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Dinuclear and Mononuclear Chromium Acetylide Complexes

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Dedicated to Professor Gerhard Erker on the occasion of his 65th birthday

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Reaction of *trans*-$Cl_2Cr(dmpe)_2$ (**1**) [dmpe = 1,2-bis(dimethylphosphanyl)ethane] with 0.5 equiv. of $Me_3Sn{-}C{\equiv}C{-}C{\equiv}C{-}SnMe_3$ or $Me_3Sn{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}SnMe_3$ afforded the dinuclear complexes *trans*-$[Cl(dmpe)_2Cr{\equiv}C{-}C{\equiv}C{-}C{\equiv}Cr(dmpe)_2Cl]$ (**2**), *trans*-$[Cl(dmpe)_2Cr{-}C{\equiv}C{-}C{\equiv}C{-}Cr(dmpe)_2Cl][SnMe_3Cl_2]_2$ (**2**$[SnMe_3Cl_2]_2$), and *trans*-$[Cl(dmpe)_2Cr{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}Cr(dmpe)_2Cl][SnMe_3Cl_2]_2$ (**3**$[SnMe_3Cl_2]_2$), which could be transformed to the **2**$[PF_6]_2$ and **3**$[BPh_4]_2$ salts. Substitutions of the chloride groups in **2** were carried out to achieve the corresponding iodo (**4**) and (trimethylsilyl)alkynyl (**5**) complexes. Utilizing similar reactions and treatment with only 1 equiv. of the corresponding alkynyl ligand [$Me_3Sn{-}C{\equiv}C{-}R$ (R = $-SnMe_3$, $-C_6H_5$), $Me_3Sn{-}C{\equiv}C{-}C{\equiv}C{-}R$ (R = $-SiMe_3$, $-SnMe_3$), and $Me_3Sn{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}SnMe_3$] allowed us to prepare a series of mononuclear monoacetylide complexes: *trans*-$[Cl(dmpe)_2Cr{-}C{\equiv}C{-}R]$ [R = $-SnMe_3$(**6**), $-C_6H_5$(**7**)], *trans*-$[Cl(dmpe)_2Cr{-}C{\equiv}C{-}C{\equiv}C{-}R]$ [R = $-SiMe_3$(**8**), $-SnMe_3$(**9**)], and *trans*-$[Cl(dmpe)_2Cr{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}SnMe_3]$ (**10**), respectively. The complexes **2**, **2**$[SnMe_3Cl_2]_2$, **2**$[PF_6]_2$, **3**$[SnMe_3Cl_2]_2$, **3**$[BPh_4]_2$, and **6**–**10** displayed paramagnetic behavior. Electrochemical studies performed on the dinuclear complexes (**2**), (**2**$[SnMe_3Cl_2]_2$), (**3**$[SnMe_3Cl_2]_2$), and (**5**) showed one two-electron redox wave revealing a class-I type behavior based on the Robin–Day classification, which is untypical for dinuclear complexes bridged by a butadiyne ligand. The complexes were characterized by NMR, ESI–MS, cyclic voltammetry, EPR spectroscopy, magnetic measurements, and exemplary single-crystal X-ray diffraction studies for **2**, **2**$[SnMe_3Cl_2]_2$, **8**, **9**, and **10**.

Introduction

Over the last two decades organometallic complexes bridged by acetylenic units were investigated as rigid-rod redox-active complexes denoted as molecular wires. On the basis of through-bridge single-electron conductivity they show potential for applications in the field of molecular electronics.[1–3] Organic molecular wires studied to date were constructed entirely of delocalized orbital systems. However, they often revealed lower molecular single-electron conductivities than that predicted theoretically.[4,5] The incorporation of transition-metal centers in these chains was found to increase the delocalization due to the strong electronic coupling between the metal center and the conjugated organic ligands.[6,7] The electronic properties of molecular wires built from organometallic complexes can be fine-tuned by modifying the extent of conjugation in the bridge or changing the metal center or by switching the oxidation states of the metal. Bridged or terminal ligands based on linear C_n polycarbon chains emerged as important candidates for the construction of molecular wires. They were in addition extensively investigated to explore their physical properties.[8–10] Homo- or heterometallic complexes in which unsaturated elemental-carbon chains span two metals of the type $L_mMC_nM'L'_m$ were thus reported[11,12] and turned out to be especially suited for the study of the electronic interaction between the two metal centers.[13–17] These complexes constitute the most fundamental class of carbon-based rigid-rod-type molecular wires,[18,19] and represent attractive synthetic targets that allow the study of their electronic, optical, and electrochemical properties.[20]

Among the known bimetallic complexes most of them are bismetallocene complexes.[21] One of the disadvantages associated with this type of compound is that the coordination sphere does not allow any further substitution thereby acting as a stopper unit to the wire. Complexes of the type $L_mMC_nM'L'_m$ with $n = 4$ have been reported for M = Fe,[22,23] Re,[12,24–26] Ru,[27] Pt,[28] Mo,[29,30] Mn,[31–33] Os,[34] and the most recent for W.[35] These kinds of complexes normally reveal high delocalization of the electrons. Metal complexes belonging to class-III compounds, based on the Robin–Day classification of electron transfer, are considered as good candidates for the construction of molecular

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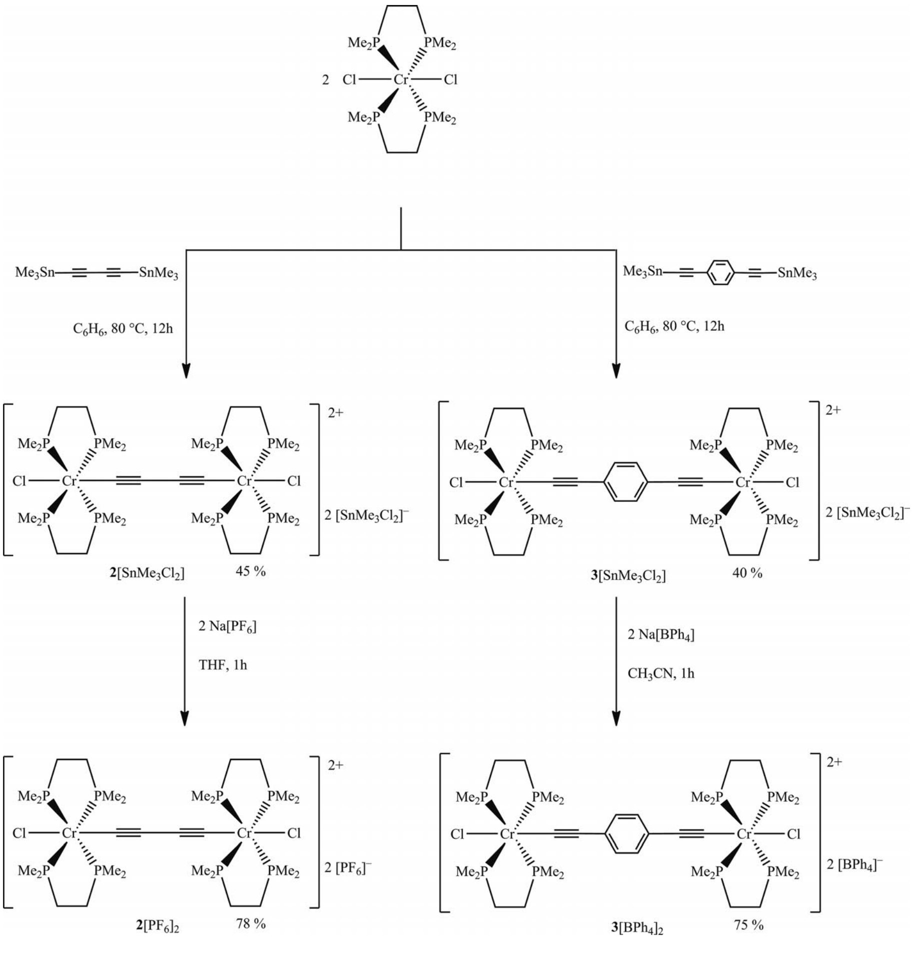
wires, possessing no or almost no barrier for electron transfer.[36] On the other hand compounds corresponding to class I or II are expected to show barriers for electron transfer that make these complexes useful for controlling the extent of electron-transfer functions and to serve for instance as resistors, diodes, or single-electron transistors.

We have recently reported investigations on dinuclear butadiyne tungsten carbyne complexes and further their functionalization of the terminal ends with Fe(depe)$_2$Cl caps [depe = 1,2-bis(diethylphosphanyl)ethane]. In continuation with the ongoing investigations in our group, chromium based dinuclear butadiyne complexes were also expected to possess appropriate energy–work functions suitable for the construction of molecular wires. The first chromium complexes bearing the chelating ligand 1,2-bis(dimethylphosphanyl)ethane (dmpe) was reported by Wilkinson and coworkers,[37] and several chromium bis(acetylide) complexes using these chelating phosphane ligands were previously prepared by our group.[38] In this context a dinuclear bis(acetylide)-chromium(I) complex bridged by a dinitrogen ligand has been reported.[39] The synthesis of the monoacetylide complexes would create a new set of building blocks for heterodinuclear compounds after coupling these monosubstituted species with different metal precursors containing Fe, Re, or W. In this work, we report on the syntheses and properties of the dinuclear chromium complexes possessing a butadiyne bridge and exhibiting an unusual class-I behavior based on the Robin–Day classification,[40] and mononuclear chromium monoacetylide complexes with trimethylstannyl end groups.

Results and Discussion

Substitution reactions of the Cl$_2$Cr(dmpe)$_2$ complex with lithium acetylides to form bis(acetylide) complexes were investigated earlier in our group,[38] however similar conditions could not be adopted for the synthesis of the monosubstituted alkyne complexes and the dinuclear butadiyne complexes. Hence, a different synthetic strategy was sought that involved the use of trimethylstannyl alkynyl reagents with the starting Cl$_2$Cr(dmpe)$_2$ complex. The dinuclear complexes **2**, **2**[SnMe$_3$Cl$_2$]$_2$, and **3**[SnMe$_3$Cl$_2$]$_2$ were obtained by heating Cl$_2$Cr(dmpe)$_2$[37] with 0.5 equiv. of bis(trimethylstannyl)butadiyne (Scheme 1) in benzene for 12 h at 80 °C. An anion exchange was performed for **2**[SnMe$_3$Cl$_2$]$_2$ by treatment with a stoichiometric amount of NaPF$_6$ in CH$_2$Cl$_2$ to form the corresponding salt **2**[PF$_6$]$_2$. In order to obtain the neutral complex **2**, the reaction was carried out in the presence of Zn powder as a reducing agent and the



Scheme 1.

corresponding neutral complex was obtained in 55% yield. However, using this route we were only able to obtain the dicationic complex **3**$[SnMe_3Cl_2]_2$ when $Me_3Sn–C{\equiv}C–C_6H_4–C{\equiv}C–SnMe_3$ was used. An anion exchange was performed on complex **3**$[SnMe_3Cl_2]_2$, as well, to form the corresponding **3**$[BPh_4]_2$ by treatment with a stoichiometric amount of $NaBPh_4$ in acetonitrile.

Strong paramagnetic behavior for the complexes **2**$[SnMe_3Cl_2]_2$, **2**$[PF_6]_2$, **3**$[SnMe_3Cl_2]_2$, and **3**$[BPh_4]_2$ was observed in the ^1H NMR and ^{31}P NMR spectra. The ^1H NMR resonances of these complexes appeared at high field as broad signals at –14.5 and –33.7 ppm for the methylene and methyl protons, respectively.

A study of the Curie–Weiss behavior using a temperature range between 30 °C and –70 °C was carried out to confirm the paramagnetic character of **2**$[SnMe_3Cl_2]_2$ (Figure 1). The resonances (PCH_2 and PCH_3) for the dmpe ligand showed a shift from –19.6 to –14.7 ppm over the temperature range from 30 °C to –70 °C.

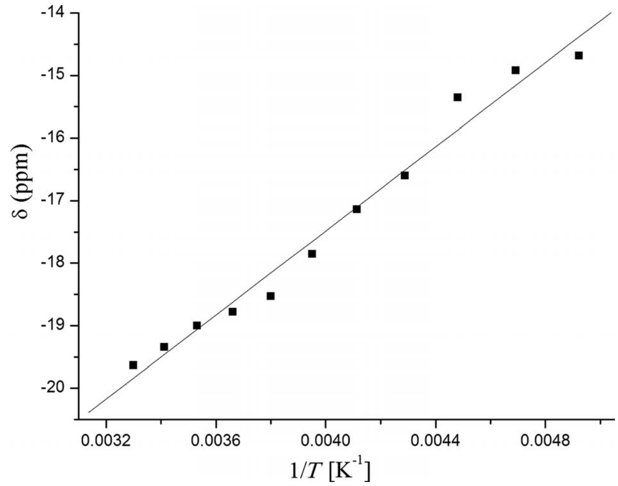


Figure 1. Curie–Weiss behavior for the proton resonances of **2**$[SnMe_3Cl_2]_2$ in CD_2Cl_2 over a temperature range from 30 °C to –70 °C (R = 0.990).

The ^1H NMR spectrum of **2** exhibits signals at δ = 1.3 and 1.6 ppm for the methylene protons and the methyl protons of the dmpe ligands, respectively. In the IR spectra these chromium complexes reveal bands at $\tilde{\nu} \approx 2050$ and 2000 cm^{-1} for **2**, $\tilde{\nu} \approx 1990$ and 1940 cm^{-1} for **2**$[SnMe_3Cl_2]_2$, and at 1950 and 1580 cm^{-1} for **3**$[SnMe_3Cl_2]_2$; these variations correspond to different vibrations of the C_4 chain.[41] The structures of **2** (Figure 2) and **2**$[SnMe_3Cl_2]_2$ (Figure 3) were confirmed by X-ray diffraction studies. In both molecules the ligand geometry around the chromium atoms are approximately octahedral with the Cl and the butadiyne ligand in the *trans* positions and the P atoms in an equatorial arrangement displaying Cr–P distances between 2.315(1) and 2.443(1) Å.

The $C_\alpha–C_\beta$ bond lengths are longer than the central $C_\beta–C_\beta'$ distance of **2** and the $Cr–C_\alpha$ bond length is close to that of a triple bond[42] confirming a biscarbyne canonical structure (Scheme 2).[42–44] In the case of complex **2**$[SnMe_3Cl_2]_2$ the $C_\alpha–C_\beta$ and $C_\beta–C_\beta'$ distances are 1.218(5) and 1.377(5) Å, respectively, confirming the C_4 chain of **2**$[SnMe_3Cl_2]_2$ as prevailingly bisacetylenic.[42,45] This clearly indicates that the oxidation of **2** causes a transformation of the C_4 bridge, from biscarbynic to bisacetylenic, and as a consequence the electronic configuration of the complex changes from an 18 e^- complex to a 15 e^- complex.

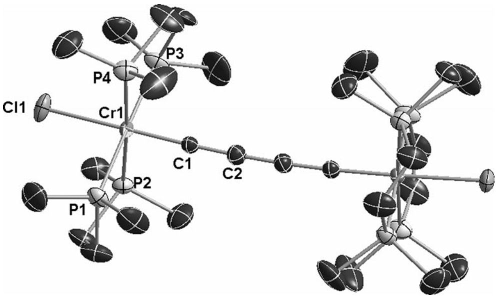


Figure 2. Crystal structure of **2** (ellipsoids set at the 50% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–Cl1 2.4107(9), Cr1–C1 1.789(3), C1–C2 1.301(4), C2–C2′ 1.286(4), Cr1–P1 2.325(1), Cr1–P2 2.3350(9), Cr1–P3 2.322(1), Cr1–P4 2.315(1), Cr1–C1–C2 177.2(2), C1–C2–C2′ 176.9(3).

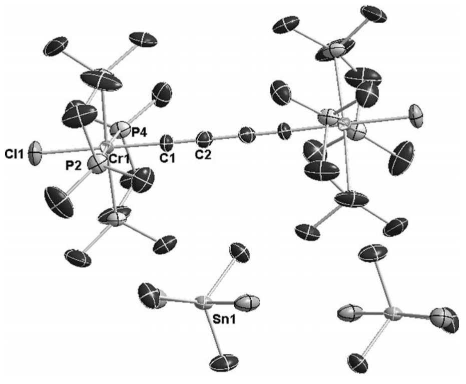


Figure 3. Crystal structure of **2**$[SnMe_3Cl_2]_2$ (ellipsoids set at the 50% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–Cl1 2.328(1), Cr1–C1 1.951(3), C1–C2 1.218(5), C2–C2′ 1.377(5), Cr1–P1 2.441(1), Cr1–P2 2.427(2), Cr1–P3 2.443(1), Cr1–P4 2.435(2), Cr1–C1–C2 177.0(4), C1–C2–C2′ 179.4(5).

$$\cdot C{\equiv}C{-}C{\equiv}C\cdot \longleftrightarrow :C{=}C{=}C{=}C: \longleftrightarrow \vdots C{-}C{\equiv}C{-}C\vdots$$

Acetylenic Carbenic Carbynic

Scheme 2. Canonical forms of a C_4 unit in $[M]C_4[M]$ structures.

Electrochemical studies of the complexes **2**, **2**$[SnMe_3Cl_2]_2$, and **3**$[SnMe_3Cl_2]_2$ (Figure 4) were employed to evaluate the abilities of electronic communication between the chromium centers. All complexes displayed one reversible two-electron redox wave with $E_{1/2}$ at –1.08 V (**2**), –1.20 V (**2**$[SnMe_3Cl_2]_2$), and –1.29 V (**3**$[SnMe_3Cl_2]_2$). This behavior is in contrast to that observed in related $W–C_4–W$ complexes. Also the redox potentials are significantly lower than that observed for the tungsten complexes, which are at –0.253 and –0.543 V vs. $F_c^{0/+}$.[35] The presence of only one redox wave for the chromium complexes corresponds to the kind of behavior expected for a class-I system according to the Robin–Day classification (localized).[40] For class-I complexes, the barrier to electron transfer is very high, such that electrons are permanently "locked" in one position,[46] and the properties of these systems are essentially those of the separate sites.[47] Mixed-valent complexes of this type of dinuclear complex are often not stable since they tend to disproportionate. As it was already discussed for a tungsten carbyne-type system, under rigorous symmetry conditions the HOMO is expected to be of δ-type and hence through bridge interactions from π orbitals are not possible. Therefore, the electron transfer observed in a tungsten complex is attributed to lowering of the symmetry of the molecule exemplified in the W–C_α–C_β angle of 172° of the tungsten carbyne chain.[35] Such a strong distortion is not observed in the chromium dinuclear complexes of this work where the Cr–C_α–C_β angle in the complexes was found to be approximately 177°. This could be a plausible reason for the total absence of electronic interaction between the two metal centers.

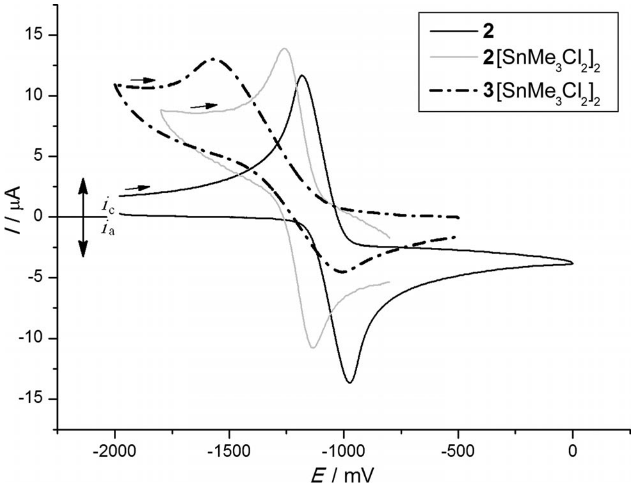


Figure 4. Cyclic voltammograms for **2**, **2**[$SnMe_3Cl_2$]$_2$, and **3**[$SnMe_3Cl_2$]$_2$ in 0.1 M [nBu$_4$N][PF_6] (Au electrode, scan rate: 100 mV s^{-1} 20 °C. *E* vs. Ag$^{0/+}$).

Further confirmation of the class-I behavior was obtained from the absence of an intervalence charge-transfer band of a 1:1 mixture of complexes **2** and **2**[$SnMe_3Cl_2$]$_2$ in CH_2Cl_2 in the NIR spectrum, which for class-III compounds would be expected to comproportionate to a mixed-valent species and for class-I compounds the equilibrium would lie on the left side forming no mixed-valent species at all (Scheme 3). It is important to mention that we could not observe or isolate any mixed-valence complex, which would exclude the formation of a mixed-valent compound (class-I).

$$[\mathbf{2}] + [\mathbf{2}[SnMe_3Cl_2]_2] \underset{K_c}{\overset{\text{comproportionation}}{\rightleftharpoons}} 2\,[\mathbf{2}[SnMe_3Cl_2]]$$

Scheme 3.

The magnetic susceptibility curve of **2**[$SnMe_3Cl_2$]$_2$ (Figure 5) shows the typical paramagnetic behavior of a d^3 high-spin complex, with a magnetic moment of 2.19 μ_B, which further confirms the observation from the ^{1}H NMR spectroscopy of a temperature-dependent paramagnetic left-shift behavior. The EPR spectrum of **2**[PF_6]$_2$ in CH_2Cl_2 at 6 K (Figure 6) showed one signal corresponding to the unpaired electron of the orbital d_{xy} of the metal center. This can be attributed to a strong antiferromagnetic coupling of the unpaired electrons of the d_{xz} and d_{yz} orbital of the chromium(III) centers through the bridge. A hyperfine coupling is detected because of the coupling with the phosphorus nuclei, but has not been resolved well enough to be quantified. Further EPR studies of **2** under the same conditions showed EPR silent behavior.

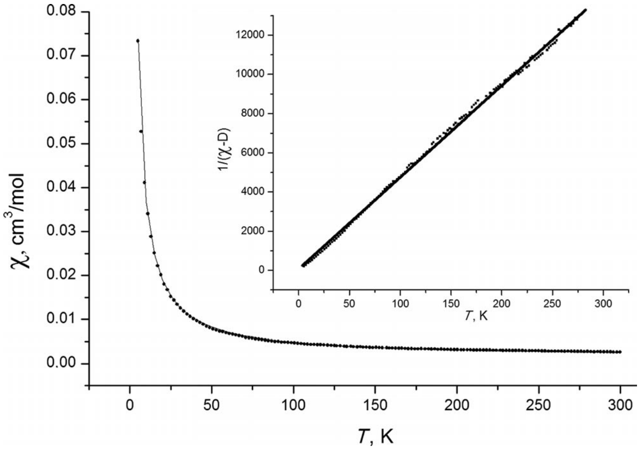


Figure 5. Temperature dependence of χ vs. T and $1/(\chi - D)$ vs. T (inset) for complex **2**[$SnMe_3Cl_2$]$_2$.

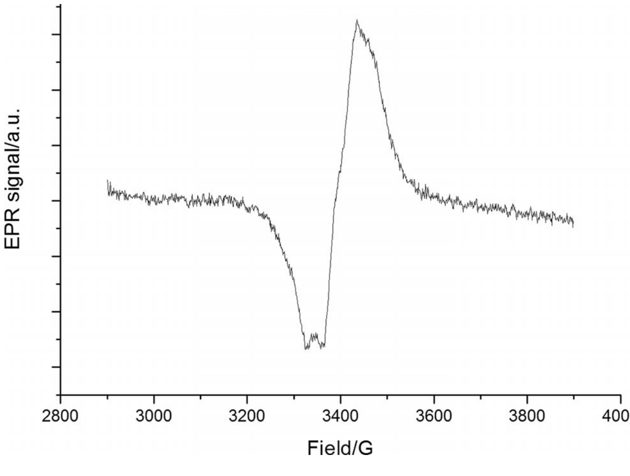
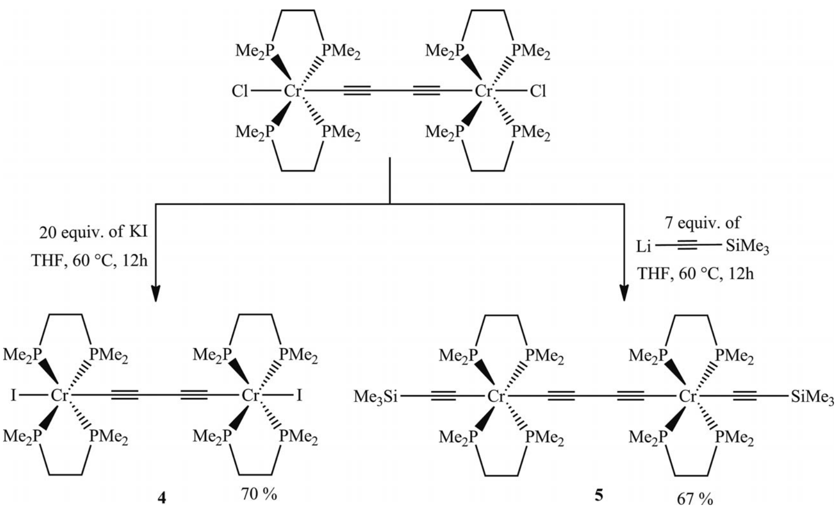


Figure 6. EPR of **2**[PF_6]$_2$ in CH_2Cl_2 glass at 6 K.

In order to further elucidate the effect of the axial ligand on the electronic properties of these chromium complexes, a preparation for complexes with different electronic properties of these groups was sought (Scheme 4).

The iodo derivative **4** was obtained in a Finkelstein-type reaction by stirring 20 equiv. of KI with **2** in THF. Such an excess was probably required because of the low solubility



Scheme 4.

of KI in THF. In the case of **5**, substitution of the Cl group could be achieved by using an excess of lithium trimethylsilyl acetylide in THF at 60 °C for 12 h. The dinuclear species **4** and **5** were isolated in 70 and 67% yield, respectively. Such end-group replacements of the halides with acetylide ligands open up possibilities for further functionalization of the dinuclear complexes. Electrochemical studies were performed on **5**. It exhibits a single redox wave at $E_{1/2}$ = –1.21 V (Figure 7) corresponding to two electrons, similar to the behavior already observed for the dinuclear complexes **2**, **2**$[SnMe_3Cl_2]_2$, and **3**$[SnMe_3Cl_2]_2$ (Table 1).

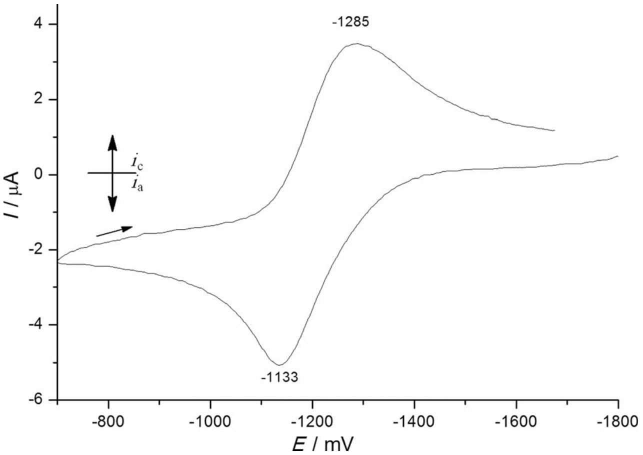


Figure 7. Cyclic voltammogram for **5** in 0.1 M $[nBu_4N][PF_6]$ (Au electrode, scan rate: 100 mVs^{-1}, 20 °C. E vs. $Ag^{0/+}$).

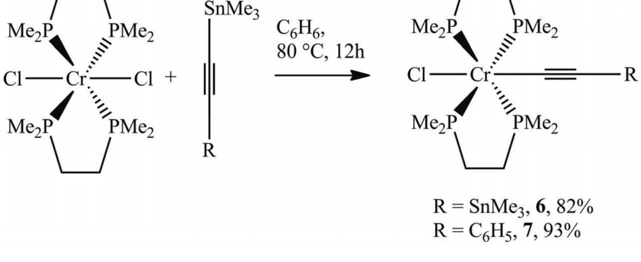
Table 1. Electrochemical data for complexes **2**, **2**$[SnMe_3Cl_2]_2$, **3**$[SnMe_3Cl_2]_2$, and **5**.

Complex	$E_{1/2}$ [V]	ΔE_p [mV]
2	–1.077	115
2$[SnMe_3Cl_2]_2$	–1.200	228
3$[SnMe_3Cl_2]_2$	–1.288	560
5	–1.209	152

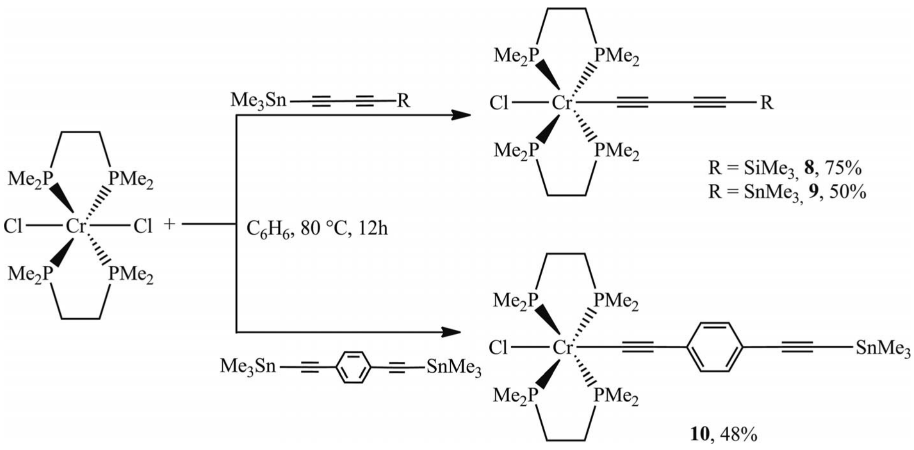
The presence of the anion in complex **2**$[SnMe_3Cl_2]_2$ decreases the $E_{1/2}$ value by about 123 mV in comparison with complex **2** and under CV conditions was oxidized to **2**$[PF_6]_2$, which could possibly arise from enhanced ion paring. Complex **2** with chloride end groups shows a higher redox potential than **5** with acetylide end groups, which is consistent with the stronger σ-donating property of the acetylide ligands. In the case of complex **3**$[SnMe_3Cl_2]_2$ the difference in the i_{pa} and i_{pc} values (ΔE_p = 560 mV) increases in comparison with the complexes bearing the butadiyne bridge, which is indicative of the decrease in the reversibility of the process.[48] This is in agreement with results reported by Gladysz et al., with different chain lengths for the rhenium complexes.[19]

Since the electronic communication between the homonuclear chromium complexes remained elusive, we thought to eventually achieve one-way electronic communication by preparation of heterodinuclear complexes. We previously demonstrated that trimethylstannyl alkynes can be excellent precursors for reactions with $Fe(depe)_2Cl_2$.[49] In this context substitutions of the halides with trimethylstannyl alkynes in the chromium complexes would indeed allow the preparation of heteronuclear complexes.

A series of mononuclear monoacetylide complexes was obtained by treatment of $Cl_2Cr(dmpe)_2$ with 1 equiv. of the corresponding trimethylstannyl alkynyl reagent in benzene at 80 °C for 12 h (Schemes 5 and 6). All these mononuclear



Scheme 5.



Scheme 6.

complexes were obtained in good yields, except for the cases of **9** and **10** with SnMe$_3$ end groups, where the yields were lower than those of the other mononuclear complexes because of the formation of small amounts of the dinuclear complexes. In the case of 1,2-bis(trimethylstannyl)ethyne (**6**), the formation of the corresponding C$_2$ dinuclear complex was not observed and this was attributed to a high steric congestion of the ligands. In the IR spectrum of **6**–**10** the characteristic bands for the (C≡C) vibrations were observed at 2010–1950 cm^{-1} for the acetylene units and between 2900–2965 cm^{-1} for the C–H vibrations of the methyl and methylene groups.

The ^{1}H NMR spectra of **6**–**10** showed strong paramagnetic behavior. Resonances at –13 and –30 ppm were observed for the methylene and methyl protons, respectively. For **7** and **10** two broad signals were found at 33 and –52 ppm corresponding to the aromatic protons. All the complexes were additionally characterized by ESI–MS and elemental analysis.

Cyclic voltammetry of **9** showed a reversible one-electron redox wave at $E_{1/2}$ = –1.339 V (ΔE_p = 364 mV) corresponding to the Cr^{II}/Cr^{III} redox couple. The structures of **8**–**10** were confirmed by X-ray diffraction studies (see Figures 8, 9, and 10). The chromium centers possess octahedral coordination with the alkyne ligand and the Cl group in a *trans* position. The Cr–C$_\alpha$ bond lengths in all complexes are close to 2 Å confirming the ligand structures as acetylides.

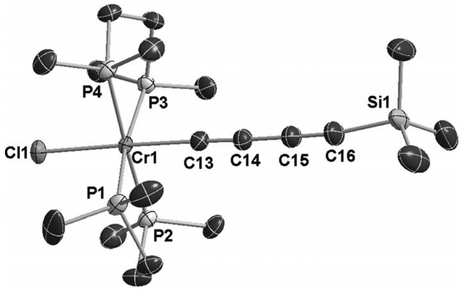


Figure 8. Crystal structure of **8** (ellipsoids set at the 50% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Cr1–Cl1 2.3682(4), Cr1–C13 2.0192(14), C13–C14 1.2171(19), C14–C15 1.378(2), C15–C16 1.214(2), C16–Si1 1.8383(16).

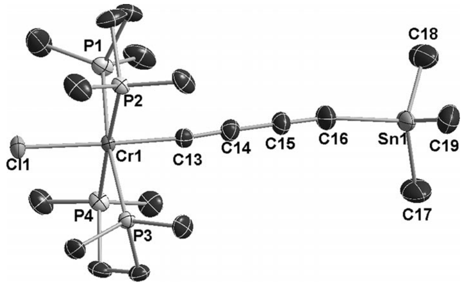


Figure 9. Crystal structure of **9** (ellipsoids set at the 50% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Cr1–Cl1 2.3632(14), Cr1–C13 1.995(5), C13–C14 1.229(8), C14–C15 1.364(8), C15–C16 1.199(9), C16–Sn1 2.115(5).

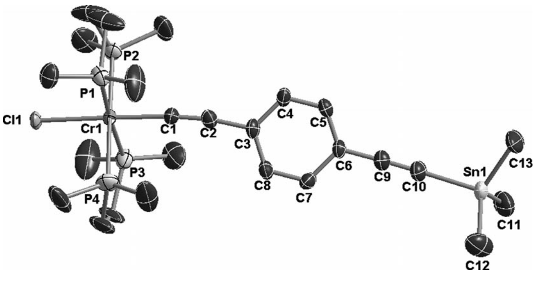


Figure 10. Crystal structure of **10** (ellipsoids set at the 50% probability level). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Cr1–Cl1 2.4042(11), Cr1–C1 2.000(4), C1–C2 1.224(6), C2–C3 1.432(6), C6–C9 1.418(6), C9–C10 1.208(6), C10–Sn1 2.108(5).

The C16–Sn1 and C10–Sn1 distances in **9** and **10** are 2.115(7) and 2.108(5) Å, respectively. These distances are longer than the C–Si distance of 1.8383(16) Å observed in **8** and in other mononuclear chromium acetylene derivatives;[38] confirming the high reactivity of the Me$_3$Sn end group in comparison to the Me$_3$Si end groups, which is consistent with the lower dissociation energy of the C–Sn bond.[50]

Conclusions

We have reported dinuclear and mononuclear chromium acetylide complexes. The dinuclear complexes with the butadiyne bridge show a class-I type electron-transfer behavior, which is very untypical of dinuclear complexes bridged by a C_4 unit. Further substitution of the chlorido ligand for the corresponding iodido group and the trimethylsilyl alkynyl terminated complexes did not have a significant influence on the electronic properties of the C_4 bridge and the chromium metal center. Also synthetic access to the reactive trimethylstannyl alkynyl mononuclear complexes was achieved. These complexes can be utilized as new building blocks for the synthesis and investigation of electron-transfer properties of heterodinuclear and further on oligonuclear complexes with various metal centers, which is currently ongoing in our group.

Experimental Section

All the manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or a glovebox (M. Braun 150B-G-II). The solvents benzene, toluene, pentane, diethyl ether, and tetrahydrofuran were dried and distilled from sodium benzophenone prior to use. Dichloromethane and acetonitrile were distilled from CaH_2. CHN elemental analyses were performed with a LECO CHN-932 microanalyzer. IR spectra were obtained with a Bio-Rad FTS-45 instrument. NMR spectra were measured with a Varian Mercury spectrometer at 200 MHz for the ^1H NMR and Varian Gemini-2000 spectrometer at 300 MHz for ^1H NMR. The chemical shift for the ^1H NMR is given in ppm relative to TMS and for ^{31}P NMR relative to phosphoric acid. Cyclic voltammograms were obtained with a BAS 100W voltammetric analyzer. The cell was equipped with a Au working and Pt counter electrode, and a non-aqueous reference electrode. All sample solutions were approximately 5×10^{-3} M in the substrate and 0.1 M in Bu_4NPF_6, and were prepared under nitrogen. The BAS 100W program was employed for data analysis. X-band EPR spectra were obtained using a Bruker EMX electron spin resonance system. The starting material $Cr(dmpe)_2Cl_2$ (**1**) was prepared as described in the literature.[38]

X-ray Diffraction Studies: Single-crystal X-ray diffraction data were collected at 183(2) K with an Xcalibur diffractometer (Agilent Technologies, Ruby CCD detector) for compounds **2**, **2**[$SnMe_3Cl_2$]$_2$, **8**, and **10**, and with a SuperNova Dual diffractometer (Agilent Technologies, Atlas CCD detector) for compound **9** using a single wavelength Enhance X-ray source with Mo-K_α radiation (λ = 0.71073 Å).[51] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed onto a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction, and analytical absorption corrections[52] were performed with the program suite CrysAlis^{Pro}.[51] The crystal structures were solved with the program SHELXS97[53] using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL97.[53] All programs used during the crystal structure determination process are included in the WINGX software.[54] The program PLATON[55] was used to check the result of the X-ray analyses and DIAMOND[56] was used for the molecular graphics.

CCDC-841965 (for **2**), -841966 (for **2**[$SnMe_3Cl_2$]$_2$), -841967 (for **8**), -841968 (for **9**), and -841969 (for **10**) contain the supplementary crystallographic data (excluding structure factors) 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.

Table 2. Crystallographic data for compounds **2** and **2**[$SnMe_3Cl_2$]$_2$.

	2	**2**[$SnMe_3Cl_2$]$_2$
Empirical formula	$C_{28}H_{64}Cl_2Cr_2P_8$	$C_{28}H_{64}Cl_2Cr_2P8$, **2**($C_3H_9Cl_2Sn$), **2**(CH_2Cl_2)
M_r [g mol^{-1}]	823.45	1462.73
T [K]	183(2)	183(2)
λ [Å]	0.71073	0.71073
Crystal system, Space group	orthorhombic, $C222_1$	monoclinic, $C2/c$
a [Å]	12.4500(3)	31.1484(12)
b [Å]	13.6928(3)	10.7228(2)
c [Å]	25.2013(7)	22.6263(9)
α [°]	90	90
β [°]	90	117.419(5)
γ [°]	90	90
V [Å^3]	4296.20(18)	6708.2(5)
Z, ρ_{calcd} [Mg m^{-3}]	4, 1.273	4, 1.448
μ [mm^{-1}]	0.946	1.664
F(000)	1736	2960
Crystal size [mm]	0.35 × 0.29 × 0.025	0.24 × 0.13 × 0.04
θ range [°]	2.21–28.28	2.62–25.68
Measured reflections	14101	18095
Unique reflections	5334 [R_{int} = 0.058]	6349 [R_{int} = 0.058]
Completeness to θ [%]	99.8	99.9
Absorption correction	analytical	analytical
Max./min. transmission	0.980 and 0.800	0.959 and 0.823
Data/restraints/parameters	3768/7/209	3818/0/273
Gof on F^2	0.900	0.859
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0431, 0.0688	0.0401, 0.0688
R_1 and wR_2 indices (all data)	0.0726, 0.0739	0.0858, 0.0752
Absolute structure parameter	0.10(2)	
Largest diff. peak and hole (e Å^{-3})	0.647 and –0.440	0.673 and –0.639

The unweighted R factor is $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$ and the weighted R factor is $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 3. Crystallographic data for compounds **8**, **9**, and **10**.

	8	**9**	**10**
Empirical formula	$C_{19}H_{41}ClCrP_4Si$	$C_{19}H_{41}ClCrP_4Sn$	$C_{25}H_{45}ClCrP_4Sn$
M_r [g mol^{-1}]	508.94	599.56	675.65
T [K]	183(2)	183(2)	183(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	orthorhombic, $Iba2$
a [Å]	9.2024(6)	9.1399(13)	19.6605(4)
b [Å]	11.7569(5)	11.7256(4)	28.1754(5)
c [Å]	26.235(5)	26.5608(10)	11.9620(2)
α [°]	90	90	90
β [°]	92.944(10)	92.761(6)	90
γ [°]	90	90	90
V [Å^3]	2834.7(6)	2843.2(4)	6626.3(2)
Z, $\rho_{calcd.}$ [Mg m^{-3}]	4, 1.193	4, 1.401	8, 1.355
μ [mm^{-1}]	0.769	1.583	1.367
F(000)	1080	1224	2768
Crystal size [mm]	0.33 × 0.28 × 0.15	0.31 × 0.09 × 0.08	0.37 × 0.20 × 0.08
θ range [°]	2.64–30.51	2.23–28.28	2.78–30.51
Measured reflections	51206	15141	20775
Unique reflections	8642 [R_{int} = 0.028]	7725	9810 [R_{int} = 0.060]
Completeness to θ [%]	100.0	94.4	99.9
Absorption correction	analytical	analytical	analytical
Max./min. transmission	0.908 and 0.819	0.971 and 0.923	0.954 and 0.828
Data/restraints/parameters	7749/0/246	7080/0/247	6604/46/319
Gof on F^2	1.088	1.081	0.920
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0300, 0.0717	0.0611, 0.1752	0.0505, 0.1102
R_1 and wR_2 indices (all data)	0.0355, 0.0743	0.0658, 0.1791	0.0752, 0.1159
Absolute structure parameter			0.06(2)
Largest diff. peak and hole (e Å^{-3})	0.604 and –0.390	3.971 and –0.914	1.007 and –1.053

The unweighted R factor is $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$ and the weighted R factor is $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

In the crystal structure of **2** the asymmetric unit consists of one half of the molecule. The second part of the molecule is generated by a symmetry from a twofold axis. The ethane group (C9–C10) of one dmpe ligand is disordered over two sets of positions with site-occupancy factors of 0.459(19) and 0.541(19). Some restraints were used to correct the geometry of the disordered group. In the crystal structure of **2**[SnMe$_3$Cl$_2$]$_2$, the asymmetric unit consists of one half of the dicationic chromium species, one anionic dichlorotrimethyltin molecule, and one solvent molecule of dichloromethane. The dinuclear species lies on a twofold axis, one part is refined and the second part is reproduced by a symmetry operation. The crystal data for compounds **2** and **2**[SnMe$_3$Cl$_2$]$_2$ are given in Table 2. The structure of compound **9** has been refined as a nonmerohedral twin with the CrysAlis^{Pro} twin data module.[51] The nonmerohedral twin matrix has been identified and a single *HKLF-5* file containing reflections from both domains was employed for the final structure refinement. Refinement using a single lattice and no twin treatment afforded R_1 = 19.5%, with residual peaks as large as 6.85 e Å^{-3}. Full treatment as a twin with application of an analytical absorption correction resulted in R_1 = 6.1% with the strongest residual peak of 3.97 e Å^{-3}. In the crystal structure of **10**, the ethane group (C20–C21) of one dmpe ligand is disordered over two sets of positions with site-occupancy factors of 0.452(17) and 0.548(17). Some restraints were used to correct the geometry of the disordered group and the thermal parameters of the corresponding carbon atoms. The crystal data for compounds **8**, **9**, and **10** are given in Table 3. For all five refinements, all hydrogen positions were calculated after each cycle of refinement using a riding model, with C–H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms, and with C–H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

***trans*-[Cl(dmpe)$_2$Cr≡C–C≡C–C≡Cr(dmpe)$_2$Cl] (2):** A benzene solution (20 mL) of Me$_3$Sn–C≡C–C≡C–SnMe$_3$[57] (53.34 mg, 0.142 mmol) was added to a solution of Cr(dmpe)$_2$Cl$_2$ (120 mg, 0.284 mmol) in benzene (35 mL) in the presence of metallic Zn. The reaction mixture was heated to 80 °C and the mixture was stirred overnight. The solvent was removed in vacuo and the solid residue was washed with pentane and subsequently extracted with benzene. Recrystallization from THF/pentane at –30 °C gave red crystals; yield 64.2 mg (55%). ^{1}H NMR (200 MHz, [D$_8$]THF, 25 °C): δ = 1.28 (s, 12 H, PCH$_3$), 1.31 (s, 12 H, PCH$_3$), 1.55 (m, 8 H, CH$_2$), 1.67 (m, 8 H, PCH$_2$) ppm. ^{31}P{^{1}H} NMR (81 MHz, [D$_8$]THF, 25 °C): δ = 64.54 (s) ppm. IR (ATR): $\tilde{\nu}$ = 2950 (C–H), 2050 (C≡C), 922 (C–P) cm^{-1}. ESI–MS ($C_{28}H_{64}Cl_2Cr_2P_8$): m/z = 822 [M]$^+$. $C_{28}H_{64}Cl_2Cr_2P_8$ (822.27): calcd. C 40.83, H 7.78; found C 40.69, H 7.74.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–C≡C–Cr(dmpe)$_2$Cl][SnMe$_3$Cl$_2$]$_2$ (2[SnMe$_3$Cl$_2$]$_2$):** A benzene solution (15 mL) of Me$_3$SnC≡C–C≡C–SnMe$_3$ (44.3 mg, 0.118 mmol) was added to a solution of Cr(dmpe)$_2$Cl$_2$ (100 mg, 0.237 mmol) in benzene (30 mL). The temperature was raised to 80 °C and the mixture was stirred overnight. The solvent was removed and the red solid was washed with THF and extracted with dichloromethane. Recrystallization with CH$_2$Cl$_2$/pentane at –30 °C gave red crystals; yield 68.9 mg (45%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, 25 °C): δ = –19.63 (br., 8 H, PCH$_2$, 24 H, PCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2986 (C–H), 1917 (C=C), 953 (C–P) cm^{-1}. ESI–MS ($C_{34}H_{82}Cl_2Cr_2P_8Sn_2$): m/z = 411 [M]$^{2+}$. $C_{34}H_{82}Cl_2Cr_2P_8Sn_2$ (1151.09): calcd. C 31.59, H 6.35; found C 31.70, H 6.41.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–C≡C–Cr(dmpe)$_2$Cl][PF$_6$]$_2$ (2[PF$_6$]$_2$):** A CH$_2$Cl$_2$ suspension of NaPF$_6$ (25.87 mg, 0.154 mmol) was added to a CH$_2$Cl$_2$ solution of (**2**[SnMe$_3$Cl$_2$]$_2$) (100 mg, 0.077 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated and the product was extracted with THF. The THF solution was evaporated in vacuo to give the title compound.

Crystallization from a mixture of dichloromethane and ether at –35 °C produced single red crystals; yield 87 mg, 0.08 mmol (78%). ^{1}H NMR (300 MHz, CD_2Cl_2, 22 °C): δ = –17.92 (br., 8 H, PCH_2, 24 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 22 °C): δ = –146.1 (sept, $^1J_{PF}$ = 714 Hz, PF_6^-) ppm. ^{19}F {^{1}H} NMR (282.3 MHz, CD_2Cl_2, 22 °C): δ = –74.8 (d, $^1J_{FP}$ = 714 Hz, PF_6^-) ppm. IR (ATR): $\tilde{\nu}$ = 2927 (w), 2888 (w) (C–H), 2083 (m) (C≡C), 980 (s), 941 (s) (P–C), 865 (vs) (P–F) cm^{-1}. $C_{28}H_{64}Cl_2Cr_2F_{12}P_{10}$ (1113.42): calcd. C 30.20, H 5.79; found C 29.98, H 5.60.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–Ph–C≡C–Cr(dmpe)$_2$Cl][SnMe$_3$Cl$_2$]$_2$ (3[SnMe$_3$Cl$_2$]$_2$):** Cr(dmpe)$_2$Cl$_2$ (90 mg, 0.213 mmol) and Me$_3$Sn–C≡C–Ph–C≡C–SnMe$_3$ (48.1 mg, 0.107 mmol) were dissolved in benzene (40 mL). The mixture was stirred for 12 h at 80 °C. After evaporation of the solvent the product was washed with THF and extracted with CH_3CN and then the solvent was removed in vacuo; yield 58.3 mg (40%). ^{1}H NMR (200 MHz, [D$_8$]THF, 25 °C): δ = –14.5 (br., 8 H, PCH_2), –35.9 (br., 12 H, PCH_3), –37.8 (br., 12 H, PCH_3) ppm. ESI–MS ($C_{40}H_{86}B_2Cl_6Cr_2P_8Sn_2$): *m*/*z* = 449.2 [M]$^{2+}$. $C_{40}H_{86}B_2Cl_6Cr_2P_8Sn_2$ (1369.0): calcd. C 35.09, H 7.33; found C 29.8, H 4.86.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–Ph–C≡C–Cr(dmpe)$_2$Cl][BPh$_4$]$_2$ (3[BPh$_4$]$_2$):** A CH_3CN solution of (**3**[SnMe$_3$Cl$_2$]$_2$) (100 mg, 0.073 mmol) was added to a CH_3CN suspension of NaBPh$_4$ (25.0 mg, 0.073 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated and the product was extracted with THF. The solvent was evaporated in vacuo to give the title compound; yield 84.1 mg (75%). NMR (200 MHz, CD_3CN, 25 °C): δ = –17.3 (br., 8 H, PCH_2), –24.2 (br., 8 H, PCH_2), –45.7 (br., 12 H, PCH_3), –55.5 (br., 12 H, PCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2909 (C–H), 2196 (C≡C), 1580 (C=C), 949 (C–P) cm^{-1}. ESI–MS ($C_{82}H_{108}B_2Cl_2Cr_2P_8$): *m*/*z* = 449.2 [M]$^{2+}$. $C_{82}H_{108}B_2Cl_2Cr_2P_8$ (1536.5): calcd. C 64.03, H 7.08; found C 63.91, H 7.01.

***trans*-[I(dmpe)$_2$Cr≡C–C≡C–C≡Cr(dmpe)$_2$I] (4):** KI (323.3 mg, 1.947 mmol) in THF (20 mL) was added to complex **2** (80 mg, 0.097 mmol) in THF (30 mL). The temperature was raised to 60 °C and the solution was stirred overnight. After removal of the solvent in vacuo the product was extracted with pentane and the solvent was removed in vacuo; yield 68.44 mg (70%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 1.28 (s, 12 H, PCH_3), 1.64 (s, 12 H, PCH_3), 1.35 (m, 8 H, CH_2), 1.71 (m, 8 H PCH_2) ppm. ^{31}P{^{1}H} NMR (81 MHz, [D$_8$]THF, 25 °C): δ = 49.8 (s) ppm. IR (ATR): $\tilde{\nu}$ = 2961 (C–H), 2150 (C≡C), 921 (C–P) cm^{-1}. ESI–MS ($C_{28}H_{64}I_2Cr_2P_8$): *m*/*z* = 1006.0 [M]$^+$. $C_{28}H_{64}Cr_2I_2P_8$ (1005.98): calcd. C 33.42, H 6.41; found C 33.29, H 6.30.

***trans*-[Me$_3$Si–C≡C(dmpe)$_2$Cr≡C–C≡C–C≡Cr(dmpe)$_2$C≡C–SiMe$_3$] (5):** Complex **2** (100 mg, 0.122 mmol) in THF (30 mL) and a freshly prepared solution of Li–C≡C–SiMe$_3$ (88.6 mg, 0.852 mmol) in THF (20 mL) were mixed and stirred at 60 °C overnight. The solvent was then evaporated and the red-brown solid was extracted with pentane and the solvent was removed in vacuo; yield 77 mg. (67%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.18 [s, 18 H, Si(CH$_3$)$_3$], 1.31 (m, 12 H, PCH_3), 1.42 (m, 12 H, PCH_3), 1.55 (m, 8 H, CH_2), 1.69 (m, 8 H, PCH_2) ppm. IR (ATR): $\tilde{\nu}$ = 2959 (C–H), 2190 (C≡C), 934 (C–P) cm^{-1}. ESI–MS ($C_{38}H_{82}Si_2Cr_2P_8$): *m*/*z* = 946.3 [M]$^+$. $C_{38}H_{82}Cr_2P_8Si_2$ (946.3): calcd. C 48.19, H 8.73; found C 47.98, H 8.66.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–SnMe$_3$] (6):** Cr(dmpe)$_2$Cl$_2$ (50 mg, 0.118 mmol) and Me$_3$Sn–C≡C–SnMe$_3$ (43.8 mg, 0.124 mmol) were dissolved in benzene (40 mL). The mixture was stirred for 12 h at 80 °C. After evaporation of the solvent the product was washed with a small amount of cold pentane, extracted in pentane, and then the solvent was removed in vacuo; yield 58.0 mg (82%). ^{1}H NMR (200 MHz, [D$_8$]toluene, 25 °C): δ = –13.9 (br., 8 H, PCH_2), –29.1 (br., 12 H, PCH_3), –33.7 (br., 12 H, PCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2900 (C–H), 1950 (C≡C), 920 (C–P) cm^{-1}. ESI–MS ($C_{17}H_{41}ClCrP_4Sn$): *m*/*z* = 576.1 [M]$^+$. $C_{17}H_{41}ClCrP_4Sn$ (576.1): calcd. C 35.47, H 7.13; found C 35.25, H 7.12.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–Ph] (7):** A benzene solution (20 mL) of Cr(dmpe)$_2$Cl$_2$ (40 mg, 0.095 mmol) and a benzene solution (15 mL) of Me$_3$Sn–C≡C–Ph (26.3 mg, 0.099 mmol) were mixed and stirred for 12 h at 80 °C. After evaporation of the solvent, the product was washed with cool pentane, extracted with pentane, and dried in vacuo; yield 43 mg (93%). ^{1}H NMR (200 MHz, [D$_8$]toluene, 25 °C): δ = 33.2, (br., 4 H, Ph), –51.3 (br., 4 H, Ph), –6.9 (br., 8 H, PCH_2), –9.3 (br., 8 H, PCH_2), –29.4 (br., 12 H, PCH_3), –32.5 (br., 12 H, PCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2965 (C–H), 2032 (C≡C), 1587 (C=C), 984 (C–P) cm^{-1}. ESI–MS ($C_{20}H_{37}ClCrP_4$): *m*/*z* = 488.2 [M]$^+$. $C_{20}H_{37}ClCrP_4$ (488.5): calcd. C 49.13, H 7.6; found C 49.26, H 7.48.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–C≡C–C–SiMe$_3$] (8):** Me$_3$Sn–C≡C–C≡C–C–SiMe$_3$ (40.8 mg, 0.143 mmol) in benzene (20 mL) was added to a benzene solution (20 mL) of Cr(dmpe)$_2$Cl$_2$ (55 mg, 0.130 mmol). The mixture was stirred overnight at 80 °C. After evaporation of the solvent the product was extracted with pentane and dried in vacuo. Recrystallization from pentane at –30 °C gave red crystals; yield 49.7 mg (75%). ^{1}H NMR (200 MHz, [D$_6$]toluene, 25 °C): δ = –5.6 (br., 8 H, PCH_2), –10.6 (br., 8 H, PCH_2), –13.1 (br., 8 H, PCH_2), –28.5 (br., 12 H, PCH_3), –31.2 (br., 12 H, PCH_3), –33.3 (br., 12 H, PCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2964 (C–H), 2093 (C≡C), 988 (C–P) cm^{-1}. ESI–MS ($C_{19}H_{41}ClCrP_4Si$): *m*/*z* = 508.1 [M]$^+$. $C_{19}H_{41}ClCrP_4Si$ (508.0): calcd. C 44.84, H 8.12; found C 44.98, H 8.21.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–C≡C–SnMe$_3$] (9):** Cr(dmpe)$_2$Cl$_2$ (50 mg, 0.142 mmol) and Me$_3$Sn–C≡C–C≡C–SnMe$_3$ (58.7 mg, 0.156 mmol) were dissolved in benzene (50 mL), the mixture was stirred overnight at 80 °C. The solvent was then evaporated and the red solid was extracted with pentane, and then the solvent was removed in vacuo. Recrystallization from pentane gave red crystals; yield 42.6 mg (50%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = –6.2 (br., 8 H, PCH_2), –10.5 (br., 8 H, PCH_2), –13.3 (br., 8 H, PCH_2), –29.1 (br., 12 H, PCH_3), –31.7 (br., 12 H, PCH_3), –33.9 (br., 12 H, PCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2964 (C–H), 2100 (C≡C), 936 (C–P) cm^{-1}. ESI–MS ($C_{19}H_{41}ClCrP_4Sn$): *m*/*z* = 600.0 [M]$^+$. $C_{19}H_{41}ClCrP_4Sn$ (600.0): calcd. C 38.06, H 6.89; found C 37.78, H, 6.55.

***trans*-[Cl(dmpe)$_2$Cr–C≡C–Ph–C≡C–SnMe$_3$] (10):** Cr(dmpe)$_2$Cl$_2$ (60 mg, 0.118 mmol) and Me$_3$Sn–C≡C–Ph–C≡C–SnMe$_3$ (70.4 mg, 0.156 mmol) were dissolved in benzene (25 mL). The mixture was stirred for 12 h at 80 °C. After evaporation of the solvent the product was extracted in pentane and dried in vacuo. Recrystallization from pentane gave red crystals; yield 46.1 mg (48%). ^{1}H NMR (200 MHz, [D$_8$]toluene, 25 °C): δ = 37.6 (br., 4 H, Ph), –53.8 (br., 4 H, Ph), –9.4 (br., 8 H, PCH_2), –29.8 (br., 12 H, PCH_3), –32.6 (br., 12 H, PCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2900 (C–H), 2018 (C≡C), 1592 (C=C), 984 (C–P) cm^{-1}. ESI–MS($C_{25}H_{45}ClCrP_4Sn$): *m*/*z* = 676.7 [M]$^+$. $C_{25}H_{45}ClCrP_4Sn$ (676.3): calcd. C 49.13, H 7.6; found C 49.26, H 7.48.

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