Di-, Tri-, and Tetranuclear Cyclobutenylidene Complexes☆

Frédéric Leroux, Rüdiger Stumpf, and Helmut Fischer*

Fakultät für Chemie, Universität Konstanz, Fach M727,
D-78457 Konstanz, Germany
Fax: (internat.) + 49(0)7531/88-2783
E-mail: hfischer@dg6.chemie.uni-konstanz.de

Received April 24, 1998

Keywords: Vinylidene complexes / Cyclobutenylidene complexes / Bridging ligands / Cycloadditions / Cross-coupling

Pentacarbonyl(dimethylvinylidene)chromium, $[(CO)_5Cr=C=CMe_2]$ (**1**), reacts with the butadiynyl complexes $[Cp(CO)_2FeC{\equiv}CC{\equiv}CR]$ [**2**; R = $SiMe_3$ (**a**), *n*Bu (**b**), Ph (**c**)] and $[Cp(CO)(PPh_3)FeC{\equiv}CC{\equiv}CSiMe_3]$ (**3a**) by regiospecific cycloaddition of the $C^{\alpha}{\equiv}C^{\beta}$ bond of the butadiynyl complexes to the C=C bond of **1** to form the 1,3-*hetero*binuclear cyclobutenylidene complexes **4a–c** and **5a** with an alkynyl substituent at C-2 of the bridging ring. Desilylation of the 2-$C{\equiv}CSiMe_3$ substituent in **4a** and **5a** with tetrabutylammonium fluoride affords the 2-C≡CH-substituted complexes **6** and **7**. Complex **4a** reacts with $HNMe_2$ and $HN(CH_2)_5$ by substitution of NR_2 for the 3-$Fe(CO)_2Cp$ fragment to form the corresponding 3-aminocyclobutenylidene complexes **10** and **11**. Sequential reactions of **4a** with $[nBu_4N]F$ and nBu_3SnNEt_2 give the trinuclear 2-$C{\equiv}CSnnBu_3$-substituted complex **12**. Coupling of **12** with $C_6H_4I_2$-*p* yields the 2-$C{\equiv}CC_6H_4I$-*p*-substituted complex **13**. Coupling of **7** with $C_6H_4I_2$-*p* yields a mixture of the mono-coupling product **14** and the tetranuclear $C{\equiv}C–C_6H_4–C{\equiv}C$-bridged bis(cyclobutenylidene) complex **15**. Coupling of **7** with *trans*-$[(Et_3P)_2MCl_2]$ in the presence of CuI/$[Pd(PPh_3)_4]$ gives the trinuclear 2-$C{\equiv}C–M(PEt_3)_2X$-substituted complexes **16** (M = Pd, X = I) and **17** (M = Pt, X = Cl). The spectroscopic data as well as the results of the X-ray-structural analysis of **5a** indicate strong electronic communication between the metal centers. In the solid state, **5a** exhibits a "butterfly" conformation.

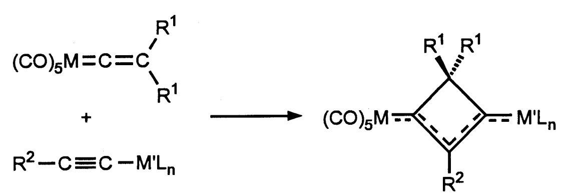
Introduction

Electronic communication between the metal centers in bi- and polynuclear transition-metal complexes containing unsaturated carbon bridges should lead to unusual physical and chemical properties[1]. For example, carbon-bridged bimetallic π-conjugated complexes of the type $[L_nMC_mM'(L')_{n'}]$ have been proposed as a new class of one-dimensional molecular wires[2]. Rigid-rod polymers like $[L_nMC{\equiv}CXC{\equiv}C]_m$ (X = aryl) can exhibit both liquid-crystalline[3] and nonlinear optical properties[4] similar to certain metal acetylides[5]. Binuclear complexes with different L_nM end groups at a conjugated π system should exhibit second-order nonlinear optical (NLO) properties.

Related to linear C_n bridges are rigid cyclic bridges with a delocalized π system. We recently reported on the syntheses of 1,3-*hetero*binuclear complexes with a cyclic C_4R_3 bridging ligand (cyclobutenylidene complexes)[6]. By variation of the substituents at the bridging ligand a fine-tuning of the magnetic, electronic, and spectroscopic properties of such binuclear complexes should be possible. Until now, 1,3-*hetero*binuclear cyclobutenylidene complexes with alkyl and aryl substituents as well as with functional groups at the bridging ligand, and with various metal-ligand fragments in 1- and 3-position of the ring have been prepared by reaction of suitable vinylidene complexes of chromium and tungsten, $[(CO)_5M=C=CR^1_2]$, with alkynyl complexes, $[L_nM'\text{-}C{\equiv}CR^2]$ (Scheme 1)[6a].

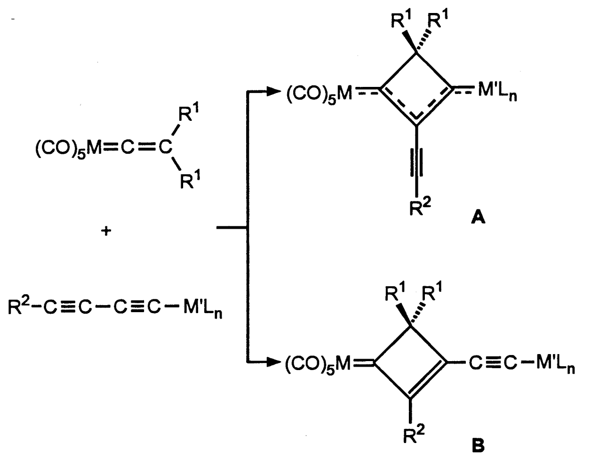
Cyclobutenylidene complexes with an exocyclic C=C bond were accessible by a regiospecific cycloaddition of alkynyl complexes to the $C^{\alpha}{=}C^{\beta}$ bond of allenylidene(pentacarbonyl)chromium and -tungsten complexes[6b]. The properties of these 1,3-*hetero*binuclear complexes are strongly influenced by the substituents at both non-metal-bonded ring atoms.

Scheme 1



Transition-metal butadiynyl complexes, $[L_nMC^{\alpha}{\equiv}C^{\beta}C^{\gamma}{\equiv}C^{\delta}R]$, are related to alkynyl complexes $[L_nMC{\equiv}CR]$. In alkynyl complexes the HOMO is mainly localized at the terminal C atom. Therefore, electrophiles add to this carbon atom. Spectroscopic investigations of butadiynyl complexes indicate a strong communication between the metal center and the butadiynyl ligand[7][8]. In contrast to alkynyl complexes, two pathways are conceivable for the reactions of butadiynyl with vinylidene complexes as electrophiles depending on whether initial electrophilic attack of the vinylidene C^{α} atom in $[L_nM{=}C^{\alpha}{=}C^{\beta}R^1_2]$ is directed towards the C^{β} or the C^{δ} atom of the butadiynyl ligand. Attack at the C^{β} atom and subsequent ring closure would lead to 1,3-*hetero*binuclear cyclobutenylidene complexes with an alkynyl functionality at C-2 of the ring (**A**; Scheme 2). Such complexes should constitute interesting starting compounds for further derivatization by coupling reactions. An attack at the butadiynyl C^{δ} atom followed by ring closure would lead to complexes of type **B** (Scheme 2) thus extending the conjugated system between the metal centers in cyclobutenylidene complexes.

Scheme 2

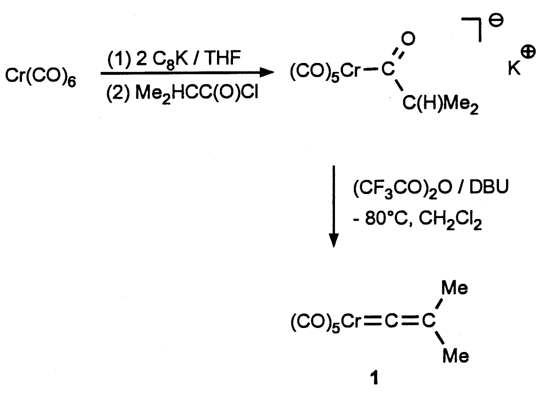


In this paper we report on the syntheses of the first 1,3-*hetero*binuclear cyclobutenylidene complexes with an alkynyl substituent at the bridging ring and on coupling reactions of these complexes leading to new di-, tri-, and tetrametallic systems.

Results and Discussion

The vinylidene complex $[(CO)_5Cr{=}C{=}CMe_2]$ (**1**)[6a] was chosen as the starting compound. Complex **1** was generated by the reaction sequence shown in Scheme 3.

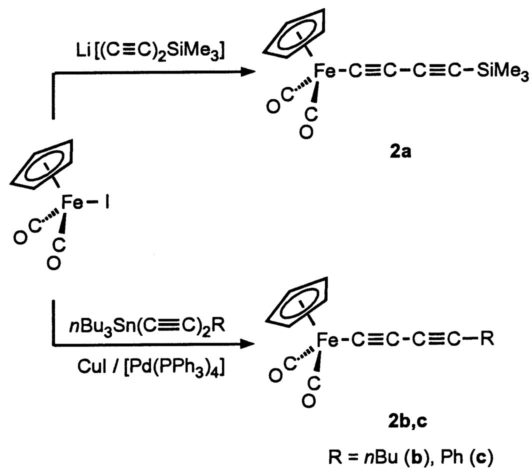
Scheme 3



Reduction of $Cr(CO)_6$ with potassium-graphite (C_8K) laminate in tetrahydrofuran at 0°C followed by reaction with isobutyryl chloride afforded pentacarbonyl(isobutyryl) chromate by a method described by M. F. Semmelhack et al.[9]. Treatment of the chromate with trifluoroacetic anhydride/DBU finally gave the vinylidene complex **1**. Compound **1** is thermally very labile. Therefore, **1** was not isolated and its solutions were immediately employed in the subsequent reactions with butadiynyl complexes.

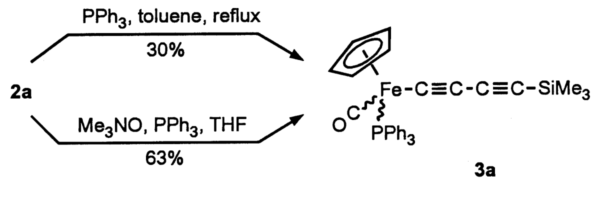
The dicarbonyl-butadiynyl complex $[Cp(CO)_2FeC{\equiv}CC{\equiv}CSiMe_3]$ (**2a**) was prepared in analogy to a previously published procedure[7a] by reaction of $[Cp(CO)_2FeI]$ with $Li[(C{\equiv}C)_2SiMe_3]$, obtained by monodesilylation of 1,4-bis(trimethylsilyl)-1,3-butadiyne with MeLi·LiBr (Scheme 4)[10]. The corresponding phenyl- and *n*-butyl-substituted butadiynyl complexes [**2b** (R = *n*Bu) and **2c** (R = Ph)] were accessible by coupling of $[Cp(CO)_2FeI]$ with $nBu_3Sn{-}C{\equiv}CC{\equiv}C{-}R$ (R = *n*Bu, Ph) in THF with CuI/$[Pd(PPh_3)_4]$ as the catalyst (Scheme 4).

Scheme 4



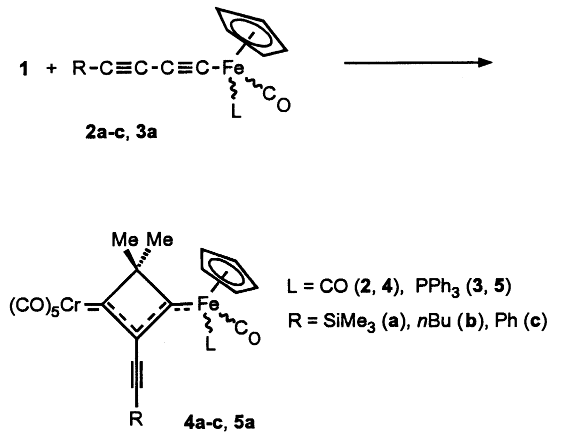
Thermal decarbonylation of **2a** by refluxing in toluene in the presence of PPh_3 yielded the monocarbonyl-butadiynyl complex $[Cp(CO)(PPh_3)FeC{\equiv}CC{\equiv}CSiMe_3]$ (**3a**)[7a] albeit in rather low yield (about 30%). Significantly higher yields were achieved by oxidative decarbonylation of **2a** with trimethylamine *N*-oxide in the presence of PPh_3 at room temperature. By this procedure, complex **3a** was obtained in 63% yield (Scheme 5). The lower yield in the former route is presumably due to competition between formation and decomposition of **3a** at the temperature of boiling toluene.

Scheme 5



When solutions of the vinylidene complex **1** and the butadiynyl complexes **2a−c** or **3a** in CH_2Cl_2 were combined at −60°C and then warmed to room temperature, the color of the solutions changed within about 30 minutes from green to red. Chromatographic workup of the reaction mixtures afforded the novel 2-alkynyl-substituted 1,3-*hetero*binuclear cyclobutenylidene complexes **4a−c** and **5a** (Scheme 6) in 45−65% yield. Alternatively, complex **5a** was also formed when **4a** was oxidatively decarbonylated with trimethylamine *N*-oxide in the presence of PPh_3.

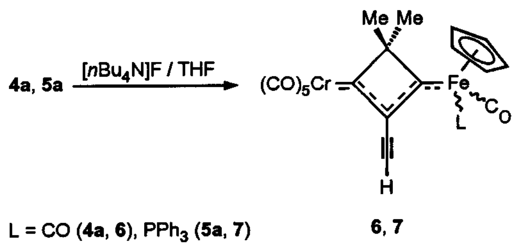
Scheme 6



The addition of the butadiynyl complexes $[L_nM-C^{\alpha}\equiv C^{\beta}-C^{\gamma}\equiv C^{\delta}-R]$ to the vinylidene ligand in **1** is highly regioselective. In each case, only the product of cycloaddition of the $C^{\alpha}\equiv C^{\beta}$ bond of the butadiynyl ligand to the C=C bond of the vinylidene ligand was obtained (complex type **A**; Scheme 2). The formation of isomers derived from cycloaddition of the $C^{\gamma}\equiv C^{\delta}$ bond to the C=C bond of the vinylidene ligand (complex type **B**; Scheme 2) was not detected. Likewise, 1,2-dimetallated cyclobutenylidenes, derived from the inverse regiochemistry of the cycloaddition of either the $C^{\alpha}\equiv C^{\beta}$ or the $C^{\gamma}\equiv C^{\delta}$ bond of the butadiynyl ligand to the C=C bond of the vinylidene ligand, were not observed.

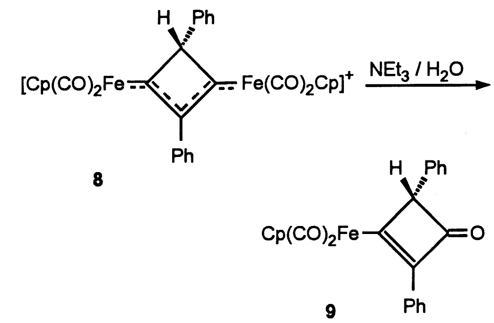
Desilylation of **4a** and **5a** with tetrabutylammonium fluoride (TBAF) in THF afforded the 2-ethynylcyclobutenylidene complexes **6** and **7** after chromatographic workup in 67% and 57% yield, respectively (Scheme 7). The highest yields were obtained when 0.4 equivalents of TBAF was used instead of the stoichiometric amount. Similar observations have been reported for the desilylation of other compounds with TBAF[7a].

Scheme 7



The complexes **4a**, **5a**, **6**, and **7** should constitute convenient starting compounds for the synthesis of tri- and tetranuclear complexes by coupling reactions. In coupling reactions, often amines are employed as the solvent. Therefore, we investigated the reactivity of these 2-alkynyl-substituted cyclobutenylidene complexes towards amines with the example of **4a** and **5a**. In earlier experiments it was observed that a cationic 1,3-*homo*binuclear cyclobutenylidene complex **8** reacts with aqueous Et_3N yielding the iron complex **9** by a formal substitution of "O" for $[Cp(CO)_2Fe]^+$ (Scheme 8)[11]. In contrast, 2-*alkyl*-substituted 1,3-*hetero*-binuclear cyclobutenylidene complexes are inert towards amines.

Scheme 8



The dicarbonyl complex **4a** reacted rapidly at room temperature in THF with aqueous dimethylamine or with piperidine by substitution of NR_2 for the 3-dicarbonyl(cyclopentadienyl)iron fragment to form the 3-aminocyclobutenylidene complexes **10** and **11** (Scheme 9).

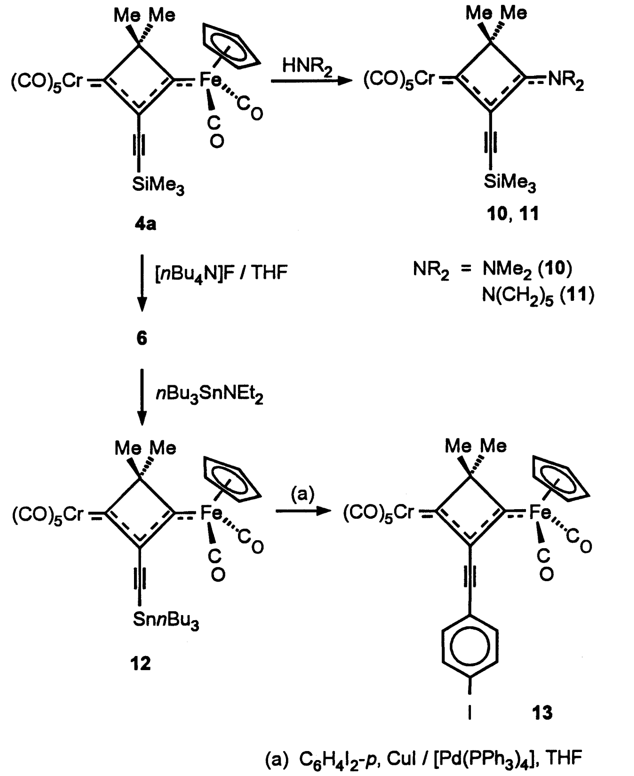
3-Alkoxy-substituted cyclobutenylidene complexes of chromium analogously react with secondary amines HNR_2 by displacement of OR by NR_2 to form 3-aminocyclobutenylidene complexes[12]. These substitution reactions are reminiscent of the aminolysis of alkoxycarbene complexes[13] and emphasize the close relationship of these cyclobutenylidene complexes with π-donor-substituted carbene complexes. Thus, cyclobutenylidene complexes can be regarded as a novel type of vinylogous heteroatom-stabilized carbene complexes. However, the ready displacement of the substituent in 3-position of the cyclobutenylidene complex by amines excludes the use of primary and secondary amines as solvents in coupling reactions with **4a** and **6**. Therefore, palladium-catalyzed C−C coupling reactions require the use of the corresponding *C*-stannylated compound (Stille coupling)[14].

The heterotrinuclear tributyltin-substituted compound **12** was obtained as a red oil by transformation of **4a** with $[nBu_4N]F$ in THF into **6** and subsequent reaction of **6** with nBu_3SnNEt_2 in toluene[15] (Scheme 9). The palladium-catalyzed coupling of **12** with half an equivalent of 1,4-diiodobenzene in the presence of CuI[16] afforded only the monocoupling product **13** (Scheme 9). The formation of a tetranuclear complex by coupling of two molecules of **12** with one molecule of 1,4-diiodobenzene was not observed.

In contrast to **4a**, the triphenylphosphane-substituted cyclobutenylidene complex **5a** did not react with amines to give 3-aminocyclobutenylidene complexes but was inert towards amines presumably due to the better back-bonding properties of $Cp(CO)(PPh_3)Fe$ compared to $Cp(CO)_2Fe$ and thus the reduced electrophilicity of 3-C in **5a**. Therefore, coupling reactions of 3-$Cp(CO)(PPh_3)Fe$-substituted cyclobutenylidene complexes in amines as the solvent should be possible.

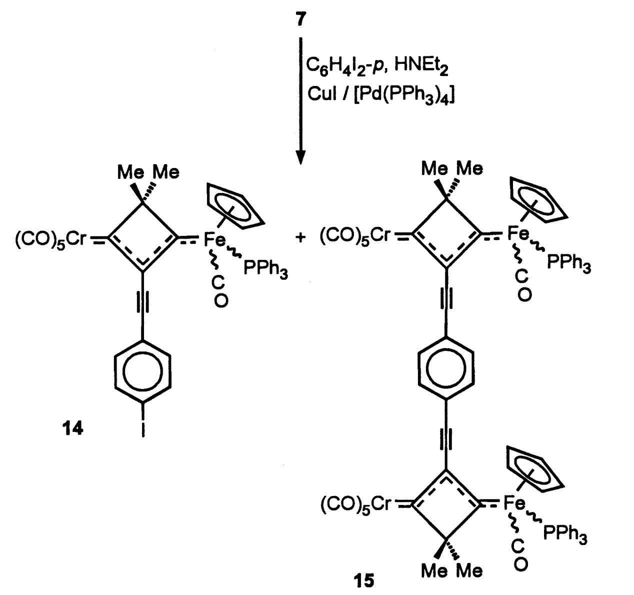
This was confirmed by the reaction of **7** with half an equivalent of 1,4-diiodobenzene in $HNEt_2$ and $[Pd(PPh_3)_4]$/

Scheme 9



CuI as the catalyst. The mono-coupling product **14** as well as the tetranuclear complex **15** were formed within several hours (Scheme 10) and, after chromatographic workup, obtained in 35% (**14**) and 10% (**15**) yield. Complex **15** was isolated in form of a single diastereomer (*meso* or *R*/*S*).

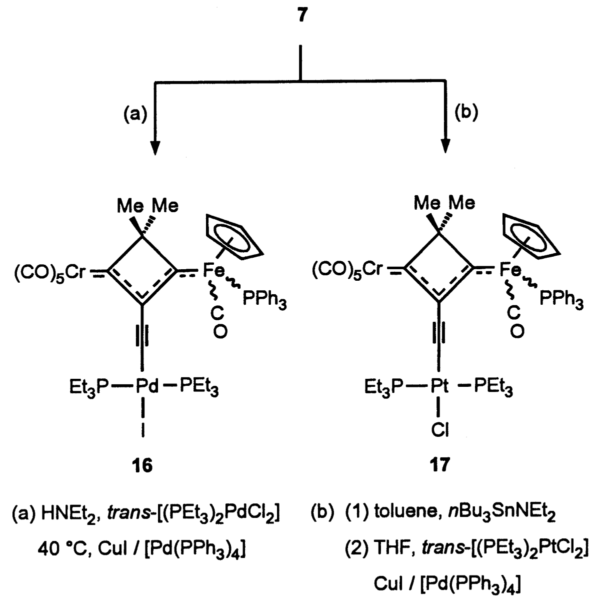
Scheme 10



The [Pd(PPh$_3$)$_4$]/CuI-catalyzed reaction of **7** with *trans*-[(PEt$_3$)$_2$PdCl$_2$] in HNEt$_2$ afforded the mono-coupling product **16** in 23% yield (Scheme 11). In addition to the coupling of both complexes, Pd-coordinated chloride was replaced by iodide from CuI. Presumably, the substitution took place in the trinuclear complex initially formed from **7** and *trans*-[(PEt$_3$)$_2$PdCl$_2$]. The displacement of Cl^- for X^- in *trans*-[(PEt$_3$)$_2$Pd(C≡CR)Cl] complexes in the presence of NaX (X = Br, I) has been observed several times[17]. Although a threefold excess of **7** over *trans*-[(PEt$_3$)$_2$PdCl$_2$] was used, the formation of a pentanuclear complex by coupling of *trans*-[(PEt$_3$)$_2$PdCl$_2$] with two molecules of **7** was not detected.

The trimetallic *trans*-chloroplatinum complex **17** was obtained by initial *C*-stannylation of **7** with nBu$_3$SnNEt$_2$ in toluene followed by [Pd(PPh$_3$)$_4$]/CuI-catalyzed coupling of the product with *trans*-[(PEt$_3$)$_2$PtCl$_2$] in THF. A halide exchange was not observed in these reactions. Presumably, free iodide was trapped as nBu$_3$SnI (Scheme 11). A pentanuclear complex was likewise not detected.

Scheme 11



When **11** was stannylated in situ and the resulting derivative then coupled with iodobenzene under Stille conditions complex **5c** was obtained (see Scheme 6).

Spectroscopic Investigations and Molecular Structure of 5a

All new compounds were stable at room temperature and fully characterized by spectroscopic means and by elemental analyses.

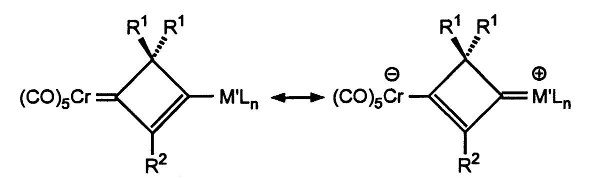
The $\tilde{\nu}$(CO) absorptions of the pentacarbonyl chromium moiety in **4−7** and **10−17** are at rather low wave numbers indicating considerable transfer of electron density from C_4R_3−FeCO(L)Cp to (CO)$_5$Cr. The $\tilde{\nu}$(CO) spectra are similar to those of aminocarbene complexes (e. g. [(CO)$_5$Cr=C(NHMe)Me])[18] and 3-amino-substituted cyclobutenylidene complexes[19] as well as to those of the previously described 1,3-*hetero*binuclear[6] cyclobutenylidene complexes. The positions of the absorptions are strongly influenced by the donor capacity of the substituent in 3-position and shift in the series Fe(CO)$_2$Cp, NR$_2$, Fe(CO)(PPh$_3$)Cp towards smaller wave numbers. In contrast, the influence of the substituent in 2-position (alkyl, C≡C−R) is only small. With increasing donor capacity of R the ṽ(C≡C) absorption shifts towards smaller wave numbers [R = $SiMe_3$: ṽ(C≡C) = 2141 cm^{-1} (**5a**); R = *trans*-$(PEt_3)_2PdI$: ṽ(C≡C) = 2092 cm^{-1} (**16**)].

The ^{13}C resonances of both the chromium- (1-C) and the iron-bound (3-C) ring carbon atoms appear at low field. The 1-C resonance is in the range usually observed for alkoxycarbene complexes (δ = 290−320)[20]. The resonance of the 3-C atom is in the region characteristic for alkenyliron complexes[21]. Increasing the ability of the alkynyl group C≡C−R at 2-C to donate electron density {R = Ph (**4c**) → $SiMe_3$ (**5a**) → *trans*-[$(PEt_3)_2PdI$] (**16**)} leads to an upfield shift of the 1-C and 3-C resonances and to a downfield shift of the 2-C resonance. These results are consistent with earlier observations with 1,3-*hetero*binuclear cyclobutenylidene complexes[6].

In general, the UV/Vis spectra of these cyclobutenylidene complexes are solvent-dependent. The UV/Vis absorption at lowest energy is shifted to shorter wavelength when a nonpolar solvent like pentane is replaced by a more polar one (DMF). However, whereas the solvent dependence of the 3-aminocyclobutenylidene complexes **10** and **11** is pronounced [Δṽ = 1930 (**10**), 1820 cm^{-1} (**11**)] that of the 3-Fe(CO)LCp-substituted complexes **5a**, **7**, **14**, and **15** is rather small [Δṽ = 80−300 cm^{-1}].

The structure of the complex **5a** was additionally established by an X-ray-structural analysis (Table 1, Figure 1). The C(6)−C(9) [1.401(4) Å] and the C(8)−C(9) distance [1.410(5) Å] are almost equal in length indicating that the resonance structures **C** and **D** (Scheme 12) contribute to almost the same extent to the overall bonding description. The distances are in between the characteristic bond lengths of a $C(sp^2)-C(sp^2)$ single bond (1.46 Å)[22] and a $C(sp^2)=C(sp^2)$ double bond (1.32 Å)[22]. The Cr(1)−C(6) distance [2.054(4) Å] is typical for heteroatom-stabilized carbene complexes[13].

Scheme 12

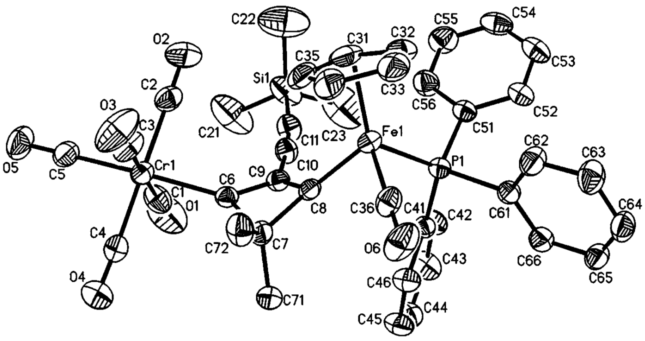


C **D**

The Fe−C(8) distance is comparable to that in cyclobut-1-en-3-one complexes[21a][21c]. The Fe−C(36) axis in **5a** is almost coplanar with the plane formed by the atoms C(7), C(8), C(9) [torsion angle C(9)−C(8)−Fe(1)−C(36) = 170.9°]. This conformation allows for maximal Fe→C(8) backdonation.

The most striking feature is the nonplanarity of the bridging ligand in **5a**. The puckering angle [angle between the planes formed by the atoms C(7), C(6), C(9) and C(7), C(8), C(9)] is 148.2°. A similar puckering has been observed with other 1,3-*hetero*binuclear cyclobutenylidene complexes[6], however, usually the four-membered ring in 3-amino- and 3-ethoxy-substituted cyclobutenylidene complexes[19], (cyclobut-1-en-3-one)iron complexes[21a][21c], free cyclobut-1-en-3-ones[23], and 1,3-*homo*binuclear cyclobutenylidene complexes[24] is nearly planar. As a consequence of the puckering, the transannular distance C(6)−C(8) in **5a** is small (1.986 Å) and the distance is well below the sum of the van der Waals radii. Therefore, direct electronic exchange cannot be excluded.

Figure 1. Molecular structure of complex **5a** in the crystal (hydrogen atoms are omitted for clarity)[a]



[a] Selected bond lengths [Å], bond angles, and torsion angles [°]: Cr(1)−C(6) 2.054(4), C(6)−C(9) 1.401(4), C(8)−C(9) 1.410(5), C(9)−C(10) 1.428(4), C(10)−C(11) 1.199(5), C(8)−Fe(1) 1.910(4); C(6)−C(9)−C(8) 89.9(3), C(7)−C(6)−C(9) 91.3(3), C(7)−C(8)−C(9) 91.0(3); C(7)−C(6)−C(9)−C(8) 22.7(2).

Conclusion

Our results demonstrate that an alkynyl functionality is readily introduced into the 2-position of 1,3-*hetero*binuclear cyclobutenylidene complexes by [2+2] cycloaddition of butadiynyl complexes to vinylidene complexes. These cyclobutenylidene complexes offer an easy access to a wide range of di-, tri-, and tetranuclear cyclobutenylidene complexes by derivatization of the alkynyl group and coupling reactions. In addition, the substituents in 4- and 3-position can be modified by use of other vinylidene complexes and by variation of the starting butadiynyl complexes.

By substitution of amines for the $Fe(CO)_2Cp$ fragment in **5a** a large variety of amines such as chiral amines can be introduced into the 3-position which is crucial for the nonlinear optical properties of these compounds. Thus, the synthesis of butadiynes R−C≡CC≡C−NR_2[25], which are rather difficult to prepare, can be avoided.

The nonplanarity of the cyclobutenylidene ring in **5a** decreases the symmetry of the molecule. Thus, taking into account the chirality of the iron center the existence of two diastereomers might be expected. However, only one isomer of **5a** could be isolated and the NMR spectra of **5a** exhibit only one set of signals. Obviously, in solution a rapid inversion of the four-membered ring occurs. For the analogous compound with an *n*Bu substituent at 2-C and a $Cp(PEt_3)Ni$ fragment at 3-C this dynamic process is still fast even at −80°C[6a].

The geometry of the complexes **7** and **15** is similarly flexible. However, for the diastereoselective coupling of **7** to **15** a second effect has to be considered. Probably due to the steric demand of the bulky PPh_3 substituent, only one isomer of **15** (*meso* or *R*/*S*) was formed. A similar selectivity has been reported by Gladysz et al. for the formation of comparable cyclobutenylidene complexes[24a].

Support of this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged. We also thank *B. Weibert* for collecting the data set for the X-ray-structural analysis.

Experimental Section

General: All operations were performed under either nitrogen or argon by using standard Schlenk techniques. Solvents were dried by refluxing over CaH_2 (CH_2Cl_2) or sodium/benzophenone ketyl (pentane, Et_2O, THF) and were freshly distilled prior to use. Silica gel (Fa. J. T. Baker; silica gel for flash chromatography) and alumina (Fa. Fluka) used for chromatography were nitrogen-saturated. Flash chromatography was performed at a nitrogen pressure of 1.4 bar. The complexes **1**[6a], **2a**[7a], **3a**[7a], [Cp(CO)$_2$FeI][26], and [Pd(PPh$_3$)$_4$][26] as well as R−C≡C−C≡C−Sn*n*Bu$_3$ (R = *n*Bu, Ph)[27] and *n*Bu$_3$SnNEt$_2$[28] were prepared according to literature procedures. − NMR: Bruker AC 250 (^{1}H and ^{13}C) and Jeol JNX 400 (^{1}H, ^{13}C, and ^{31}P); chemical shifts are reported relative to internal TMS (^{1}H and ^{13}C) or external H_3PO_4 (^{31}P). Unless mentioned otherwise, NMR spectra were recorded in $CDCl_3$ at room temperature. − IR: Biorad FTS 60. − MS: Finnigan MAT 312, modified either for EI or FAB (NBOH or NBOE used as solvent for FAB). − UV/Vis: Hewlett-Packard diode-array spectrophotometer 8452A. − Elemental analyses: Heraeus CHN-O-RAPID.

Dicarbonyl(η^5-cyclopentadienyl)(octa-1,3-diynyl)iron (**2b**): 9.9 g (25.0 mmol) of *n*Bu$_3$Sn−C≡C−C≡C−*n*Bu, 0.3 g (2.0 mmol) of CuI, and 2.5 g (2.0 mmol) of [Pd(PPh$_3$)$_4$] were added to a solution of 6.1 g (20.0 mmol) of [Cp(CO)$_2$FeI] in 150 ml of THF. The reaction mixture was stirred at room temp. for about 1 h. The solvent was evaporated in vacuo and the residue was chromatographed at −20°C first two times with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 4:1) on alumina and then two times with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 3:2) on silica gel. The solvent was evaporated in vacuo. The residue was recrystallized from 40 ml of pentane/CH_2Cl_2 (3:2) to give **2b** as a yellow powder. Yield: 2.3 g (32%, based on [Cp(CO)$_2$FeI]), m.p. 45°C. − IR (CH_2Cl_2): ṽ(CO) = 2040 cm^{-1} vs, 1997 vs; ṽ(C≡C) = 2203 cm^{-1} vw. − ^{1}H NMR (250 MHz): δ = 0.88 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH$_3$), 1.32−1.51 (m, 4 H, CH$_2$), 2.24 (t, $^3J_{HH}$ = 6.7 Hz, 2 H, CH$_2$), 5.06 (s, 5 H, C$_5$H$_5$). − ^{13}C NMR (250 MHz): δ = 13.5 (CH$_3$), 18.7, 21.9, 30.9 (CH$_2$), 67.1, 67.9, 83.8 (C≡C), 85.2 (C$_5$H$_5$), 97.4 (C≡C), 211.4 (CO). − $C_{15}H_{14}FeO_2 \cdot CH_2Cl_2$ (367.0): calcd. C 52.36, H 4.39; found C 51.86, H 3.97.

Dicarbonyl(η^5-cyclopentadienyl)(phenylbuta-1,3-diynyl)iron (**2c**): The synthesis of **2c** from 6.1 g (20.0 mmol) of [Cp(CO)$_2$FeI], 10.4 g (25.0 mmol) of *n*Bu$_3$Sn−C≡C−C≡C−Ph, 0.3 g (2.0 mmol) of CuI, and 2.5 g (2.0 mmol) of [Pd(PPh$_3$)$_4$] in 150 ml of THF and the purification of the product by chromatography first with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 3:1) on alumina and then with pentane/CH_2Cl_2 (ratio slowly decreasing from 1:0 to 1:1) on silica gel] were carried out similarly to that of **2b**. Recrystallization from 40 ml of pentane/CH_2Cl_2 (1:1) gave **2c**. Yellow powder. Yield: 2.7 g (45%, based on [Cp(CO)$_2$FeI]), m.p. 91°C. − IR (CH_2Cl_2): ṽ(CO) = 2042 cm^{-1} vs, 1994 vs; ṽ(C≡C) = 2184 cm^{-1} m. − ^{1}H NMR (250 MHz): δ = 5.06 (s, 5 H, C$_5$H$_5$), 7.24, 7.39 (m, br., 5 H, C$_6$H$_4$). − ^{13}C NMR (250 MHz): δ = 64.8, 77.3 (C≡C), 85.4 (C$_5$H$_5$), 96.2, 97.3 (C≡C), 123.6, 127.5, 128.1, 132.4 (C$_6$H$_5$), 211.1 (CO). − MS (EI, 70 eV); *m/z* (%): 302 (38) [M$^+$], 274 (23), 246 (100) [M$^+$ − *n* CO; *n* = 1, 2]. − Although the product was chromatographed several times, it still contained small amounts of tin compounds. Therefore, a satisfactory elemental analysis could not be obtained.

Carbonyl(η^5-cyclopentadienyl)(trimethylsilyl-1,3-diynyl)(triphenylphosphane)iron (**3a**): A THF solution (50 ml) of 3.0 g (10.0 mmol) of **2a**, 0.8 g (10.0 mmol) of Me$_3$NO, and 4.0 g (15.0 mmol) of PPh$_3$ was stirred at room temp. The reaction was monitored by IR spectroscopy. After ca. 2 h, the solvent was removed in vacuo, the residue dissolved in 30 ml of CH_2Cl_2 and transferred to a column packed with silica gel. Gradient elution at 0°C with a mixture of pentane/CH_2Cl_2 (ratio slowly decreasing from 1:0 to 3:7) yielded the product as an orange band. After evaporation of the solvent in vacuo, the product was obtained as an orange oil. Yield: 3.4 g (63%, based on **2a**). The product was identified by comparison with literature data.[7a]

Pentacarbonyl{3-dicarbonyl(η^5-cyclopentadienyl)ferrio]-4,4-dimethyl-2-(trimethylsilylethynyl)cyclobut-2-en-1-ylidene}chromium (**4a**): At −60°C, a solution of 1.49 g (5.0 mmol) of **2a** in 50 ml of CH_2Cl_2 was added to a solution of **1**[6a]. The reaction mixture was allowed to slowly warm up to room temp. Then, 50 ml of pentane was added. The resulting suspension was filtered through a 2-cm layer of alumina and the alumina was eluted with CH_2Cl_2. The solvent was removed in vacuo and the residue was chromatographed at −30°C on silica gel. Elution with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 4:1) gave a red solution. The solvent was removed in vacuo and the residue recrystallized from 20 ml of pentane/CH_2Cl_2 (3:1). Red crystals of **4a**. Yield: 1.79 g (65%, based on [Cr(CO)$_6$]), m.p. 84°C. − IR (CH_2Cl_2): ṽ(CO) = 2053 cm^{-1} s, 2034 s, 1990 s, 1939 vs; ṽ(C≡C) = 2148 cm^{-1} vw. − UV/Vis (pentane): λ_{max} (lg ε) = 494 nm (4.212); (DMF): λ_{max} (lg ε) = 492 nm (4.178). − ^{1}H NMR (250 MHz): δ = 0.25 (s, 9 H, SiMe$_3$), 1.33 (s, 6 H, CH$_3$), 5.25 (s, 5 H, C$_5$H$_5$). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = −0.4 (SiMe$_3$), 26.4 (CH$_3$), 74.3 (4-C), 87.1 (C$_5$H$_5$), 100.2, 104.4 (C≡C), 180.6 (2-C), 211.9 (Fe−CO), 217.9 (*cis*-CO), 229.2 (*trans*-CO), 251.5 (3-C), 313.3 (1-C). − $C_{23}H_{20}CrFeO_7Si$ (544.3): calcd. C 50.75, H 3.70; found C 50.52, H 3.88.

Pentacarbonyl{3-dicarbonyl(η^5-cyclopentadienyl)ferrio]-4,4-dimethyl-2-(hexa-1-ynyl)cyclobut-2-en-1-ylidene}chromium (**4b**): The synthesis of **4b** from **1** and 1.4 g (5.0 mmol) of **2b** in 50 ml of CH_2Cl_2 at −60°C and the purification of the product with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 2:1) were carried out analogously to that of **4a**. Red oil. Yield: 1.19 g (45%, based on [Cr(CO)$_6$]). − IR (CH_2Cl_2): ṽ(CO) = 2051 cm^{-1} m, 2031 s, 1981 vs, 1935 vs; ṽ(C≡C) = 2142 cm^{-1} vw. − UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 490 nm (4.116), (DMF) 486 nm (4.161). − ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 0.86 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH$_3$), 1.27 (s, 6 H, CH$_3$), 1.39−1.54 (m, 4 H, CH$_2$), 2.41 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, CH$_2$), 5.14 (s, 5 H, C$_5$H$_5$). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = 13.8 (CH$_3$), 19.8, 22.5 (CH$_2$), 26.8 (CH$_3$), 30.9 (CH$_2$), 74.3 (4-C), 75.9 (C≡C), 86.9 (C$_5$H$_5$), 100.6 (C≡C), 182.7 (2-C), 212.1 (Fe−CO), 218.3 (*cis*-CO), 228.9 (*trans*-CO), 245.3 (3-C), 304.8 (1-C). − $C_{24}H_{20}CrFeO_7$ (528.0): calcd. C 54.55, H 3.82; found C 54.29, H 4.11. − MS (FAB); *m/z* (%): 528 (22) [M$^+$], 500 (14), 472 (38), 444 (10), 416 (100), 388 (50), 360 (10), 332 (12) [M$^+$ − *n* CO; *n* = 1−7].

Pentacarbonyl{3-dicarbonyl(η^5-cyclopentadienyl)ferrio]-4,4-dimethyl-2-(phenylethynyl)cyclobut-2-en-1-ylidene}chromium (**4c**): The synthesis of **4c** from **1** and 1.5 g (5.0 mmol) of **2c** and the purification of the product were carried out analogously to **4b**. Recrystallization from 20 ml of pentane/CH_2Cl_2 (3:1) gave red crystals of **4c**. Yield: 1.65 g (60%, based on [Cr(CO)$_6$]), m.p. 84°C. − IR (CH_2Cl_2): ṽ(CO) = 2052 cm^{-1} m, 2033 m, 1989 m, 1937 vs; ṽ(C≡C) = 2146 cm^{-1} vw. − UV/Vis (pentane): λ_{max} (lg ε) = 494 nm (4.062); (DMF): λ_{max} (lg ε) = 492 nm (4.183). − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.40 (s, 6 H, CH_3), 5.29 (s, 5 H, C_5H_5), 7.38−7.56 (m, 5 H, C_6H_5). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = 26.6 (CH_3), 74.8 (4-C), 84.8 (C≡C), 87.0 (C_5H_5), 98.0 (C≡C), 123.3, 128.9, 131.5, 132.3 (C_6H_5), 180.7 (2-C), 211.9 (Fe−CO), 218.1 (*cis*-CO), 229.0 (*trans*-CO), 250.6 (3-C), 311.5 (1-C). − $C_{26}H_{16}CrFeO_7$ (548.3): calcd. C 56.96, H 2.94; found C 57.12, H 3.06. − MS (FAB); *m/z* (%): 548 (38) [M^+], 520 (22), 492 (40), 464 (10), 436 (100), 408 (52), 380 (10), 352 (30) [$M^+ - n$ CO; $n = 1-7$].

Pentacarbonyl{3-[carbonyl(η^5-cyclopentadienyl)(triphenylphosphane)ferrio]-4,4-dimethyl-2-(trimethylsilylethynyl)cyclobut-2-en-1-ylidene}chromium (**5a**): The synthesis of **5a** from **1** and 2.7 g (5.0 mmol) of **3a** in 50 ml of CH_2Cl_2 at −60°C, the purification, and the chromatography of the product were carried out analogously to that of **4a**. The red fraction was eluted with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 1:1). Recrystallization from 20 ml of pentane/CH_2Cl_2 (3:1) gave red crystals of **5a**. Yield: 2.53 g (65%, based on [$Cr(CO)_6$]), m.p. 152°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2043 cm^{-1} m, 1950 sh, 1927 vs; $\tilde{\nu}$(C≡C) = 2141 cm^{-1} vw. − UV/Vis (pentane): λ_{max} (lg ε) = 520 nm (4.246); (DMF): λ_{max} (lg ε) = 512 nm (3.889). − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.26 (s, 9 H, $SiMe_3$), 0.49 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 4.82 (d, $^3J_{PH}$ = 1.5 Hz, 5 H, C_5H_5), 7.41−7.56 (m, 15 H, Ph). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = −0.1 ($SiMe_3$), 25.8, 27.9 (CH_3), 76.2 (4-C), 87.2 (C_5H_5), 102.9, 104.1 (C≡C), 128.9, 129.0, 130.8, 130.9, 133.7, 133.9, 135.2, 135.9 (C_6H_5), 183.2 (2-C), 218.4 (d, $^2J_{PC}$ = 30 Hz, Fe−CO), 219.1 (*cis*-CO), 228.6 (*trans*-CO), 276.5 (d, $^2J_{PC}$ = 19 Hz, 3-C), 288.5 (1-C). − $C_{40}H_{35}CrFeO_6PSi$ (778.6): calcd. C 61.69, H 4.53; found C 61.91, H 4.63.

Decarbonylation of **4a** *with Me_3NO in the Presence of PPh_3:* A solution of 1.6 g (3.0 mmol) of **4a**, 0.3 g (3.0 mmol) of Me_3NO, and 1.6 g (6.0 mmol) of PPh_3 in 30 ml of THF was stirred at room temp. The progress of the reaction was monitored by IR spectroscopy. After about 1 h, the solvent was removed in vacuo, the residue dissolved in 15 ml of CH_2Cl_2, and the solution transferred to a chromatography column packed with silica gel. Gradient elution at −20°C with pentane/CH_2Cl_2 (ratio slowly decreasing from 1:0 to 1:1) yielded 1.71 g (72%, based on **4a**) of **5a**.

Pentacarbonyl{3-[carbonyl(η^5-cyclopentadienyl)(triphenylphosphane)ferrio]-4,4-dimethyl-2-(phenylethynyl)cyclobut-2-en-1-ylidene}chromium (**5c**): A solution of 1.4 g (2.0 mmol) of **7** in 5 ml of toluene was treated at room temp. with 0.5 g (2.5 mmol) of Me_3SnNMe_2. The reaction was followed by thin-layer chomatography. After 30 min, the solvent was removed in vacuo. The remaining oil was dissolved in THF (30 ml) and 0.5 g (2.5 mmol) of iodobenzene, 30 mg (0.2 mmol) of CuI, and 280 mg (0.2 mmol) of [$Pd(PPh_3)_4$] were added. The reaction mixture was stirred for 30 min at 40°C. The solvent was removed in vacuo, the residue dissolved in 15 ml of CH_2Cl_2 and chromatographed at −30°C with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 3:2) on silica gel. A red band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (1:1) gave red crystals of **5c**. Yield: 1.25 g (76%, based on **7**), m.p. 95°C (dec.). − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2043 cm^{-1} m, 1950 sh, 1925 vs, 1901 sh. − UV/Vis (pentane): λ_{max} (lg ε) = 522 nm (3.891); (DMF): λ_{max} (lg ε) = 516 nm (4.122). − ^1H NMR (250 MHz): δ = 0.56 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 4.80 (d, $^3J_{PH}$ = 1.5 Hz, 5 H, C_5H_5), 7.28−7.57 (m, 20 H, C_6H_5, PPh_3). − ^{13}C NMR (250 MHz): δ = 25.5, 27.7 (CH_3), 76.0 (4-C), 86.5 (C_5H_5), 97.5, 123.6 (C≡C), 128.2, 128.4, 128.6, 129.5, 130.5, 131.1, 132.8, 133.2, 134.1, 134.4, 134.8, 135.5 (C_6H_5, PPh_3), 182.0 (2-C), 217.8 (d, $^2J_{PC}$ = 29 Hz, Fe−CO), 218.7 (*cis*-CO), 228.1 (*trans*-CO), 275.8 (d, $^2J_{PC}$ = 17 Hz, 3-C), 291.8 (1-C). − ^{31}P NMR: δ = 68.8 (s). − $C_{43}H_{31}CrFeO_6P \cdot 1/2\ CH_2Cl_2$ (824.6): calcd. C 63.35, H 3.91; found C 63.51, H 4.40. − MS (FAB); *m/z* (%): 782 (16) [M^+], 754 (2), 698 (2), 670 (16), 642 (30), 614 (46) [$M^+ - n$ CO; n = 1, 3−6].

Pentacarbonyl{3-dicarbonyl(η^5-cyclopentadienyl)ferrio]-4,4-dimethyl-2-(ethynyl)cyclobut-2-en-1-ylidene}chromium (**6**): At −90°C, 0.4 equiv. of tetrabutylammonium fluoride (1 M solution in THF) was added to a solution of **4a** (5.4 g, 10.0 mmol) in 100 ml of THF. The mixture was warmed to room temp. and stirred for ca. 3 h at room temp. The progress of the reaction was monitored by thin-layer chromatography. The solvent was removed in vacuo and the residue dissolved in 30 ml of CH_2Cl_2. Chromatography at −40°C with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 1:1) and recrystallization from 20 ml of pentane/CH_2Cl_2 (1:1) afforded red crystals of **6**. Yield: 3.16 g (67%, based on **4a**), m.p. 68°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2054 cm^{-1} s, 2033 s, 1990 m, 1938 vs; $\tilde{\nu}$(C≡C) = 2139 cm^{-1} vw, br. − UV/Vis (pentane): λ_{max} (lg ε) = 492 nm (4.206); (DMF): λ_{max} (lg ε) = 486 nm (4.238). − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.35 (s, 6 H, CH_3), 3.68 (s, 1 H, C≡CH), 5.25 (s, 5 H, C_5H_5). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = 26.3 (CH_3), 74.2 (4-C), 79.0, 86.3 (C≡C), 87.0 (C_5H_5), 179.5 (2-C), 211.8 (Fe−CO), 217.8 (*cis*-CO), 229.1 (*trans*-CO), 253.7 (3-C), 315.1 (1-C). − $C_{20}H_{12}CrFeO_7$ (472.2): calcd. C 50.88, H 2.52; found C 50.80, H 2.61.

Pentacarbonyl{3-[carbonyl(η^5-cyclopentadienyl)(triphenylphosphane)ferrio]-4,4-dimethyl-2-(ethynyl)cyclobut-2-en-1-ylidene}chromium (**7**): The synthesis of **7** by reaction of **5a** (7.8 g, 10.0 mmol) with 0.4 equiv of tetrabutylammonium fluoride and the purification were performed analogously to **6**. Red crystals of **7**. Yield: 4.24 g (57%, based on **5a**), m.p. 72°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2043 cm^{-1} s, 1950 sh, 1927 vs, 1888 sh; $\tilde{\nu}$(C≡C) = 2143 cm^{-1} vw, br. − UV/Vis (pentane): λ_{max} (lg ε) = 518 nm (4.030); (DMF): λ_{max} (lg ε) = 512 nm (4.166). − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.62 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 3.58 (s, 1 H, C≡C-H), 4.80 (d, $^3J_{PH}$ = 1.5 Hz, 5 H, C_5H_5), 7.39−7.54 (m, 15 H, Ph). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = 25.9, 27.4 (CH_3), 76.3 (4-C), 81.3, 86.1 (C≡C), 86.9 (C_5H_5), 128.4, 128.6, 129.0, 129.7, 130.9, 133.2, 133.7, 133.9, 135.1, 135.8 (C_6H_5), 181.8 (2-C), 218.1 (d, $^2J_{PC}$ = 29 Hz, Fe−CO), 219.0 (*cis*-CO), 228.4 (*trans*-CO), 280.7 (d, $^2J_{PC}$ = 17 Hz, 3-C), 289.9 (1-C). − ^{31}P NMR: δ = 68.8 (s). − $C_{37}H_{27}CrFeO_6P \cdot 1/2\ C_5H_{12}$ (742.5): calcd. C 63.98, H 4.35; found C 63.95, H, 4.51. − MS (FAB); *m/z* (%): 706 (8) [M^+], 594 (15), 566 (20), 538 (35) [$M^+ - n$ CO; n = 4, 5, 6], 263 (100) [$HPPh_3^+$].

Pentacarbonyl[3-dimethylamino-4,4-dimethyl-2-(trimethylsilylethynyl)cyclobut-2-en-1-ylidene]chromium (**10**): An aqueous solution of $HNMe_2$ (40%, 0.25 ml, 2.0 mmol) was added at room temp. to a solution of 0.5 g (1.0 mmol) of **4a** in 10 ml of THF. The color of the solution changed within a few minutes from red to yellow. The solvent was removed in vacuo and the residue chromatographed at −20°C on silica gel. With pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 1:1) a yellow band was eluted. Recrystallization from 5 ml of pentane/CH_2Cl_2 (3:1) gave yellow crystals of **10**. Yield: 0.35 g (83%, based on **4a**), m.p. 113°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2046 cm^{-1} m, 1971 vw, 1929 vs, 1893 sh; $\tilde{\nu}$(C≡C) = 2146 cm^{-1} w. − UV/Vis (pentane): λ_{max} (lg ε) = 450 nm (4.383); (DMF): λ_{max} (lg ε) = 414 nm (4.290). − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.20 (s, 9 H, $SiMe_3$), 1.41 (s, 6 H, CH_3), 3.06, 3.42 (s, 6 H, NMe_2). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = −0.4 ($SiMe_3$), 23.8 (CH_3), 39.8, 49.9 (NMe_2), 60.7 (4-C), 98.4, 102.0 (C≡C), 134.2 (2-C), 176.1 (3-C), 219.1 (*cis*-CO), 227.2 (*trans*-CO), 307.1 (1-C). − $C_{18}H_{21}CrNO_5Si \cdot 1/10\ CH_2Cl_2$ (420.0): calcd. C 51.82, H 5.08, N, 3.88; found C 51.78, H 5.09, N 3.34. − MS (EI, 70 eV); *m/z* (%): 411 (9) [M^+], 355 (4), 299 (20), 271 (100) [$M^+ - n$ CO; n = 2, 4, 5].

Pentacarbonyl[4,4-dimethyl-3-piperidino-2-(trimethylsilylethynyl)cyclobut-2-en-1-ylidene]chromium (**11**): The synthesis of **11** from 0.5 g (1.0 mmol) of **4a** and 1.5 equiv. of piperidine in 10 ml of THF and the purification of the product were carried out similarly to **10**. On chromatography, pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 7:1) was used as the eluant. Recrystallization from 5 ml of pentane/CH_2Cl_2 (6:1) afforded yellow crystals of **11**. Yield: 0.18 g (40%, based on **4a**), m.p. 120°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2046 cm^{-1} m, 1970 w, 1926 vs, 1896 sh; $\tilde{\nu}$(C≡C) = 2145 cm^{-1} w. − UV/Vis (pentane): λ_{max} (lg ε) = 450 nm (4.325); (DMF): λ_{max} (lg ε) = 416 nm (4.360). − ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 0.20 (s, 9 H, $SiMe_3$), 1.40 (s, 6 H, CH_3), 1.77, 3.40, 3.94 (m, br., 10 H, $N(CH_2)_5$). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = −0.3 ($SiMe_3$), 23.6 (CH_2), 23.8 (CH_3), 26.3, 26.7, 49.0, 49.9 (CH_2), 60.6 (4-C), 98.5, 102.1 (C≡C), 133.3 (2-C), 173.6 (3-C), 219.2 (*cis*-CO), 227.1 (*trans*-CO), 305.3 (1-C). − $C_{21}H_{25}CrNO_5Si$ (451.5): calcd. C 55.86, H 5.58, N 3.10; found C 55.80, H 5.59, N 3.37. − MS (FAB); *m/z* (%): 451 (45) [M^+], 423 (8), 395 (42), 367 (18), 339 (100), 311 (82) [$M^+ - n$ CO; n = 1−5], 260 (50) [$(C_{16}H_{25}NSi)^+$].

Pentacarbonyl{3-dicarbonyl(η⁵-cyclopentadienyl)ferrio]-4,4-dimethyl-2-(tri-n-butylstannylethynyl)cyclobut-2-en-1-ylidene}-chromium (**12**): At room temp., 0.9 g (2.5 mmol) of nBu_3SnNEt_2 was added to a solution of 0.9 g (2.0 mmol) of **6** in 5 ml of toluene. The progress of the reaction was monitored by thin-layer chomatography. After ca. 5 min, the solvent was removed in vacuo, the residue dissolved in 10 ml of CH_2Cl_2, and chromatographed at −20°C on silica gel with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 1:1). Complex **12** was obtained as a red oil. Yield: 1.29 g (85%, based on **6**). − IR (pentane): $\tilde{\nu}$(CO) = 2054 cm^{-1} m, 2033 s, 1990 s, 1951 vs, 1938 sh; $\tilde{\nu}$(C≡C) = 2131 cm^{-1} vw, br. − ^{1}H NMR (250 MHz): δ = 0.91 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3), 1.03−1.09 (m, 6 H, CH_2), 1.29−1.43 (m, 6 H, CH_2), 1.34 (s, 6 H, CH_3), 1.55−1.68 (m, 6 H, CH_2), 5.24 (s, 5 H, C_5H_5). − ^{13}C NMR (250 MHz): δ = 11.1 (CH_3), 13.6, 26.4, 27.0 (CH_2), 28.9 (CH_3), 73.7 (4-C), 86.4 (C_5H_5), 104.2, 105.0 (C≡C), 181.6 (2-C), 211.4 (Fe−CO), 217.5 (*cis*-CO), 228.6 (*trans*-CO), 243.9 (3-C), 308.1 (1-C). −It was not possible to completely remove small amounts of tin compounds. Therefore, a satisfactory elemental analysis was not obtained.

Pentacarbonyl{3-dicarbonyl(η⁵-cyclopentadienyl)ferrio]-2-(p-iodophenylethynyl)-4,4-(dimethyl)cyclobut-2-en-1-ylidene}-chromium (**13**): Compound **12** was generated in situ from 2.8 g (6.0 mmol) of **6** and 2.2 g (6.0 mmol) of nBu_3SnNEt_2 in 10 ml of toluene as described above. After changing the solvent to THF (100 ml), 1.0 g (3.0 mmol) of $C_6H_4I_2$-*p*, 30 mg (0.2 mmol) of CuI, and 280 mg (0.2 mmol) of [$Pd(PPh_3)_4$] were added. The reaction mixture was stirred for 30 min at 40°C. The solvent was removed in vacuo, the residue dissolved in 20 ml of CH_2Cl_2, and chromatographed at −30°C with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 2:1) on silica gel. A red band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (1:1) gave red crystals of **13**. Yield: 0.41 g (20%, based on $C_6H_5I_2$-*p*), m.p. 77°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2053 cm^{-1} m, 2033 m, 1984 m, 1937 vs; $\tilde{\nu}$(C≡C) = 2197 cm^{-1} vw. − UV/Vis (pentane): λ_{max} (lg ε) = 494 nm (3.900); (DMF): λ_{max} (lg ε) = 492 nm (4.187). − ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.39 (s, 6 H, CH_3), 5.28 (s, 5 H, C_5H_5), 7.26−7.28, 7.72−7.74 (m, 4 H, C_6H_4I). − ^{13}C NMR (CD_2Cl_2, 400 MHz): δ = 26.2 (CH_3), 74.6 (4-C), 86.8 (C_5H_5), 94.6, 96.7 (C≡C), 122.6, 132.7, 133.5, 137.8 (C_6H_4I), 179.8 (2-C), 211.5 (Fe−CO), 217.7 (*cis*-CO), 228.7 (*trans*-CO), 251.6 (3-C), 313.2 (1-C). − $C_{27}H_{15}CrFeIO_7$ (686.2): calcd. C 47.26, H 2.20; found C 47.36, H 2.29.

Pentacarbonyl{3-[carbonyl(η⁵-cyclopentadienyl)-(triphenylphosphane)ferrio]-2-(p-iodophenyl)ethynyl-4,4-(dimethyl)cyclobut-2-en-1-ylidene}chromium (**14**) *and 1,4-Bis({4-pentacarbonylchromium-2-[carbonyl(η⁵-cyclopentadienyl)-(triphenylphosphane)ferrio]-3,3-(dimethyl)cyclobut-1-en-4-ylidene}ethynyl)benzene* (**15**): 0.2 g (0.5 mmol) of $C_6H_4I_2$-*p*, 20 mg (0.1 mmol) of CuI, and 120 mg (0.1 mmol) of [$Pd(PPh_3)_4$] were added to a solution of 0.7 g (1.0 mmol) of **7** in 30 ml of $HNEt_2$. The reaction mixture was stirred for 5 h at 40°C. The solvent was removed in vacuo, the residue dissolved in 4 ml of CH_2Cl_2 and then chromatographed at −20°C with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 4:1) on silica gel. Two slightly different red bands were eluted. The first band contained **14**, the second one **15**.

14: Yield: 0.18 g (38%, based on $C_6H_4I_2$-*p*), m.p. 87°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2042 cm^{-1} m, 1948 sh, 1926 vs, 1901 sh. − UV/Vis (pentane): λ_{max} (lg ε) = 522 nm (4.213); (DMF): λ_{max} (lg ε) = 516 nm (4.216). − ^{1}H NMR (400 MHz): δ = 0.58 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 4.79 (s, 5 H, C_5H_5), 7.14−7.69 (m, 19 H, C_6H_4, C_6H_5). − ^{13}C NMR (400 MHz): δ = 25.4, 27.8 (CH_3), 86.5 (C_5H_5), 88.9 (4-C), 94.0, 96.5 (C≡C), 123.2, 128.1, 128.5, 128.6, 128.8, 129.2, 130.5, 132.5, 133.0, 133.3, 133.5, 133.7, 134.9, 135.4, 137.6 (C_6H_4, C_6H_5), 181.5 (2-C), 217.7 (d, $^2J_{PC}$ = 29 Hz, Fe−CO), 218.6 (*cis*-CO), 228.1 (*trans*-CO), 277.3 (d, $^2J_{PC}$ = 17 Hz, 3-C), 294.2 (1-C). − ^{31}P NMR: δ = 68.5 (s). − $C_{43}H_{30}CrFeIO_6P \cdot 1/2\ C_5H_{12}$ (944.1): calcd. C 57.88, H 3.84; found C 57.74, H 3.74. − MS (FAB); *m/z* (%): 908 (6) [M^+], 796 (12), 768 (26), 740 (52) [$M^+ - n$ CO; n = 4, 5, 6], 478 (30) [M^+ − 6 CO − PPh_3], 383 (100) [$(CpFePPh_3)^+$].

15: Yield: 0.07 g (10%, based on $C_6H_4I_2$-*p*), m.p. 72°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2043 cm^{-1} s, 1947 sh, 1925 vs; $\tilde{\nu}$(C≡C) = 2067 cm^{-1} vw. − UV/Vis (pentane): λ_{max} (lg ε) = 522 nm (3.890); (DMF): λ_{max} (lg ε) = 516 nm (4.348). − ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 0.61 (s, 6 H, CH_3), 1.28 (s, 6 H, CH_3), 4.86 (d, $^3J_{PH}$ = 1.2 Hz, 10 H, C_5H_5), 7.30−7.57 (m, 34 H, C_6H_4, C_6H_5). − ^{13}C NMR (CD_2Cl_2, 250 MHz): δ = 25.9, 27.9 (CH_3), 76.6 (4-C), 87.1 (C_5H_5), 89.7, 97.6 (C≡C), 123.7, 128.9, 129.1, 130.9, 131.4, 133.7, 133.8, 135.2, 135.9 (C_6H_4, C_6H_5), 182.1 (2-C), 218.3 (d, $^2J_{PC}$ = 29 Hz, Fe−CO), 219.2 (*cis*-CO), 228.6 (*trans*-CO), 280.0 (d, $^2J_{PC}$ = 18 Hz, 3-C), 291.1 (1-C). − ^{31}P NMR: δ = 68.5 (s). − $C_{80}H_{56}Cr_2Fe_2O_{12}P_2$ (1487.0): calcd. C 64.62, H 3.80; found C 64.90, H 4.52. − MS (FAB); *m/z* (%): 1487 (25) [M^+], 1402 (4), 1374 (15), 1347 (40), 1319 (88) [$M^+ - n$ CO; n = 3−6], 944 (38), 916 (58), 888 (60) [$M^+ - HPPh_3 - n$ CO; n = 10−12].

Pentacarbonyl{3-[carbonyl(η⁵-cyclopentadienyl)(triphenylphosphane)ferrio]-2-[trans-iodobis(triethylphosphane)palladio]-ethynyl-4,4-(dimethyl)cyclobut-2-en-1-ylidene}]chromium (**16**): 0.4 g (1.0 mmol) of *trans*-[$(PEt_3)_2PdCl_2$], 60 mg (0.3 mmol) of CuI, and 350 mg (0.3 mmol) of [$Pd(PPh_3)_4$] were added to a solution of 2.1 g (3.0 mmol) of **7** in 30 ml of $HNEt_2$. The reaction mixture was stirred for 1 d at 40°C. The solvent was removed in vacuo, the residue dissolved in 15 ml of CH_2Cl_2, and chromatographed at −20°C with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 1:1) on alumina. An orange band was eluted which was then chromatographed two times at −20°C with pentane/CH_2Cl_2 (ratio decreasing from 1:0 to 1:1) on silica gel. Recrystallization yielded **16** as an orange powder. Yield: 0.27 g (22%, based on *trans*-[$(PEt_3)_2PdCl_2$]), m.p. 82°C. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2042 cm^{-1} m, 1965 sh, 1942 sh, 1919 vs, 1888 sh; $\tilde{\nu}$(C≡C) = 2092 cm^{-1} vw. − ^{1}H NMR (250 MHz): δ = 0.84 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 0.88−1.29 (m, br., 18 H, CH_2CH_3), 2.00−2.30 (m, br., 12 H, CH_2), 4.63 (s, 5 H, C_5H_5), 7.21−7.56 (m, 15 H, C_6H_5). − ^{13}C NMR (250 MHz): δ = 8.4 (PEt_3), 17.5 (m, PEt_3), 27.1, 30.7 (CH_3), 78.2 (4-C), 86.3 (C_5H_5), 103.4 (t, $^3J_{PC}$ = 5 Hz, C≡C), 117.5 (t, $^2J_{PC}$ = 14 Hz, C≡C), 128.0, 128.4, 128.8, 129.4, 130.5, 130.8, 132.9, 133.2, 133.4, 133.6, 135.2, 135.9 (C_6H_5), 192.2 (2-C), 218.7 (d, $^2J_{PC}$ = 32 Hz, Fe−CO), 219.7 (*cis*-CO), 226.3 (*trans*-CO), 236.2 (d, $^2J_{PC}$ = 18 Hz, 3-C), 241.4 (1-C). − ^{31}P NMR: δ = 72.8 (s, PPh_3), 13.8 (s, PEt_3). − $C_{49}H_{56}CrFeIO_6P_3Pd \cdot C_5H_{12}$ (1246.2): calcd. C 52.09, H 5.35; found C 52.20, H 5.06. − MS (FAB); *m/z* (%): 1174 (28) [M$^+$], 1062 (25), 1034 (10), 1006 (5) [M$^+$ − *n* CO; *n* = 4−6], 916 (10), 888 (12) [M$^+$ − *n* CO − PEt_3; *n* = 5, 6], 800 (10), 772 (15), 744 (15) [M$^+$ − PPh_3 − *n* CO; *n* = 4−6], 383 (100) [$CpFePPh_3^+$].

Pentacarbonyl{3-[carbonyl(η^5-cyclopentadienyl)(triphenylphosphane)ferrio]-2-[trans-chlorobis(triethylphosphane)platinio]ethynyl-4,4-(dimethyl)cyclobut-2-en-1-ylidene}chromium (**17**): 1.1 g (3.0 mmol) of nBu_3SnNEt_2 was added at room temp. to a solution of 2.1 g (3.0 mmol) of **7** in 5 ml of toluene. The progress of the reaction was followed by thin-layer chomatography. After 30 min, the solvent was removed in vacuo and the remaining oil dissolved in THF (50 ml). This solution was treated with 0.5 g (1.0 mmol) of *trans*-[$(PEt_3)_2PtCl_2$], 57 mg (0.3 mmol) of CuI, and 350 mg (0.3 mmol) of [$Pd(PPh_3)_4$]. The reaction mixture was stirred for 12 h at room temp. The solvent was removed in vacuo, the residue dissolved in 15 ml of CH_2Cl_2 and chromatographed at −30°C with pentane/acetone (ratio decreasing from 1:0 to 7:3) on silica gel. An orange fraction was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (1:1) yielded **17** as an orange powder. Yield: 0.42 g (36%, based on *trans*-[$(PEt_3)_2PtCl_2$]), m.p. 78°C. − IR (CH_2Cl_2): ṽ(CO) = 2041 cm^{-1} m, 1963 sh, 1940 sh, 1918 vs , 1889 sh; ṽ(C≡C) = 2096 cm^{-1} vw. − ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 0.80 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.09−1.26 (m, br., 18 H, CH_2CH_3), 1.85−2.10 (m, br., 12 H, CH_2), 4.62 (s, 5 H, C_5H_5), 7.42−7.59 (m, 15 H, C_6H_5). − ^{13}C NMR (400 MHz): δ = 7.9 (PEt_3), 14.1−14.6 (m, PEt_3), 25.5, 26.8 (CH_3), 77.6 (4-C), 86.3 (C_5H_5), 99.9 (m, C≡C), 128.5, 128.6, 130.3, 133.5, 133.6, 135.4, 135.8 (C_6H_5), 193.2 (2-C), 218.9 (d, $^2J_{PC}$ = 32 Hz, Fe−CO), 219.8 (*cis*-CO), 226.4 (*trans*-CO), 233.9 (3-C), 239.9 (1-C). − ^{31}P NMR: δ = 72.9 (s, PPh_3), 14.1 (s and d, $^1J_{PtP}$ = 2371 Hz, PEt_3). − $C_{49}H_{56}ClCrFeO_6P_3Pt$ (1172.3): calcd. C 50.20, H 4.81; found C 50.00, H 5.06. − MS (FAB); *m/z* (%): 1172 (2) [M$^+$], 1060 (16), 1032 (38), 1004 (38) [M$^+$ − 6 CO; *n* = 4−6], 886 (34) [M$^+$ − 6 CO − PEt_3], 769 (26) [M$^+$ − 6 CO − 2 PEt_3 + H], 742 (92) [M$^+$ − 6 CO − PPh_3], 624 (100) [M$^+$ − 6 CO − PPh_3 − PEt_3].

X-ray-Structural Analysis of **5a**: $C_{40}H_{35}CrFeO_6PSi$ (778.6), crystal size 0.3 × 0.3 × 0.3 mm (obtained from pentane/CH_2Cl_2, 3:1), triclinic, $P\bar{1}$, a = 11.555(2), b = 12.599(2), c = 15.382(2) Å, α = 83.83(2), β = 75.10(1), γ = 63.62(1)°, V = 1937.4(5) Å^3, Z = 2, $d_{calcd.}$ = 1.335 g cm^{-3}, μ(Mo-$K_α$) = 0.760 mm^{-1}, F(000) = 804, Wyckoff scan 4° < 2Θ < 54°, scan rate variable 4.00−30.00° min^{-1} in ω; Δω = 1.40°, T = 244 K, 8873 reflections collected, 8446 independent reflections, 6373 reflections with F > 4.0 σ(F); 451 refined parameters; R = 0.047, R_w = 0.051. Largest difference peak (hole): +0.45 e Å^{-3} (−0.38 e Å^{-3}). Data were collected with a crystal mounted in a glass capillary on a Siemens P4 diffractometer (graphite monochromator, Mo-$K_α$ radiation, λ = 0.71073 Å). The structure was solved by Patterson methods and refined by full-matrix least-squares techniques (Siemens SHELXTL PLUS program package). The positions of the hydrogen atoms were calculated by assuming ideal geometries (d_{C-H} = 0.96 Å) and their coordinates were refined together with the attached C atoms as "riding models". Complete lists of atom coordinates and their thermal parameters have been deposited[29].

☆ Dedicated to Professor *Ernst Otto Fischer* on the occasion of his 80th birthday.

[1] For example: [1a] E. A. Maatta, D. D. Devore, *Angew. Chem.* **1988**, *100*, 583−585; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 569−571. − [1b] M. H. Chisholm, *Angew. Chem.* **1991**, *103*, 690−691; *Angew. Chem. Int. Ed. Engl.* **1991**, *103*, 673−674. − [1c] F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123−1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101−1123. − [1d] W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* **1993**, *105*, 969−996; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 923−949. − [1e] H. Lang, *Angew. Chem.* **1994**, *106*, 569−572; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 547−550. − [1f] M. J. Irwin, G. Jia, N. C. Payne, R. J. Puddephatt, *Organometallics* **1996**, *15*, 51−57. − [1g] U. H. F. Bunz, *Angew. Chem.* **1996**, *108*, 1047−1049; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 968−971. − [1h] W. Weng, T. Bartik, J. A. Gladysz, *Angew. Chem.* **1994**, *106*, 2269−2272; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2199−22021 and literature cited therein.

[2] [2a] J. S. Schumm, D. L. Pearson, J. M. Tour, *Angew. Chem.* **1994**, *106*, 1445−1448; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1360−1363. − [2b] T. Bartik, B. Bartik, M. Brady, R. Dembinski, J. A. Gladysz, *Angew. Chem.* **1996**, *108*, 467−469; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 414−417.

[3] A.-M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem.* **1991**, *103*, 370−398; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 375−402.

[4] See e.g.: [4a] *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), Wiley, Chichester, **1992**. − [4b] "Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates", *ACS Symp. Ser. 572* (Eds.: P. Wisian-Neilson, H. R. Allcock, K. J. Wynne), American Chemical Society, Washington, DC, **1994**.

[5] H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor, T. B. Marder, *J. Chem. Soc., Chem. Commun.* **1991**, 188−190.

[6] [6a] H. Fischer, F. Leroux, G. Roth, R. Stumpf, *Organometallics* **1996**, *15*, 3723−3731. − [6b] H. Fischer, F. Leroux, R. Stumpf, G. Roth, *Chem. Ber.* **1996**, *129*, 1475−1482.

[7] [7a] A. Wong, P. C. W. Kang, C. D. Tagge, D. R. Leon, *Organometallics* **1990**, *9*, 1992−1994. − [7b] R. Crescenzi, C. Lo Sterzo, *Organometallics* **1992**, *11*, 4301−4305. − [7c] P. J. Stang, R. Tykwinski, *J. Am. Chem. Soc.* **1992**, *114*, 4411−4412. − [7d] Y. Sun, N. J. Taylor, A. J. Carty, *Organometallics* **1992**, *11*, 4293−4300. − [7e] P. J. Kim, H. Masai, K. Sonogashira, N. Hagihara, *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181−185. − [7f] Y. Sun, N. J. Taylor, A. J. Carty, *J. Organomet. Chem.* **1992**, *423*, C43−C47. − [7g] A. Romero, D. Peron, P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.* **1990**, 1410−1412. − [7h] L. D. Field, A. V. George, E. Y. Malouf, I. H. M. Slip, T. W. Hambley, *Organometallics* **1991**, *10*, 3842−3848. − [7i] G. H. Worth, B. H. Robinson, J. Simpson, *Organometallics* **1992**, *11*, 501−513.

[8] D. L. Lichtenberger, S. K. Renshaw, A. Wong, C. D. Tagge, *Organometallics* **1993**, *12*, 3522−3526.

[9] M. F. Semmelhack, G. R. Lee, *Organometallics* **1987**, *6*, 1839−1844.

[10] [10a] A. B. Holmes, G. E. Jones, *Tetrahedron Lett.* **1980**, *21*, 3111−3112. − [10b] A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, *J. Chem. Soc., Chem. Commun.* **1979**, 840−842.

[11] [11a] Yu. L. Slovokhotov, A. I. Yanovskyi, V. G. Andrianov, Yu. T. Struchkov, *J. Organomet. Chem.* **1980**, *184*, C57−C60. − [11b] N. E. Kolobova, T. V. Rozantseva, Yu. T. Struchkov, A. S. Batsanov, V. I. Bakhmutov, *J. Organomet. Chem.* **1985**, *292*, 247−256.

[12] C. C. Karl, H. Fischer, unpublished results.

[13] *Transition Metal Carbene Complexes* (Eds.: K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss), Verlag Chemie, Weinheim, **1983**.

[14] [14a] C. Lo Sterzo, M. M. Miller, J. K. Stille, *Organometallics* **1989**, *8*, 2331−2337. − [14b] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504−519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508−523. − [14c] C. Lo Sterzo, J. K. Stille, *Organometallics* **1990**, *9*, 687−694.

[15] [15a] C. Cauletti, C. Furlani, A. Sebald, *Gazz. Chim. Ital.* **1988**, *118*, 1−23. − [15b] K. Jones, M. F. Lappert, *J. Organomet. Chem.* **1965**, *3*, 295−307.

[16] V. Farina, *Pure Appl. Chem.* **1996**, *68*, 73−78.

[17] H.-F. Klein, B. D. Zettel, *Chem. Ber.* **1995**, *128*, 343−350.

[18] E. Moser, E. O. Fischer, *J. Organomet. Chem.* **1969**, *16*, 275−282.

[19] H. Fischer, O. Podschadly, A. Früh, C. Troll, R. Stumpf, A. Schlageter, *Chem. Ber.* **1992**, *125*, 2667−2673.

[20] B. E. Mann, B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds*, Academic Press, London, **1981**.

[21] [21a] A. G. M. Barrett, N. E. Carpenter, J. Mortier, M. Sabat, *Organometallics* **1990**, *9*, 151−156. − [21b] L. S. Chen, D. W. Lichtenberg, P. W. Robinson, Y. Yamamoto, A. Wojcicki, *Inorg. Chim. Acta* **1977**, *25*, 165−172. − [21c] G. G. Alexandrov, V. V. Skripkin, N. E. Kolobova, Yu. T. Struchkov, *Koord. Khim.* **1979**, *5*, 453−458 (*Chem. Abstr.* **1979**, *90*: 178495m).
[22] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.
[23] [23a] L. S. Trifonov, A. S. Orahovats, R. Prewo, J. H. Bieri, H. Heimgartner, *J. Chem. Soc., Chem. Commun.* **1986**, 708−709. − [23b] S. Hirokami, T. Takahashi, M. Nagata, T. Yamazaki, *J. Org. Chem.* **1987**, *52*, 2455−2468.
[24] [24a] W. Weng, T. Bartik, M. T. Johnson, A. M. Arif, J. A. Gladysz, *Organometallics* **1995**, *14*, 889−897. − [24b] Yu. L. Slovokhotov, A. I. Yanovskyi, V. G. Andrianov, Yu. T. Struchkov, *J. Organomet. Chem.* **1980**, *184*, C57−C60.
[25] J.-L. Dumont, W. Chodkiewicz, P. Cadiot, *Bull. Soc. Chim. Fr.* **1967**, 1197−1203.
[26] *Handbuch der präparativen Anorganischen Chemie* (Ed.: G. Brauer), Ferdinand Enke Verlag, Stuttgart, **1978**, vol. 2.
[27] G. Himbert, H. Umbach, M. Barz, *Z. Naturforsch.* **1984**, *39b*, 661−667.
[28] K. Sisido, S. Kozima, *J. Org. Chem.* **1962**, *27*, 4051−4052.
[29] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101439. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

[98127]