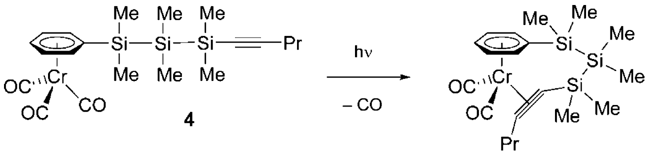
However, it crystallizes as a racemate (space group type *Cc*, *Z* = 4).

Whereas the preceding experiments aimed at intermolecular reactions of the triple bond to form multinuclear complexes, intramolecular reactions of the alkynylsilyl group with the transition-metal complex moiety are also possible.[6,37]

Irradiation-induced ligand substitutions are quite common also for silyl[38] and stannyl[39] complexes with unsaturated hydrocarbons. Admittedly, oligosilane chains rearrange and shorten under these conditions.[38b,c,40] Even cyclic benzenetricarbonylchromium−alkyne derivatives with alkyl ether bridges are known.[6] Consequently, solutions of compounds **1**, **3**, **4**, and **6** were irradiated with UV light[6a,41] and the progress of the reaction was monitored with IR and NMR spectroscopy. Except for the UV treatment of compound **4**, only decomposition occurred and the free silane ligands were detected.

Upon irradiation of complex **4** a low-field shift of the ^{29}Si NMR signal of the silicon atom bearing the alkyne group by about 10 ppm suggested that complexation of the C≡C bond had taken place.[42] However, the anticipated main product dicarbonyl{hexamethyl-1-[(1,2-*η*)-pent-1-yn-1-yl]-3-(η^6-phenyl)trisilane}chromium(0) (*n*-PrC≡CMe$_2$Si−SiMe$_2$−SiMe$_2$PhCr(CO)$_2$, Scheme 6) could not be isolated. Instead, a mixture of **4** and the free trisilane ligand *n*-PrC≡CMe$_2$Si−SiMe$_2$−SiMe$_2$Ph was obtained. These were most likely formed by decomposition of the irradiation product, as the ^{29}Si NMR spectrum had indicated that they were present after irradiation only in minor amounts. Nevertheless, this indicates that the trisilane backbone is maintained throughout the irradiation without rearrangement.

Scheme 6. Intramolecular Reaction of Complex 4 upon UV Irradiation As Indicated by ^{29}Si NMR Spectroscopy



CONCLUSIONS

Alkynylsilylarene complexes can be synthesized with good results both by direct complexation of substituted benzenes or silylation of preformed arene complexes (except for the reaction of lithiated (C$_6$H$_6$)Cr(CO)$_3$ with an alkynylchlorosilane). Therefore, derivatives of (C$_6$H$_6$)Cr(CO)$_3$ are more easily to synthesize than the corresponding CpMn(CO)$_3$ derivatives.[3b] In case of direct arene complex formation of a silane bearing phenylethynyl and phenyl substituents, complexation of the silicon-bound phenyl group is preferred.

Complexes with an *n*-propyl substituent at the C≡C triple bond are more sensitive to decomposition than those with a phenyl substituent. This is likely to be more an electronic than a steric effect, as their molecular structures are very similar including a weak CH···*π* contact.

The alkynyl groups undergo further complexation reactions with additional metal compounds leading to various hetero- and homomultinuclear compounds. With appropriate reagents, such as CpCo(PPh$_3$)$_2$, complexation is accompanied by carbon−carbon bond coupling reactions resulting, e.g., in a dinuclear cyclobutadiene complex.

Thus, alkynylsilylarene complexes are useful precursors to multinuclear homo- or heterometallic compounds, which may find application in the fields of catalysis (tailored catalysts) or materials science (metal- and silicon-containing polymers).[3a,7g,h]

EXPERIMENTAL SECTION

General Remarks. All operations were carried out under purified argon using standard Schlenk line or glovebox techniques. If possible, reactions were monitored by NMR or IR spectroscopy. The NMR spectra were recorded at 22 °C using tetramethylsilane (Me$_4$Si) as internal standard for ^{1}H (400.13 MHz), ^{13}C (100.63 MHz), and ^{29}Si (79.49 MHz). The external standards for ^{31}P (161.98 MHz), ^{59}Co (94.65 MHz), and ^{95}Mo (26.02 MHz) were 85% H$_3$PO$_4$, 0.1 mol/L K$_3$[Co(CN)$_6$] in D$_2$O, and 1 mol/L Na$_2$MoO$_4$ in H$_2$O, respectively.[43] For ^{29}Si NMR spectra the INEPT[44] pulse sequence was employed. Melting points were determined between thin glass plates (air) or in sealed capillaries (argon) on a Boëtius type heating microscope with a heating rate of about 4 K/min. The UV irradiation experiments were performed in a Narva UVS 125 quartz photoreactor with 125 W irradiation power and 150 mL volume.[45]

Chemicals. Solvents were dried and deoxygenated by distillation under argon from sodium−benzophenone (benzene, diethyl ether, hexane, THF, toluene), calcium hydride (acetonitrile, dibutyl ether, chloroform-*d* (CDCl$_3$), cyclohexane, heptane, propionitrile, pyridine, TMEDA), lithium aluminum hydride (pentane), sodium−potassium alloy (C$_6$D$_6$), or magnesium (methanol) and stored under argon until use. Acetyl chloride was distilled from iron powder under argon and stored under argon until use. Et$_2$NMe$_2$Si−SiMe$_2$Cl was synthesized analogously to Et$_2$NMe$_2$SiCl.[46] The other silanes were synthesized as previously published.[31c] Mo(CO)$_3$(py)$_3$ was prepared from Mo(CO)$_3$(MeCN)$_3$ and pyridine in THF.[47] CpCo(PPh$_3$)$_2$·0.5(C$_6$H$_{14}$/C$_7$H$_8$) was obtained as already described.[33] The other chemicals were prepared after common procedures or purchased from commercial suppliers and were used as received.

Crystal Structure Analyses. The X-ray single-crystal structure analyses were performed on a "Bruker-Nonius X8" diffractometer using Mo K*α* radiation (*λ* = 71.073 pm) and an APEX2-CCD area detector. For solution, refinement, and visualization of the structures the programs Bruker SMART,[48a] Bruker SAINT,[48a] Bruker SHELXTL,[48b] SHELXS-97,[48c] SHELXL-97,[48d] and ORTEP32[48e] were used. The thermal ellipsoids are drawn at the 50% probability level unless otherwise stated. The data of **9** were collected from a twin with domains of similar diffraction power (56:44 ratio, R_{int} = 0.0246 and 0.0247). Equivalent reflections were merged before scaling. Structure refinement was carried out with a HKLF5 file containing data of both domains.

Tricarbonyl[dimethyl(η^6-phenyl)phenylethynylsilane]chromium(0) (1). Cr(CO)$_6$ (2.23 g, 10.1 mmol) and PhC≡CMe$_2$SiPh (2.29 g, 9.7 mmol) were refluxed in a mixture of dibutyl ether (45 mL) and THF (5 mL) for 93 h. From time to time Cr(CO)$_6$ subliming into the condenser was pushed back into the flask with a long spatula. After it was cooled to room temperature, the mixture was evaporated in vacuo. The oily residue was dissolved in diethyl ether and filtered. The filtrate was evaporated in vacuo and the residue extracted with hexane (50 mL) by stirring overnight. The extract was concentrated in vacuo to 10 mL and cooled to −20 °C, whereupon a brown-yellow solid deposited. Repetition of extraction and cooling furnished yellow needlelike crystals, which were separated, washed with hexane (2 × 5 mL), and dried in vacuo. These needles were suitable for X-ray crystallography. **1** is air-stable for several days but should be stored under argon.

Yield: 1.53 g, 4.11 mmol, 42%. Mp: 47−48 °C (argon), 48−50 °C (air). Solubility: hexane, diethyl ether, THF, chloroform. Anal. Found (calcd) for C$_{19}$H$_{16}$CrO$_3$Si (372.416): C, 61.32 (61.28); H, 4.44 (4.33). ^{1}H NMR (0.13 mol/L in CDCl$_3$): *δ* 7.51 (m, 2 H, Ph$_{ortho}$), 7.32 (m, 3 H, Ph$_{meta+para}$), 5.61 (d, $^3J_{HH}$ = 6.4 Hz, 2 H, PhCr$_{ortho}$), 5.55 (t, $^3J_{HH}$ = 6.4 Hz, 1 H, PhCr$_{para}$), 5.17 ("t", $^3J_{HH}$ = 6.4 Hz, 2 H, PhCr$_{meta}$), 0.52 (s, $^1J_{HC}$ = 121 Hz, 6 H, SiMe$_2$) ppm. ^{13}C NMR (0.13 mol/L in

CDCl$_3$): δ 232.8 (s, 3 C, CO), 132.2 (s, 2 C, Ph$_{ortho}$), 129.1 (s, 1 C, Ph$_{para}$), 128.3 (s, 2 C, Ph$_{meta}$), 122.4 (s, 1 C, Ph$_{ipso}$), 108.0 (s, $^2J_{CSi}$ = 17 Hz, 1 C, *C*≡CSi), 99.7 (s, 2 C, PhCr$_{ortho}$), 95.8 (s, $^1J_{CSi}$ = 70 Hz, 1 C, PhCr$_{ipso}$), 95.5 (s, 1 C, PhCr$_{para}$), 90.1 (s, 2 C, PhCr$_{meta}$), 89.8 (s, $^1J_{CSi}$ = 92 Hz, 1 C, C≡*C*Si), −0.9 (s, $^1J_{CSi}$ = 60 Hz, 2 C, SiMe$_2$) ppm. ^{29}Si NMR (0.13 mol/L in CDCl$_3$): δ −18.3 (s, $^1J_{SiC(Me)}$ = 59 Hz (2 C), $^1J_{SiC(Ph)}$ = 71 Hz (1 C), $^1J_{SiC(C\equiv C)}$ = 92 Hz (1 C), $^2J_{SiC(C\equiv C)}$ = 17 Hz (1 C)) ppm. IR (hexane): $\tilde{\nu}$ 2160 (w, ν(C≡C)), 1978 (s, ν(C≡O)), 1912 (s, ν(C≡O)) cm^{-1}. IR (KBr): $\tilde{\nu}$ 2157 (m, ν(C≡C)), 1965 (vs, ν(C≡O)), 1888 (vs, ν(C≡O)) cm^{-1} (see the Supporting Information for complete data). UV/vis (hexane): λ (ε) 222 (br, 16000, PhCr(CO)$_3$), 238 (15000, PhC≡C), 248 (18000, PhC≡C), 259 (15000, PhC≡C), 319 (br, 7400, PhCr(CO)$_3$) nm (L/(mol cm)).[49]

Tricarbonyl[dimethyl(pent-1-yn-1-yl)(η^6-phenyl)silane]chromium(0) (2). *(a). Synthesis in the Ratio 1:1 in Cyclohexane.* *n*-PrC≡CMe$_2$SiPh (300 mg, 330 μL, 1.48 mmol), Cr(CO)$_3$(MeCN)$_3$ (420 mg, 1.62 mmol), and cyclohexane (17 mL) were refluxed for 16 h. After it was cooled to room temperature, the solution was filtered and concentrated in vacuo to 1 mL and hexane (1.5 mL) was added. Cooling to −78 °C afforded a yellow solid, which was separated, washed with pentane (2 × 1.5 mL), and dried in vacuo. It was recrystallized once from hexane (5 mL) to give bright yellow crystals. Crystals suitable for X-ray crystallography were grown from hexane by slow warming of a concentrated solution from −78 to −20 °C. The product is air-stable for some time but should be stored under argon in a refrigerator. Yield: 275 mg, 0.81 mmol, 55%.

(b). Synthesis in the Ratio 1:2 in Heptane. *n*-PrC≡CMe$_2$SiPh (595 mg, 660 μL, 2.94 mmol), Cr(CO)$_3$(MeCN)$_3$ (1.520 g, 5.86 mmol), and heptane (30 mL) were refluxed for 24 h. After it was cooled to room temperature, the solution was filtered and evaporated in vacuo. The brown oily residue was dissolved in hexane (4 mL) and cooled to −78 °C. The precipitated solid was separated, washed with pentane (500 μL), and dried in vacuo (815 mg, 82% crude yield). It was recrystallized once from hexane (3 mL), yielding brownish yellow crystals. Yield: 800 mg, 2.36 mmol, 80% referenced to *n*-PrC≡CMe$_2$SiPh, 40% referenced to Cr(CO)$_3$(MeCN)$_3$.

Mp: 21−23 °C (argon), 24−25 °C (air). Solubility: hexane, pentane, heptane, benzene, diethyl ether, chloroform (dec). Anal. Found (calcd) for C$_{16}$H$_{18}$CrO$_3$Si (338.399): C, 57.05 (56.79); H, 5.18 (5.36). ^{1}H NMR (0.3 mol/L in C$_6$D$_6$): δ 5.10 (d, $^3J_{HH}$ = 5.5 Hz, 2 H, PhCr$_{ortho}$), 4.70 (t, $^3J_{HH}$ = 5.5 Hz, 1 H, PhCr$_{para}$), 4.33 ("t", $^3J_{HH}$ = 5.5 Hz, 2 H, PhCr$_{meta}$), 2.01 (t, $^3J_{HH}$ = 6.4 Hz, 2 H, −*CH*$_2$CH$_2$CH$_3$), 1.37 ("sextet", $^3J_{HH}$ = 7 Hz, 2 H, −CH$_2$*CH*$_2$CH$_3$), 0.85 (t, $^3J_{HH}$ = 6.9 Hz, 3 H, −CH$_2$CH$_2$*CH*$_3$), 0.32 (s, $^1J_{HC}$ = 120 Hz, 6 H, SiMe$_2$) ppm. ^{13}C NMR (0.3 mol/L in C$_6$D$_6$): δ 233.3 (s, 3 C, CO), 111.2 (s, $^2J_{CSi}$ = 18 Hz, 1 C, *C*≡CSi), 99.6 (s, 2 C, PhCr$_{ortho}$), 96.5 (s, 1 C, PhCr$_{ipso}$), 95.3 (s, 1 C, PhCr$_{para}$), 90.1 (s, $^1J_{CC}$ = 46 Hz, 2 C, PhCr$_{meta}$), 81.0 (s, $^1J_{CSi}$ = 95 Hz, 1 C, C≡*C*Si), 22.1 (s, 1 C, CH$_2$), 22.0 (s, 1 C, CH$_2$), 13.4 (s, 1 C, CH$_3$), −0.7 (s, $^1J_{CSi}$ = 59 Hz, 2 C, SiMe$_2$) ppm. ^{29}Si NMR (0.3 mol/L in C$_6$D$_6$): δ −19.3 (s, $^1J_{SiC(Me)}$ = 59 Hz (2 C), $^1J_{SiC(Ph)}$ = 71 Hz (1 C), $^1J_{SiC(C\equiv C)}$ = 95 Hz (1 C), $^2J_{SiC(C\equiv C)}$ = 18 Hz (1 C)) ppm. IR (hexane): $\tilde{\nu}$ 2174 (w, ν(C≡C)), 1980 (s, ν(C≡O)), 1908 (s, ν(C≡O)) cm^{-1}. IR (neat liquid): $\tilde{\nu}$ 2173 (s, ν(C≡C)), 1970 (vs, ν(C≡O)), 1893 (vs, ν(C≡O)) cm^{-1} (see the Supporting Information for complete data). UV/vis (hexane): λ (ε) 218 (br, 21000, PhCr(CO)$_3$), 260 (br, 7000, PhCr(CO)$_3$), 319 (br, 11000, PhCr(CO)$_3$) nm (L/(mol cm)).[49]

Tricarbonyl[tetramethyl-1-(η^6-phenyl)-2-phenylethynyldisilane]chromium(0) (3). A 2.5 mol/L solution of *n*-BuLi in hexane (1.3 mL, 3.25 mmol) was diluted with hexane (5 mL) and added to a solution of (C$_6$H$_6$)Cr(CO)$_3$ (645 mg, 3.01 mmol) in THF (30 mL) cooled to −78 °C with exclusion of light. After 2.5 h of stirring at −78 °C Et$_2$NMe$_2$SiSiMe$_2$Cl (900 μL, 800 mg, 3.58 mmol) in hexane (5 mL) was added slowly. Warming to room temperature and stirring overnight furnished a yellow-brown solution (^{29}Si NMR (THF): δ −3.9 (s, 1 Si, −SiMe$_2$NEt$_2$), −19.8 (s, 1 Si, −SiMe$_2$PhCr(CO)$_3$) ppm).

This solution was cooled to 0 °C, and methanol (1.0 mL, 0.79 g, 24.7 mmol) was added. Stirring for 1.5 h yielded a brown solution (^{29}Si NMR (THF): δ +14.6 (s, 1 Si, −SiMe$_2$OMe), −20.1 (s, 1 Si, −SiMe$_2$PhCr(CO)$_3$) ppm).

This solution was evaporated in vacuo, and the residue was redissolved in hexane (20 mL). After this solution was cooled to 0 °C, acetyl chloride (7.0 mL, 7.73 g, 98.6 mmol) diluted with hexane (5 mL) was added. The mixture was stirred at room temperature for 2 days. Then it was filtered and the filtrate evaporated in vacuo, furnishing a dark yellow oil (^{29}Si NMR (hexane): δ +18.1 (s, 1 Si, −SiMe$_2$Cl), −19.4 (s, 1 Si, −SiMe$_2$PhCr(CO)$_3$) ppm).

This oil was dissolved in diethyl ether (15 mL), and PhC≡CMgBr in diethyl ether (prepared from magnesium (75 mg, 3.09 mmol), 1,2-dibromoethane (1 droplet), ethyl bromide (300 μL, 438 mg, 4.02 mmol), phenylacetylene (330 μL, 307 mg, 3.01 mmol), and diethyl ether (10 mL), 3 h reflux)[50] was added slowly at room temperature. After it was stirred overnight, the mixture was refluxed for 2 h. After cooling it was cautiously hydrolyzed with 10% NH$_4$Cl solution (4 × 10 mL), washed with water (3 × 10 mL), and dried over Na$_2$SO$_4$. Removal of the ether furnished **3** as a dark brown oil.

Yield: 745 mg, 1.73 mmol, 57%. Solubility: hexane, benzene. ^{1}H NMR (0.7 mol/L in C$_6$D$_6$): δ 7.38 (m/br, 2 H, Ph$_{ortho}$), 6.98 (m/br, 3 H, Ph$_{meta+para}$), 4.98 (d/br, $^3J_{HH}$ = 4.8 Hz, 2 H, PhCr$_{ortho}$), 4.69 (t/br, $^3J_{HH}$ = 5.9 Hz, 1 H, PhCr$_{para}$), 4.40 ("t"/br, $^3J_{HH}$ = 5.9 Hz, 2 H, PhCr$_{meta}$), 0.38 (s/br, 6 H, SiMe$_2$), 0.24 (s/br, 6 H, SiMe$_2$) ppm. ^{13}C NMR (0.7 mol/L in C$_6$D$_6$): δ 233.7 (s, 3 C, CO), 132.1 (s, 2 C, Ph$_{ortho}$), 128.9 (s, 1 C, Ph$_{para}$), 128.6 (s, 2 C, Ph$_{meta}$), 123.5 (s, 1 C, Ph$_{ipso}$), 109.1 (s, $^2J_{CSi}$ = 14 Hz, 1 C, *C*≡CSi), 99.2 (s, 2 C, PhCr$_{ortho}$), 98.5 (s, 1 C, PhCr$_{ipso}$), 94.8 (s, 1 C, PhCr$_{para}$), 92.1 (s, 1 C, C≡*C*Si), 91.0 (s, 2 C, PhCr$_{meta}$), −2.8 (s, 2 C, SiMe$_2$), −4.3 (s, 2 C, SiMe$_2$) ppm. ^{29}Si NMR (0.7 mol/L in C$_6$D$_6$): δ −16.5 (s, $^1J_{SiC(Me)}$ = 48 Hz (2 C), $^1J_{SiC(Ph)}$ = 53 Hz (1 C), $^2J_{SiC(C\equiv C)}$ = 18 Hz (1 C), $^1J_{SiSi}$ = 90 Hz, 1 Si, −SiMe$_2$PhCr(CO)$_3$), −36.9 (s, $^1J_{SiC(Me)}$ = 50 Hz (2 C), $^1J_{SiC(C\equiv C)}$ = 76 Hz (1 C), $^2J_{SiC(C\equiv C)}$ = 16 Hz (1 C), $^1J_{SiSi}$ = 90 Hz, 1 Si, −SiMe$_2$C≡CPh) ppm. IR (hexane): $\tilde{\nu}$ 2152 (w, ν(C≡C)), 1972 (s, ν(C≡O)), 1906 (s, ν(C≡O)) cm^{-1}.

Tricarbonyl[hexamethyl-1-(pent-1-yn-1-yl)-3-(η^6-phenyl)-trisilane]chromium(0) (4) and [μ-octamethyl-1,4-bis(η^6-phenyl)tetrasilane]bis[tricarbonylchromium(0)] (5). Cr(CO)$_6$ (1.220 g, 5.54 mmol), *n*-PrC≡CMe$_2$Si−SiMe$_2$−SiMe$_2$Ph (1.475 g, 4.63 mmol), dibutyl ether (45 mL), and THF (6 mL) were refluxed for 150 h. From time to time Cr(CO)$_6$ subliming into the condenser was pushed back into the flask with a long spatula. After it was cooled, the mixture was evaporated in vacuo, the oily residue was redissolved in diethyl ether, and this solution was filtered. The filtrate was again evaporated in vacuo, leaving a yellow-brown oil which was dissolved in hexane (5 mL). On cooling to −20 °C a greenish yellow solid precipitated (**5**), which was separated, washed with hexane (3 × 1 mL), and dried in vacuo. Crystals suitable for X-ray crystallography were grown from hexane at 5 °C. The mother liquor was evaporated to two-thirds of its volume and cooled to −78 °C, whereupon a brownish red oil deposited (**4**). It was separated, washed with hexane (1 mL), and dried in vacuo.

Data for **4** are as follows. Yield: 1.360 g, 2.99 mmol, 65%. Anal. Found (calcd) for C$_{20}$H$_{30}$CrO$_3$Si$_3$ (454.711): C, 54.23 (52.83);[51a] H, 6.89 (6.65). Solubility: hexane, benzene, diethyl ether. ^{1}H NMR (0.9 mol/L in C$_6$D$_6$): δ 4.98 (dd, $^3J_{HH}$ = 6.4 Hz, $^4J_{HH}$ = 1 Hz, 2 H, PhCr$_{ortho}$), 4.78 (tt, $^3J_{HH}$ = 6.4 Hz, $^4J_{HH}$ = 1 Hz, 1 H, PhCr$_{para}$), 4.51 ("t", $^3J_{HH}$ = 6.4 Hz, 2 H, PhCr$_{meta}$), 2.00 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, −*CH*$_2$CH$_2$CH$_3$), 1.36 ("sextet", $^3J_{HH}$ = 7.1 Hz, 2 H, −CH$_2$*CH*$_2$CH$_3$), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, −CH$_2$CH$_2$*CH*$_3$), 0.40 (s, $^2J_{HSi}$ = 6 Hz, 6 H, SiMe$_2$), 0.17 (s, $^2J_{HSi}$ = 6 Hz, 6 H, SiMe$_2$), 0.11 (s, $^2J_{HSi}$ = 6 Hz, 6 H, SiMe$_2$) ppm. ^{13}C NMR (0.9 mol/L in C$_6$D$_6$): δ 233.7 (s, 3 C, CO), 110.5 (s (^{1}H coupled: m), 1 C, *C*≡CSi), 100.2 (s (^{1}H coupled: s/br), 1 C, PhCr$_{ipso}$), 99.1 (s (^{1}H coupled: dt, $^1J_{CH}$ = 171 Hz, $^3J_{CH}$ = 7 Hz), 2 C, PhCr$_{ortho}$), 94.8 (s (^{1}H coupled: dt, $^1J_{CH}$ = 173 Hz, $^3J_{CH}$ = 6 Hz), 1 C, PhCr$_{para}$), 91.0 (s (^{1}H coupled: dd, $^1J_{CH}$ = 174 Hz, $^3J_{CH}$ = 6 Hz), 2 C, PhCr$_{meta}$), 83.0 (s (^{1}H coupled: m), 1 C, C≡*C*Si), 22.3 (s (^{1}H coupled: tm, $^1J_{CH}$ = 129 Hz, $^2J_{CH}$ = 5–6 Hz), 1 C, CH$_2$), 22.2 (s (^{1}H coupled: tm, $^1J_{CH}$ = 129 Hz, $^2J_{CH}$ = 5–6 Hz), 1 C, CH$_2$), 13.5 (s (^{1}H coupled: qt, $^1J_{CH}$ = 126 Hz, $^2J_{CH}$ = 4 Hz), 1 C, CH$_3$), −1.7 (s (^{1}H coupled: qq, $^1J_{CH}$ = 121 Hz, $^3J_{CH}$ = 2 Hz), $^1J_{CSi}$ = 49 Hz, 2 C, Si*Me*$_2$C≡C-*n*-Pr), −3.5 (s (^{1}H coupled: qq, $^1J_{\mathrm{CH}}$ = 121 Hz, $^3J_{\mathrm{CH}}$ = 2 Hz), $^1J_{\mathrm{CSi}}$ = 47 Hz, 2 C, Si*Me*$_2$PhCr(CO)$_3$), −6.9 (s (^{1}H coupled: qq, $^1J_{\mathrm{CH}}$ = 122 Hz, $^3J_{\mathrm{CH}}$ = 3 Hz), $^1J_{\mathrm{CSi}}$ = 39 Hz, 2 C, −SiMe$_2$−) ppm. ^{29}Si NMR (0.9 mol/L in C$_6$D$_6$): δ −13.2 (s, $^1J_{\mathrm{SiC(Me)}}$ = 46 Hz (2 C), $^1J_{\mathrm{SiC(Ph)}}$ = 54 Hz (1 C), $^1J_{\mathrm{SiSi}}$ = 73 Hz, $^2J_{\mathrm{SiSi}}$ = 8 Hz, 1 Si, −SiMe$_2$PhCr(CO)$_3$), −35.5 (s, $^1J_{\mathrm{SiC(Me)}}$ = 49 Hz (2 C), $^1J_{\mathrm{SiC(C{\equiv}C)}}$ = 76 Hz (1 C), $^2J_{\mathrm{SiC(C{\equiv}C)}}$ = 15 Hz (1 C), $^1J_{\mathrm{SiSi}}$ = 82 Hz, $^2J_{\mathrm{SiSi}}$ = 8 Hz, 1 Si, −*Si*Me$_2$C≡C-*n*-Pr), −47.0 (s, $^1J_{\mathrm{SiC(Me)}}$ = 38 Hz, $^1J_{\mathrm{SiSi}}$ = 73 Hz, $^1J_{\mathrm{SiSi}}$ = 81 Hz, 1 Si, −SiMe$_2$−) ppm. IR (hexane): $\tilde{\nu}$ 2169 (w, ν(C≡C)), 1975 (s, ν(C≡O)), 1909 (s, ν(C≡O)) cm^{-1}. IR (neat liquid): $\tilde{\nu}$ 2166 (m, ν(C≡C)), 1969 (vs, ν(C≡O)), 1890 (vs, ν(C≡O)) cm^{-1} (see the Supporting Information for complete data).

Data for **5** are as follows. Yield: 90 mg, 0.14 mmol. Solubility: THF, chloroform (dec), diethyl ether, hexane. ^{1}H NMR (CDCl$_3$): δ 5.5 (br, 2 H, PhCr$_{para}$), 5.3 (br, 4 H, PhCr$_{ortho/meta}$), 5.2 (br, 4 H, PhCr$_{ortho/meta}$), 0.4 (br, 12 H, SiMe$_2$), 0.1 (br, 12 H, SiMe$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ 233 (s, 3 C, CO), 100 (s, 2 C, PhCr$_{ipso}$), 99 (s, 4 C, PhCr$_{ortho}$), 95 (s, 2 C, PhCr$_{para}$), 91 (s, 4 C, PhCr$_{meta}$), −3 (s, 4 C, −Si*Me*$_2$PhCr(CO)$_3$), −5 (s, 4 C, −SiMe$_2$−) ppm. ^{29}Si NMR (CDCl$_3$): δ −13 (s, 2 Si, −SiMe$_2$PhCr(CO)$_3$), −44 (s, 2 Si, −SiMe$_2$−) ppm.

Tricarbonyl[dimethyl(η^6-phenyl)phenylethynylsilane]molybdenum(0) (6). BF$_3$·Et$_2$O (1.22 mL, 1.376 g, 9.69 mmol) was added to Mo(CO)$_3$(py)$_3$ (1.340 g, 3.21 mmol) and PhC≡CMe$_2$SiPh (790 mg, 790 μL, 3.34 mmol) in diethyl ether (40 mL) at room temperature with exclusion of light. After 1 h the molybdenum starting complex had dissolved and the orange-yellow solution had turned dark brown. It was evaporated in vacuo, and the residue was extracted with hexane (15 × 10 mL). The extract was evaporated to half its volume in vacuo and cooled to −78 °C. The precipitated solid was separated, washed with hexane (3 × 2 mL), and dried in vacuo, yielding brownish yellow crystals. Crystals suitable for X-ray crystallography were grown from hexane at −20 °C. The complex is air-stable for several days but should be stored under argon.

Yield: 620 mg, 1.49 mmol, 46%. Mp: 72−75 °C (argon), 72−74 °C (air). Solubility: benzene, diethyl ether, hexane. Anal. Found (calcd) for C$_{19}$H$_{16}$MoO$_3$Si (416.360): C, 53.71 (54.81);[51b] H, 3.88 (3.87). ^{1}H NMR (0.17 mol/L in C$_6$D$_6$): δ 7.51 (m, 2 H, Ph$_{ortho}$), 6.93 (m, 3 H, Ph$_{meta+para}$), 5.24 (dd, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $^4J_{\mathrm{HH}}$ = 1 Hz, 2 H, PhMo$_{ortho}$), 4.83 (tt, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $^4J_{\mathrm{HH}}$ = 1 Hz, 1 H, PhMo$_{para}$), 4.50 ("t", $^3J_{\mathrm{HH}}$ = 6.5 Hz, 2 H, PhMo$_{meta}$), 0.32 (s, $^1J_{\mathrm{HC}}$ = 122 Hz, $^2J_{\mathrm{HSi}}$ = 7 Hz, 6 H, SiMe$_2$) ppm. ^{13}C NMR (0.17 mol/L in C$_6$D$_6$): δ 221.1 (s, $^1J_{\mathrm{CMo}}$ = 95 Hz, 3 C, CO), 132.4 (s, $^1J_{\mathrm{CC}}$ = 56 Hz, 2 C, Ph$_{ortho}$), 129.3 (s, 1 C, Ph$_{para}$), 128.6 (s, 2 C, Ph$_{meta}$), 122.9 (s, 1 C, Ph$_{ipso}$), 108.6 (s, $^2J_{\mathrm{CSi}}$ = 16 Hz, 1 C, C≡CSi), 100.3 (s, 2 C, PhMo$_{ortho}$), 98.5 (s, $^1J_{\mathrm{CSi}}$ = 70 Hz, 1 C, PhMo$_{ipso}$), 95.9 (s, 1 C, PhMo$_{para}$), 91.7 (s, 2 C, PhMo$_{meta}$), 90.3 (s, $^1J_{\mathrm{CSi}}$ = 92 Hz, 1 C, C≡CSi), −0.6 (s, $^1J_{\mathrm{CSi}}$ = 60 Hz, 2 C, SiMe$_2$) ppm. ^{29}Si NMR (0.17 mol/L in C$_6$D$_6$): δ −18.8 (s, $^1J_{\mathrm{SiC(Me)}}$ = 59 Hz (2 C), $^1J_{\mathrm{SiC(Ph)}}$ = 70 Hz (1 C), $^1J_{\mathrm{SiC(C{\equiv}C)}}$ = 92 Hz (1 C), $^2J_{\mathrm{SiC(C{\equiv}C)}}$ = 18 Hz (1 C)) ppm. ^{95}Mo NMR (0.17 mol/L in C$_6$D$_6$): δ −2078.7 (s, $\Delta\nu_{1/2}$ = 4 Hz) ppm. IR (hexane): $\tilde{\nu}$ 2161 (w, ν(C≡C)), 1984 (s, ν(C≡O)), 1913 (s, ν(C≡O)) cm^{-1}. IR (KBr): $\tilde{\nu}$ 2157 (s, ν(C≡C)), 1964 (vs, ν(C≡O)), 1881 (vs, ν(C≡O)) cm^{-1} (see the Supporting Information for complete data). UV/vis (hexane): λ (ε) 216 (10000, PhMo(CO)$_3$), 238 (12000, PhC≡C), 248 (14000, PhC≡C), 259 (11000, PhC≡C), 325 (br, 9100, PhMo(CO)$_3$), 375 (br/sh, 960, PhMo(CO)$_3$) nm (L/(mol cm)).[49b,52]

Bis[dimethyl(η^6-phenyl)phenylethynylsilane]chromium(0) (7). (C$_6$H$_6$)$_2$Cr (416 mg, 2.00 mmol), TMEDA (700 μL, 540 mg, 4.65 mmol), and cyclohexane (20 mL) were heated to reflux, and 2.5 mol/L *n*-BuLi in hexane (2.0 mL, 5.00 mmol) diluted with cyclohexane (8 mL) was added within 1.5 h. Refluxing was stopped 30 min after the addition of *n*-BuLi had ended, and the red-brown suspension was stirred overnight. The cyclohexane was then removed with a syringe and replaced by hexane (30 mL), and the suspension was cooled to −78 °C. PhC≡CMe$_2$SiCl (845 mg, 4.34 mmol) in hexane (8 mL) was added slowly. After it was warmed to room temperature overnight, the mixture was stirred for 6 days. It was then evaporated in vacuo and the residue extracted with toluene (16 mL). The extract was evaporated in vacuo, furnishing a red oil which crystallized to a great extent on standing. The solid was layered with pentane (5 mL) and cooled to −20 °C. After removal of the supernatant liquid the dark red crystals were washed with pentane (3 × 2.5 mL) and dried in vacuo. These crystals were suitable for X-ray crystallography. The complex is very air sensitive and must be stored under argon.

Yield: 830 mg, 1.58 mmol, 79%. Mp: 131−134 °C (argon). Solubility: benzene, toluene, THF; sparingly in hexane, cyclohexane. Anal. Found (calcd) for C$_{32}$H$_{32}$CrSi$_2$ (524.776): C, 73.21 (73.24); H, 6.13 (6.15). ^{1}H NMR (0.5 mol/L in C$_6$D$_6$): δ 7.56 (m, 4 H, Ph$_{ortho}$), 6.94 (m, 6 H, Ph$_{meta+para}$), 4.7 (vbr, $\Delta\nu_{1/2}$ = 900 Hz, 10 H, PhCr), 0.52 (s, $^1J_{\mathrm{HC}}$ = 120 Hz, 12 H, SiMe$_2$) ppm. ^{1}H NMR (0.03 mol/L in cyclohexane): δ 7.47 (m/br, 4 H, Ph$_{ortho}$), 7.19 (m/br, 6 H, Ph$_{meta+para}$), 4.54 (m/br, 4 H, PhCr$_{ortho/meta}$), 4.49 (m/br, 4 H, PhCr$_{ortho/meta}$), 4.26 (m/br, 2 H, PhCr$_{para}$), 0.43 (s/br, 12 H, SiMe$_2$) ppm. ^{13}C NMR (0.5 mol/L in C$_6$D$_6$): δ 132.3 (s, 4 C, Ph$_{ortho}$), 128.8 (s, 2 C, Ph$_{para}$), 128.6 (s, 4 C, Ph$_{meta}$), 123.7 (s, 2 C, Ph$_{ipso}$), 107.1 (s, 2 C, *C*≡CSi), 93.4 (s, 2 C, C≡*C*Si), 80−75 (br, PhCr), −0.04 (s, 4 C, SiMe$_2$) ppm. ^{13}C NMR (0.03 mol/L in cyclohexane): δ 132.5 (s, 4 C, Ph$_{ortho}$), 128.6 (s, 2 C, Ph$_{para}$), 128.4 (s, 4 C, Ph$_{meta}$), 124.5 (s, 2 C, Ph$_{ipso}$), 106.8 (s, 2 C, C≡CSi), 92.9 (s, 2 C, C≡CSi), 79.4 (s, 4 C, PhCr$_{ortho/meta}$), 77.4 (s, 4 C, PhCr$_{ortho/meta}$), 75.5 (s, 2 C, PhCr$_{para}$), 76−74 (s, 2 C, PhCr$_{ipso}$), 0.0 (s, 4 C, SiMe$_2$) ppm. ^{29}Si NMR (0.5 mol/L in C$_6$D$_6$): δ −15.5 (vbr, $\Delta\nu_{1/2}$ = 200 Hz) ppm. ^{29}Si NMR (0.03 mol/L in cyclohexane): δ −15.6 (s) ppm. IR (toluene): $\tilde{\nu}$ 2157 (m, ν(C≡C)) cm^{-1}. UV/vis (hexane): λ (ε) 238 (18000, PhC≡C), 248 (25000, PhC≡C), 258 (19000, PhC≡C), 312 (br, 11000, Ph$_2$Cr), 407 (br/sh, 750, Ph$_2$Cr), 520 (br/sh, 170, Ph$_2$Cr), 700 (br, 24, Ph$_2$Cr) nm (L/(mol cm)).[53]

Tricarbonyl-1κ^3*C*-dicyclopentadienyl-2(η^5),3(η^5)-{μ_3-dimethyl[phenyl-1(η^6)](phenylethynyl-2κ^2*C*,*C*′:3κ^2*C*,*C*′)silane}-1-chromium(0)-2,3-bis[nickel(I)](*Ni*−*Ni*)−Naphthalene (4:1) (8·0.25C$_{10}$H$_8$). Cp$_2$Ni (530 mg, 2.81 mmol), **1** (540 mg, 1.45 mmol), and naphthalene (a few mg) were dissolved in THF (18 mL) and stirred with sodium metal (70 mg, 3.04 mmol) at room temperature, whereupon the green solution quickly became dark. The next day ethyl bromide (500 μL, 730 mg, 6.70 mmol) was added, resulting in a detectable rise of the temperature of the solution. After it was stirred overnight, the mixture was evaporated in vacuo and the solid black-green residue extracted with hexane (15 × 10 mL). The extract was again evaporated in vacuo, leaving a dark green semisolid mass (760 mg, 88% crude yield referenced to **8**, 80% crude yield referenced to **8**·0.25C$_{10}$H$_8$). Fourfold recrystallization from 1/1 diethyl ether/pentane (or diethyl ether/hexane; 2−5 mL each, slow cooling to −78 °C) yielded dark green microcrystals, which were washed with hexane (3 × 0.5 mL) and dried in vacuo. These crystals were suitable for X-ray crystallography. **8**·0.25C$_{10}$H$_8$ is air-stable for at least 1 day but should be stored under argon.

Yield: 230 mg, 0.35 mmol, 24%. Mp: 108−111 °C (argon), 114−116 °C (air). Solubility: hexane, pentane, benzene, diethyl ether. Anal. Found (calcd) for C$_{31.5}$H$_{28}$CrNi$_2$O$_3$Si (652.030): C, 57.90 (58.03); H, 4.44 (4.33). Calcd for **8** (C$_{29}$H$_{26}$CrNi$_2$O$_3$Si): C, 56.18; H, 4.23. ^{1}H NMR (0.03 mol/L in C$_6$D$_6$): δ 7.62 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $^1J_{\mathrm{HC}}$ = 160 Hz, 2 H, Ph$_{ortho}$), 7.25 (m, C$_{10}$H$_8$), 7.14 ("t", $^3J_{\mathrm{HH}}$ = 8 Hz, $^1J_{\mathrm{HC}}$ = 159 Hz, 2 H, Ph$_{meta}$), 7.09 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 1 H, Ph$_{para}$), 7.14−7.09 (C$_{10}$H$_8$), 5.13 (d, $^3J_{\mathrm{HH}}$ = 5.9 Hz, 2 H, PhCr$_{ortho}$), 5.04 (s, $^1J_{\mathrm{HC}}$ = 174 Hz, 10 H, Cp), 4.66 (t, $^3J_{\mathrm{HH}}$ = 6 Hz, 1 H, PhCr$_{para}$), 4.33 ("t", $^3J_{\mathrm{HH}}$ = 6.2 Hz, 2 H, PhCr$_{meta}$), 0.60 (s, $^1J_{\mathrm{HC}}$ = 121 Hz, 6 H, SiMe$_2$) ppm. ^{13}C NMR (0.03 mol/L in C$_6$D$_6$): δ 233.6 (s, 3 C, CO), 138.8 (s, 1 C, Ph$_{ipso}$), 134.1 (s, C, C$_{10}$H$_8$), 131.2 (s, 2 C, Ph$_{ortho}$), 128.6 (s, 2 C, Ph$_{meta}$), 126.0 (s, CH, C$_{10}$H$_8$), 113.4 (s, 1 C, C≡CSi·Ni$_2$), 99.4 (s, 2 C, PhCr$_{ortho}$), 98.5 (s, 1 C, PhCr$_{ipso}$), 95.2 (s, 1 C, PhCr$_{para}$), 90.3 (s, 2 C, PhCr$_{meta}$), 89.1 (s, 1 C, C≡CSi·Ni$_2$), 87.7 (s, 10 C, Cp), −0.1 (s, $^1J_{\mathrm{CSi}}$ = 58 Hz, 2 C, SiMe$_2$) ppm. ^{13}C NMR (0.15 mol/L in diethyl ether): δ 233.1 (s, 3 C, CO), 138.5 (s, 1 C, Ph$_{ipso}$), 134.0 (s, C, C$_{10}$H$_8$), 131.0 (s, 2 C, Ph$_{ortho}$), 128.2 (s, 2 C, Ph$_{meta}$), 127.9 (s, CH, C$_{10}$H$_8$), 127.6 (s, 1 C, Ph$_{para}$), 125.7 (s, CH, C$_{10}$H$_8$), 113.5 (s, 1 C, C≡CSi·Ni$_2$), 99.8 (s, 2 C, PhCr$_{ortho}$), 98.2 (s, 1 C, PhCr$_{ipso}$), 95.7 (s, 1 C, PhCr$_{para}$), 90.4 (s, 2 C, PhCr$_{meta}$), 88.4 (s, 1 C, C≡CSi·Ni$_2$), 87.4 (s, 10 C, Cp), −0.3 (s, 2 C, SiMe$_2$) ppm. ^{29}Si NMR (0.03 mol/L in C$_6$D$_6$): δ −8.9 (s, $^1J_{\mathrm{SiC(Me)}}$ = 58 Hz (2 C), $^1J_{\mathrm{SiC(PhCr)}}$ = 73 Hz (1 C), $^1J_{\mathrm{SiC(C{\equiv}C{\cdot}Ni2)}}$ = 67 Hz (1 C)) ppm. IR (hexane): $\tilde{\nu}$ 1976 (s, ν(C≡O)), 1910 (s, ν(C≡O)) cm^{-1}. IR (KBr): $\tilde{\nu}$ 1960 (vs, ν(C≡O)), 1879 (vs, ν(C≡O)), 1602 (m, ν(C≡

C)) cm^{-1} (see the Supporting Information for complete data). UV/vis (hexane): λ (ε) 221 (85000, $\mathrm{PhCr(CO)_3}$ + $\mathrm{Cp_2Ni_2{\cdot}C{\equiv}C}$), 248 (57000, PhC≡C), 253 (55000), 259 (52000, PhC≡C + $\mathrm{PhCr(CO)_3}$ + $\mathrm{Cp_2Ni_2{\cdot}C{\equiv}C}$), 321 (br, 35000, $\mathrm{PhCr(CO)_3}$), 351 (br, 34000, $\mathrm{Cp_2Ni_2{\cdot}C{\equiv}C}$), 462 (br, 4800, $\mathrm{Cp_2Ni_2{\cdot}C{\equiv}C}$), 672 (br, 1500, $\mathrm{Cp_2Ni_2{\cdot}C{\equiv}C}$) nm (L/(mol cm)).[49]

Heptacarbonyl-1κ^3*C*,2κ^2*C*,3κ^2*C*-dicyclopentadienyl-2(η^5),3-(η^5)-{μ_3-dimethyl[phenyl-1(η^6)](phenylethynyl-2κ^2*C*,*C*′:3κ^2*C*,*C*′)-silane}-1-molybdenum(0)-2,3-bis[molybdenum(I)](*Mo*^{2}–*Mo*^{3}) (9). $\mathrm{Cp_2Mo_2(CO)_4}$ (221 mg, 0.51 mmol) was dissolved in toluene (10 mL), and **9** (215 mg, 0.52 mmol) in toluene (5 mL) was added. After 2 weeks of stirring at room temperature the solution was filtered, evaporated in vacuo to a volume of 5 mL, and layered with hexane (10 mL). Solvent diffusion and cooling to −20 °C resulted in precipitation of a solid, which was isolated, washed with hexane (4 × 1.5 mL), and dried in vacuo (210 mg, 48% crude yield). The deep red-brown solid was sorted under the microscope to remove some differently colored byproducts, dissolved in toluene (5 mL), and layered with hexane (10 mL). After solvent diffusion for some days the precipitated microcrystals were isolated, washed with hexane (3 × 2 mL), and dried in vacuo. These crystals were suitable for X-ray crystallography. They can be handled in air but should be stored under argon.

Yield: 100 mg, 0.12 mmol, 23%. Mp: 220–230 °C (dec, argon), slow continuous dec (air). Solubility: benzene, toluene, THF; sparingly in hexane. Anal. Found (calcd) for $\mathrm{C_{33}H_{26}Mo_3O_7Si}$ (850.470): C, 47.96 (46.61);[51c] H, 3.23 (3.08). ^{1}H NMR (0.035 mol/L in $\mathrm{C_6D_6}$): δ 7.36 (dd, $^3J_{\mathrm{HH}}$ = 8.2 Hz, $^4J_{\mathrm{HH}}$ = 1 Hz, 2 H, Ph_{ortho}), 7.10 ("t", $^3J_{\mathrm{HH}}$ = 7.9 Hz, 2 H, Ph_{meta}), 6.89 (tt, $^3J_{\mathrm{HH}}$ = 7.3 Hz, $^4J_{\mathrm{HH}}$ = 1 Hz, 1 H, Ph_{para}), 5.34 (dd, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $^4J_{\mathrm{HH}}$ = 1 Hz, 2 H, PhMo_{ortho}), 4.86 (tt, $^3J_{\mathrm{HH}}$ = 6.4 Hz, $^4J_{\mathrm{HH}}$ = 1.3 Hz, 1 H, PhMo_{para}), 4.68 (s, $^1J_{\mathrm{HC}}$ = 176 Hz, 10 H, Cp), 4.56 ("t", $^3J_{\mathrm{HH}}$ = 6.4 Hz, 2 H, PhMo_{meta}), 0.50 (s, $^1J_{\mathrm{HC}}$ = 120 Hz, $^2J_{\mathrm{HSi}}$ = 6.6 Hz, 6 H, $\mathrm{SiMe_2}$) ppm. ^{13}C NMR (0.035 mol/L in $\mathrm{C_6D_6}$): δ 231.1 (s, $\mathrm{CO_{Mo2}}$), 230.2 (s, $\mathrm{CO_{Mo2}}$), 221.4 (s, $\mathrm{CO_{PhMo(CO)3}}$), 146.9 (s, 1 C, Ph_{ipso}), 129.9 (s, 2 C, Ph_{ortho}), 126.5 (s, 1 C, Ph_{para}), 113.8 (s, 1 C, $\mathrm{C{\equiv}CSi{\cdot}Mo_2}$), 103.7 (s, 1 C, PhMo_{ipso}), 101.1 (s, 2 C, PhMo_{ortho}), 96.5 (s, 1 C, PhMo_{para}), 92.1 (s, 1 C, $\mathrm{C{\equiv}CSi{\cdot}Mo_2}$), 91.9 (s, 10 C, Cp), 91.2 (s, 2 C, PhMo_{meta}), 0.8 (s, $^1J_{\mathrm{CSi}}$ = 57 Hz, 2 C, $\mathrm{SiMe_2}$) ppm. ^{29}Si NMR (0.035 mol/L in $\mathrm{C_6D_6}$): δ +3.8 (s, $^1J_{\mathrm{SiC(Me)}}$ = 57 Hz) ppm. ^{95}Mo NMR (0.035 mol/L in $\mathrm{C_6D_6}$): δ −1870 (br, $\Delta\nu_{1/2}$ = 1200 Hz, $\mathrm{Cp_2Mo_2(CO)_4{\cdot}C{\equiv}C}$), −2070.8 (s, $\Delta\nu_{1/2}$ = 6 Hz, $\mathrm{PhMo(CO)_3}$) ppm. IR (THF): $\tilde{\nu}$ 1984 (m, $\nu(\mathrm{Mo_2C{\equiv}O})$), 1965 (s, $\nu(\mathrm{MoC{\equiv}O})$), 1927 (s, $\nu(\mathrm{Mo_2C{\equiv}O})$), 1888 (s, $\nu(\mathrm{MoC{\equiv}O})$), 1840 (m, $\nu(\mathrm{Mo_2C{\equiv}O})$) cm^{-1}. IR (KBr): $\tilde{\nu}$ 1981 (vs, $\nu(\mathrm{Mo_2C{\equiv}O})$), 1965 (vs, $\nu(\mathrm{MoC{\equiv}O})$), 1926 (vs, $\nu(\mathrm{Mo_2C{\equiv}O})$), 1910 (vs, $\nu(\mathrm{Mo_2C{\equiv}O})$), 1870 (vs, $\nu(\mathrm{MoC{\equiv}O})$), 1836 (vs, $\nu(\mathrm{Mo_2C{\equiv}O})$), 1503 (m, $\nu(\mathrm{C{\equiv}C})$) cm^{-1} (see the Supporting Information for complete data). UV/vis (THF): λ (ε) 220 (26000, $\mathrm{PhMo(CO)_3}$ + $\mathrm{Cp_2Mo_2(CO)_4{\cdot}C{\equiv}C}$), 249 (sh, 20000, PhC≡C), 261 (sh, 17000, PhC≡C + $\mathrm{PhMo(CO)_3}$), 327 (br, 17000, $\mathrm{PhMo(CO)_3}$), 375 (br/sh, 6100, $\mathrm{PhMo(CO)_3}$ + $\mathrm{Cp_2Mo_2(CO)_4{\cdot}C{\equiv}C}$), 440 (br/sh, 1600, $\mathrm{Cp_2Mo_2(CO)_4{\cdot}C{\equiv}C}$), 565 (br, 480, $\mathrm{Cp_2Mo_2(CO)_4{\cdot}C{\equiv}C}$) nm (L/(mol cm)).[49b,52,54]

2(η^5)-Cyclopentadienyl-{μ-3,4-diphenyl-1,2-bis{dimethyl-[phenyl-1(η^6)]silyl}cyclobutadiene-2(η^4)}-1-chromium(0)-2-cobalt(I) (10). Complex 7 (304 mg, 0.58 mmol) and $\mathrm{CpCo(PPh_3)_2{\cdot}0.5(C_6H_{14}/C_7H_8)}$ (396 mg, 0.57 mmol) were stirred together in toluene (5 mL) at room temperature, whereupon the initially red solution changed its color quickly to green-brown. After 2 days it was evaporated in vacuo to a volume of 2 mL and layered with hexane (8 mL). Standing at room temperature for some days resulted in formation of dark brown crystals (some of them millimeter-sized) which were isolated, washed with hexane, and dried in vacuo. These crystals were suitable for X-ray crystallography. They were air-stable for some time but should be stored under argon.

Yield: 30 mg, 0.05 mmol, 8%. Mp: >120 °C (dec, argon), >100 °C (dec, air). Solubility: benzene, toluene; moderately in hexane. Anal. Found (calcd) for $\mathrm{C_{37}H_{37}CoCrSi_2}$ (648.804): C, 67.64 (68.50);[51d] H, 5.70 (5.75). ^{1}H NMR (0.008 mol/L in $\mathrm{C_6D_6}$): δ 7.59 (d, 4 H, Ph_{ortho}), 7.08 ("t", 4 H, Ph_{meta}), 7.04 (t, 2 H, Ph_{para}), 4.78 (s, $\Delta\nu_{1/2}$ = 4 Hz, $^1J_{\mathrm{HC}}$ = 175 Hz, 5 H, Cp), 4.2 (vbr, $\Delta\nu_{1/2}$ = 240 Hz, PhCr), 0.66 (s/br, $\Delta\nu_{1/2}$ = 10 Hz, 6 H, SiMe), 0.41 (s/br, $\Delta\nu_{1/2}$ = 6 Hz, $^1J_{\mathrm{HC}}$ = 119 Hz, 6 H, SiMe) ppm. ^{13}C NMR (0.008 mol/L in $\mathrm{C_6D_6}$): δ 138.1 (s, 2 C, Ph_{ipso}), 129.3 (s, 4 C, Ph_{ortho}), 126.6 (s, 2 C, Ph_{para}), 88.0 (s, 2 C, $\mathrm{C_4Co}$), 82.8 (s, 5 C, Cp), 81.6 (s, 2 C, $\mathrm{C_4Co}$), 75 (vbr, PhCr), 4.0 (s/br, SiMe), 1.8 (s/br, SiMe) ppm.[55a] ^{29}Si NMR (hexane/toluene): δ −3.5 (s, $^1J_{\mathrm{SiC(Me)}}$ = 54 Hz (2 C), $^1J_{\mathrm{SiC(PhCr/CbCo)}}$ = 72 Hz (2 C)) ppm.[55b] IR (KBr): see the Supporting Information. UV/vis (hexane): λ (ε) 213 (7400), 232 (br, 8600), 284 (br, 7500), 310 (br, 6900), 410 (br/sh, 820), 590 (br/sh, 65) nm (L/(mol cm)).[53]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving details of the synthesis of compound **3** (assumed intermediates, their ^{29}Si NMR data, Scheme S1, ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compound **3**), a summary of the spectroscopic properties, ^{29}Si NMR, selected IR, and selected UV/vis data, selected overlaid UV/vis spectra, detailed IR data with assignments, Figure S8, crystal structure data, bond lengths, bond angles, and torsion angles for compounds **1**, **2**, and **5**–**10**. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC entries 642190 (**1**), 642199 (**2**), 642203 (**5**), 642201 (**6**), 642193 (**7**), 642202 (**8**), 642206 (**9**), and 642209 (**10**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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(17) In contrast to the analogous procedure for the synthesis of an tricarbonyl(alkynylsilylcyclopentadienyl)manganese complex, no carbonyl substitution product was detected.[3b]

(18) The ligand 1,4-diphenyloctamethyltetrasilane ($Ph-(SiMe_2)_4-Ph$) is an impurity in $n\text{-PrC}{\equiv}\text{CMe}_2\text{Si}-\text{SiMe}_2-\text{SiMe}_2\text{Ph}$.[31c]

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(30) Data for $Cp_2Mo_2(CO)_4\cdot PhC\equiv CPh$ (prepared from $Cp_2Mo_2(CO)_4$ and $PhC\equiv CPh$ in THF at room temperature) are as follows. ^{95}Mo NMR (C_6D_6): δ −1854 ($\Delta\nu_{1/2}$ = 470 Hz) ppm. IR (THF): $\tilde{\nu}$ 1983 (m, ν(C≡O)), 1925 (s, ν(C≡O)), 1840 (m, ν(C≡O)) cm^{-1}. IR (KBr): $\tilde{\nu}$ 1978 (m, ν(C≡O)), 1919 (s, ν(C≡O)), 1906 (s, ν(C≡O)), 1846 (m, ν(C≡O)) cm^{-1}. UV/vis (hexane): λ (ε) 216 (shoulder up to 300 nm, 70000), 363 (br, 12000), 544 (br, 1500) nm (L/(mol cm)).

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(41) Reaction conditions: **1**, 0.011 mol/L in diethyl ether, 2 h; **3**, 0.014 mol/L in hexane/diethyl ether 2/1 + 2 vol % benzene, 2 h; **4**, 0.037 mol/L in diethyl ether + 2 vol % benzene, 2 h; **6**, 0.008 mol/L in diethyl ether, 2 h.

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