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Ferrocenyl-substituted allenylidene complexes of chromium, molybdenum and tungsten: Synthesis, structure and reactivity

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Dedicated to Professor Bernhard Lippert

Abstract

Bis(ferrocenyl) substituted allenylidene complexes, [(CO)$_5$M C C CFc$_2$] (**1a c**, Fc = (C$_5$H$_4$)Fe(C$_5$H$_5$), M = Cr (**a**), Mo (**b**), W (**c**)) were obtained by sequential reaction of Fc$_2$C O with Me$_3$Si C CH, KF/MeOH, *n* BuLi, and [(CO)$_5$M(THF)]. For the synthesis of related mono(ferrocenyl)allenylidene chromium complexes, [(CO)$_5$Cr C C C(Fc)R] (R = Ph, NMe$_2$), three different routes were developed: (a) reaction of the deprotonated propargylic alcohol HC CC(Fc)(Ph)OH with [(CO)$_5$Cr(THF)] followed by desoxygenation with Cl$_2$C O, (b) Lewis acid induced alcohol elimination from alkenyl(alkoxy)carbene complexes, [(CO)$_5$Cr C(OR)CH C(NMe$_2$)Fc], and (c) replacement of OMe in [(CO)$_5$Cr C C C(OMe)NMe$_2$] by Fc. Complex **1a** was also formed when the mono(ferrocenyl)alleny lidene complex [(CO)$_5$Cr C C C(Fc)NMe$_2$] was treated first with Li[Fc] and the resulting adduct then with SiO$_2$. The replacement route (c) was also applied to the synthesis of an allenylidene complex (**7a**) with a C C spacer in between the ferrocenyl unit and C$_\gamma$ of the allenylidene ligand, [(CO)$_5$Cr C C C(NMe$_2$) C CFc]. The related complex containing a CH CH spacer (**9a**) was prepared by condensation of [(CO)$_5$Cr C C C(Me)NMe$_2$] with formylferrocene in the presence of NEt$_3$. The bis(ferrocenyl) substituted alleny lidene complexes **1a c** added HNMe$_2$ across the C$_\alpha$ C$_\beta$ bond to give alkenyl(dimethylamino)carbene complexes and reacted with diethylaminopropyne by regioselective insertion of the C C bond into the C$_\beta$ C$_\gamma$ bond to afford alkenyl(diethylamino)allenylidene complexes, [(CO)$_5$M C C C(NEt$_2$)CMe CFc$_2$]. The structures of **5a**, **7a**, and **9a** were established by X ray diffraction studies.

1. Introduction

The carbon chain in allenylidene complexes, [L$_n$M=C=C=C(R^1)R^2] [1] should be able to efficiently mediate electronic communication between the terminal groups. Recently [2], we demonstrated that the ferrocenyl and the pentacarbonyl group in complexes of the type A (*n* 0, 1) strongly interact. Oxidation of the ferrocenyl unit led to a strong shift of the *ν*(CO) vibrations to higher energy. In these complexes the ferrocenyl group was connected with the allenylidene group via CC (C$_6$H$_4$ CC)$_n$ spacers and the terminal carbon atom of the allenylidene C$_3$ fragment was incorporated into a *N*-ethyl pyridine ring acting as π-donor. We were now interested in allenylidene complexes with ferrocenyl units directly attached to the terminal carbon atom (C3) of the allenylidene ligand.

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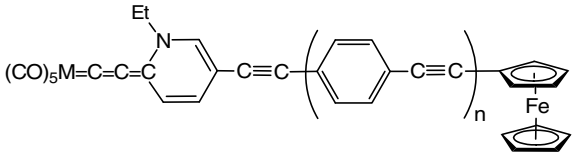


A

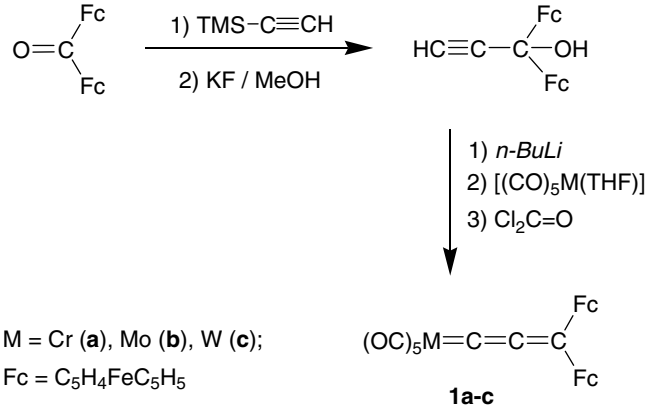
Several routes leading to allenylidene complexes have been developed in recent years [1]. Broadly applicable, among others, are (a) elimination of water or an alcohol from suitable carbene precursors or vinylidene precursors (usually obtained from substituted propargylic alcohols) [3], (b) reactions of dilithiated substituted 2-propyn-1-ols, [LiC≡CCR$_2$(OLi)], with metal carbonyls (usually [M(CO)$_6$] or [M(CO)$_5$(THF)]) and subsequent loss of oxo or alkoxy groups [4], (c) elimination of X^- from alkynyl metallates, [L_nM C≡C CR$_2$X]$^-$ [5] or *X*-alkylation of alkynyl metallates, [L_nM C≡C C(=X)R]$^-$ [6], and (d) the modification of already existing allenylidene ligands via substitution processes [7].

We now report on various synthetic approaches to (a) mono(ferrocenyl)- and bis(ferrocenyl)allenylidene complexes of chromium, molybdenum and tungsten and (b) complexes in which the ferrocenyl unit is separated from the allenylidene spine by an unsaturated spacer.

2. Results and discussion

The most promising method for the synthesis of bis(ferrocenyl)-substituted allenylidene complexes seemed to be the route successfully employed for bis(aryl)-substituted allenylidene pentacarbonyl complexes [4b].

Double deprotonation of 1,1-bis(ferrocenyl)propargylic alcohol (obtained by sequential reaction of bis(ferrocenyl)ketone with deprotonated trimethylsilylacetylene at −80 °C) and reaction with [(CO)$_5$Cr(THF)] at room temperature in THF followed by desoxygenation of the resulting alkynyl chromate with phosgene in toluene CH_2Cl_2 at −100 °C gave the bis(ferrocenyl)allenylidene chromium complex **1a** (Scheme 1). Chromatographic workup of the reaction mixture finally afforded **1a** in 39% yield.



Scheme 1.

The molybdenum and tungsten complexes **1b** and **1c** were obtained when [(CO)$_5$Mo(THF)] and [(CO)$_5$W(THF)] were employed instead of [(CO)$_5$Cr(THF)]. Whereas the chromium complex **1a** turned out to be stable at room temperature, the molybdenum and tungsten allenylidene complexes **1b** and **1c** proved to be unstable and quickly decomposed at temperature above −40 °C.

The corresponding reaction of 1-ferrocenyl-1-phenylprop-2-in-1-ol with [(CO)$_5$Cr(THF)] and subsequent desoxygenation of the resulting chromate yielded the monoferrocenylallenylidene complex **2a** (Scheme 2). The desoxygenation step could be simplified by substituting basic alumina for phosgene. Alumina is much easier to handle and can simultaneously be used as the stationary phase in the chromatographic purification step.

Analogously to **1b** and **1c**, complex **2a** proved to be unstable and rapidly decomposed above −40 °C. Therefore, its formation like that of **1b**, **c** was established by spectroscopic means only.

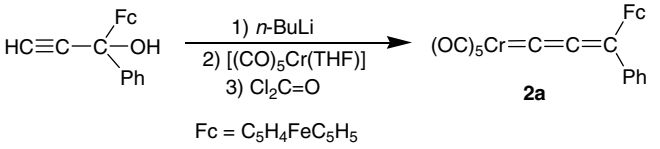
From our earlier studies it followed that π-donor substituents at C$_\gamma$ of the allenylidene ligand considerably stabilize these allenylidene pentacarbonyl complexes. Therefore, displacing the phenyl substituent by an amino group was expected to lead to stable complexes. However, the routes shown in Schemes 1, 2 could not be adapted to the synthesis of amino(ferrocenyl)allenylidene complexes and therefore another pathway had to be developed. The most feasible one was a modification of the route originally developed by Fischer et al. for the synthesis of the first allenylidene chromium complex [3a].

Addition of dimethylamine across the triple bond of the alkoxy(alkynyl)carbene complexes [(CO)$_5$Cr=C(OEt) C≡C Fc] (**3a**) [8] gave [(CO)$_5$Cr=C(OEt) CH=C(NMe$_2$) Fc] (**4a**). Subsequent alcohol elimination induced by BCl_3 yielded the amino(ferrocenyl)allenylidene complexes **5a** (Scheme 3).

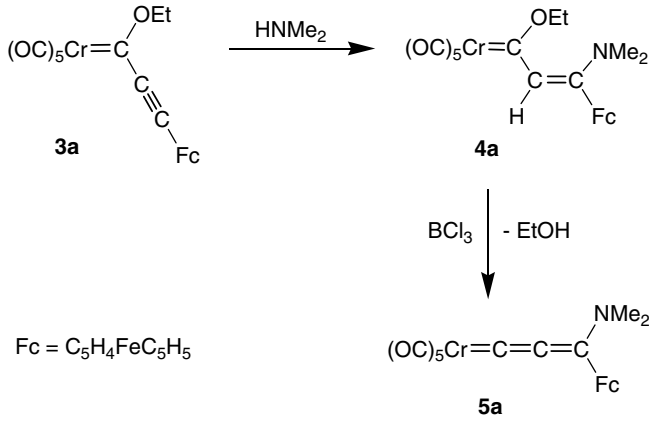
An alternative pathway likewise leading to **5a** involved replacing the methoxy substituent in **6a** by the ferrocenyl unit. Already earlier we were able to demonstrate that the alkoxy group at C$_\gamma$ in alkoxyallenylidene pentacarbonyl complexes is exchangeable [1b,6,7].

When at room temperature 1.5 equiv. of ferrocenyl lithium was added to a solution of **6a** in THF, complex **5a** quickly formed. Addition of silica led to completion of the substitution process (Scheme 4).

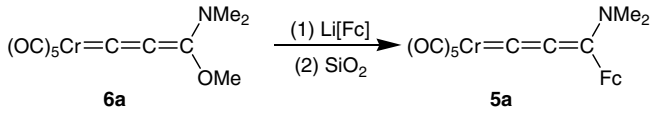
Addition of equimolar amounts of lithiated cymanthrene, Li[(CO)$_3$MnC$_5$H$_4$], or lithiated tricarbonyl(benzene)chromium, Li[(CO)$_3$CrC$_6$H$_5$], instead of Li[(C$_5$H$_4$)Fe(C$_5$H$_5$)] gave unstable compounds that decomposed rapidly even at low temperatures.



Scheme 2.



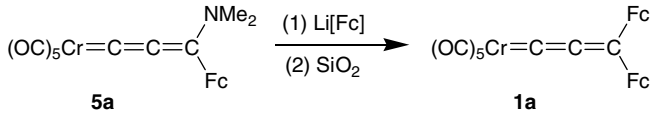
Scheme 3.



Scheme 4.

The amino substituent in **5a** could likewise be replaced by the ferrocenyl group. Treating solutions of **5a** with an excess of Li[Fc] gave rise to the formation of the bis(ferrocenyl)allenylidene complex **1a**. However, the rate for substitution of Fc for NMe_2 in **5a** is considerably less (by a factor of at least 10) than for OMe in **6a**. When solutions of **6a** in THF were treated with 5 equiv. of Li[Fc] for several hours, compound **1a** was the final product (Scheme 5) very likely formed via **5a** as intermediate.

A C≡C spacer between C_γ of the allenylidene ligand and the ferrocenyl unit could be introduced by using lithium ethynylferrocene instead of Li[Fc] in the reaction with **6a**. The resulting complex **7a** (Scheme 6) obtained in 52% yield was characterized by IR, NMR, and UV Vis spectroscopy. The structure of **7a** was additionally established by an X-ray diffraction study (see below).



Scheme 5.

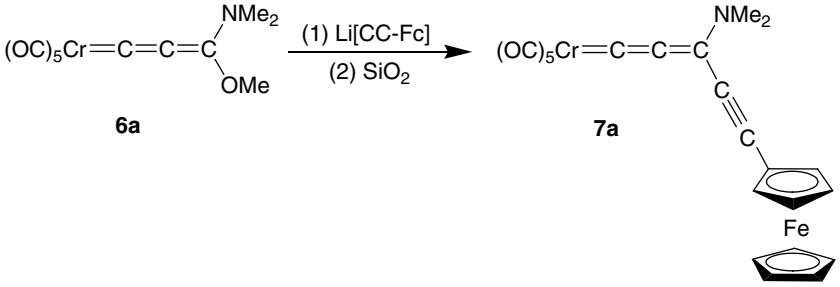
However, a CH=CH spacer could not be introduced by the same methodology. Instead, a new route had to be developed. Already earlier [9] we observed that the hydrogen atoms of the C_γ-methyl substituent in $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Me]$ (**8a**) are acidic similar to the α-CH atoms in methylcarbene complexes $[(CO)_5M{=}C(XR)Me]$ (M Cr, W; XR OMe, NHMe) [10]. Condensation of formylferrocene with **8a** in the presence of a tertiary amine offered a feasible route to an insertion of a CH=CH unit in between C_γ and the ferrocene unit and thus an extension of the unsaturated chain in **5a**. By this method the dimethylamino(*trans*-ferrocenylethenyl)allenylidene complex **9a** (Scheme 7) was obtained from **5a**, after chromatography and recrystallization, in 41% yield. Complex **9a** was characterized by spectroscopic means and by an X-ray structural analysis.

The reactivity of the new bis(ferrocenyl)allenylidene complexes **1a c** towards *C*- and *N*-nucleophiles was briefly investigated. Complexes **1a c** add dimethylamine across the C_α C_β bond of the allenylidene ligand to form alkenyl(dimethylamino)carbene complexes **10a c** (Scheme 8).

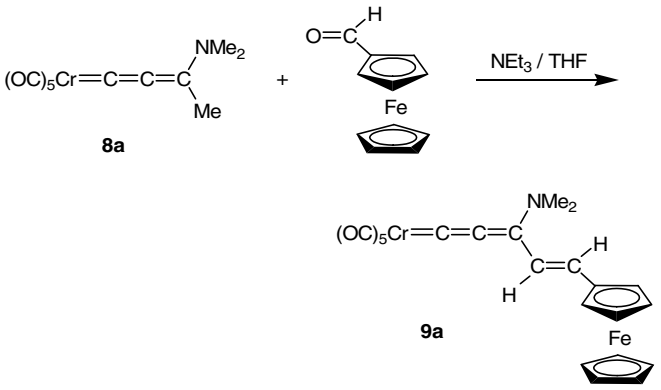
A similar C_α C_β addition was observed in the reactions of diethylamine with diarylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(Aryl)_2]$ (M Cr, W) [11] and of dimethylamine with $[(CO)_5Cr{=}C{=}C{=}C(NR_2)Ph]$ (R Et. *i*-Pr) [12]. In contrast, $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ [7a] reacts with primary amines by substitution of N(H)R for NMe_2 and primary and secondary amines displace the methoxy group in $[(CO)_5M{=}C{=}C{=}C(OMe)Ph]$ [7b,13].

The reaction of **1a c** with diethylaminopropyne proceeds by formal insertion of the C≡C triple bond into the C_β C_γ bond of the allenylidene ligand. The reaction is presumably initiated by nucleophilic attack of the *C*(Me) atom of the ynamine at C_γ of **1a c**. Subsequent cyclization of the resulting zwitterionic species followed by cycloreversion then gives **11a c** (Scheme 9).

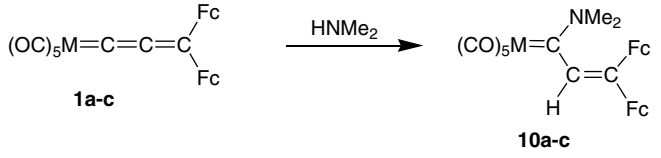
In contrast, from the corresponding reaction of diarylallenylidene complexes with diethylaminopropyne [14], mixtures of alkenyl(aryl)allenylidene complexes (comparable to **11a c**) and cyclobutenylidene complexes (formed by cycloaddition of the C≡C triple bond to the C_α C_β bond



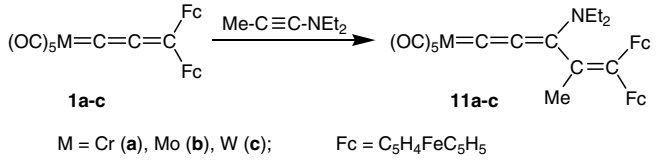
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

without subsequent cycloreversion) are obtained. The product ratios strongly depend on the solvent and the substitution pattern at C_γ. Increasing the donor capacity of the substituents at C_γ shifts the product ratio towards the insertion product. When bis(4-dimethylaminophenyl)allenylidene complexes are employed, the ratio insertion/addition product is 12.4 (Cr) and 15.0 (W). The failure to observe the formation of cyclobutenylidene complexes in the reaction of **1a c** with diethylaminopropyne indicates that the ferrocenyl unit acts as a better donor than the 4-dimethylaminophenyl substituent.

The new complexes were characterized by spectroscopic means. The structures of **5a**, **7a**, and **9a** were additionally established by X-ray structure analyses (Figs 1 3, Tables 1 and 3). Unfortunately, the crystals of **5a** were of rather poor quality leading to large standard deviations. However, the bond distances and angles measured are in accord with those of **7a** and **9a**. All three structures show some common features. The allenylidene plane (formed by C_γ and the three atoms bonded to C_γ, sum of angles at C_γ: 360°) is staggered with respect to the *cis*-CO ligands. The C_5H_4 plane of **7a** and **9a** only marginally deviates from coplanarity with the allenylidene plane (angle between both planes: 1.7° (**7a**), 2.2° (**9a**) and 12.1° (**5a**)). The significantly larger deviation in **5a** is presumably due to steric influences.

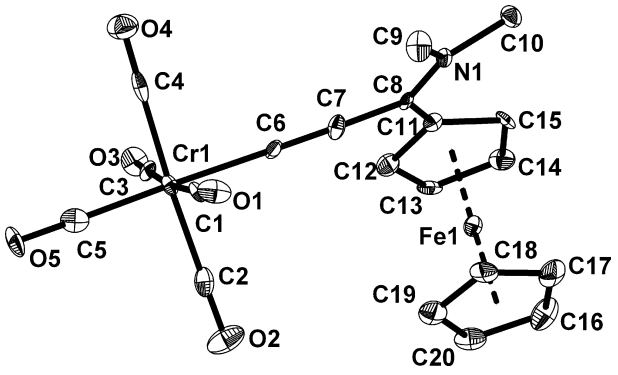


Fig. 1. Structure of complex **5a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity).

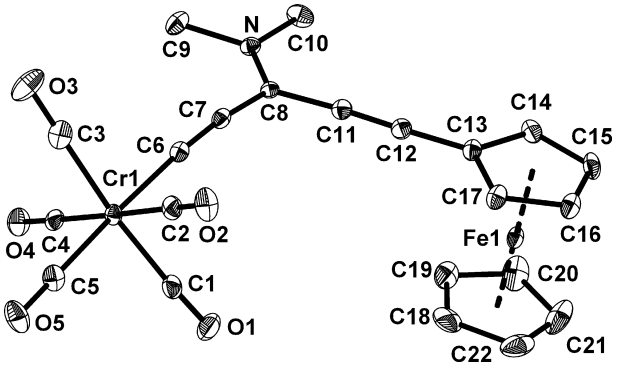


Fig. 2. Structure of complex **7a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity).

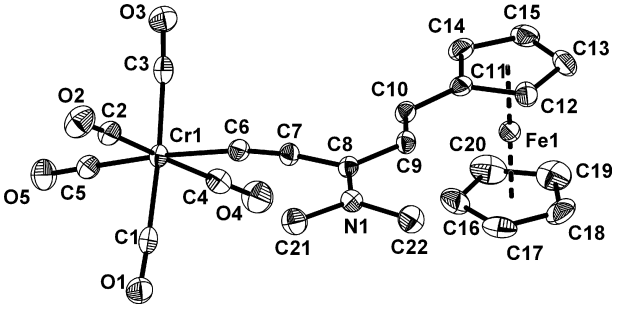
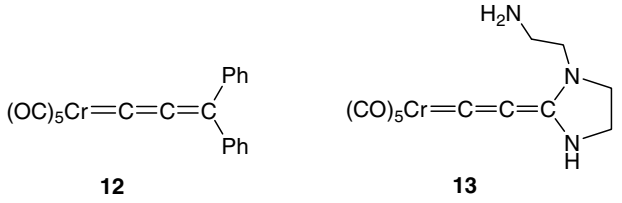


Fig. 3. Structure of complex **9a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity).

Table 1
Selected distances (Å) and angles (°) in **5a**, **7a**, and **9a**

	5a	**7a**	**9a**
Distances			
Cr(1) C(5)	1.867(8)	1.877(2)	1.873(3)
Cr(1) C(cis) av.	1.900	1.904	1.908
Cr(1) C(6)	2.022(7)	2.009(2)	2.048(3)
C(6) C(7)	1.226(9)	1.228(3)	1.227(4)
C(7) C(8)	1.409(9)	1.399(3)	1.418(4)
C(8) N(1)	1.321(8)	1.321(3)	1.327(3)
Angles			
Cr(1) C(6) C(7)	178.9(6)	174.27(2)	171.3(2)
C(6) C(7) C(8)	173.5(7)	171.3(2)	172.2(3)
C(7) C(8) N(1)	118.9(6)	122.0(2)	120.3(2)

The Cr C(6) C(7) C(8) fragment deviates from linearity, presumably due to interatomic interaction. The C6 C7 distance is short, shorter than that in the diphenylallenylidene complex **12** (1.249(3) Å) [4b], however, slightly longer than in the diaminoallenylidene complex **13** (1.214(4) Å) [7b]. Conversely, the Cr C6 and C7 C8 distances in **7a** and **9a** are significantly longer than in **12** (Cr C6 1.931(2) Å, C7 C8 1.358(3) Å) but compare well with those in **13** (Cr C6 2.030(3) Å, C7 C8 1.411(4) Å).

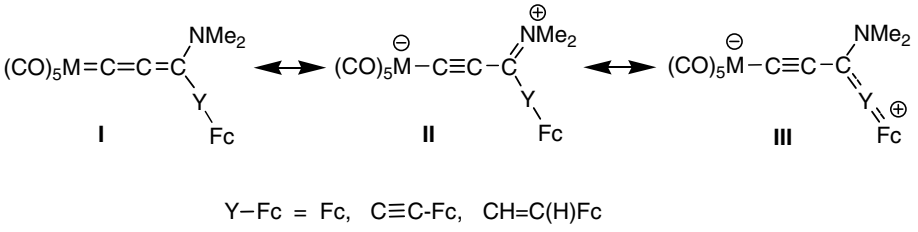


The C8 N distance in **7a**, **9a**, and **13** (1.324(3) Å) is likewise very similar. From these data it follows that the dimethylamino(ferrocenyl) unit strongly interacts with the $(CO)_5Cr$ fragment (Scheme 10) and that the spacer linking C_γ and Fc only marginally influences the interaction.

The conclusion is confirmed by the pronounced *trans* influence of the allenylidene ligand in **5a**, **7a**, and **9a**, the *trans*-Cr CO distance being significantly shorter than the average of the *cis*-Cr CO distances [1.87(1) versus 1.90(1) Å (**5a**), 1.877(2) versus 1.904(2) Å (**7a**), 1.873(3) versus 1.908(3) Å (**9a**)]. The *trans* influence is similar to and only slightly smaller than that in **13** [1.866(3) versus 1.908 Å] whereas in the diphenylallenylidene complex **12** *cis*- and *trans*-Cr CO distances are similar, the *trans*-Cr CO bond (1.912(3) Å) being even slightly longer than the average of the *cis*-Cr CO distances (1.905 Å). In all complexes the *cis*-Cr CO distances are essentially the same, the difference resulting from the influence of the allenylidene ligand on the *trans*-Cr CO bond.

The C7 C8 bond in **7a** is shorter than the C(8) C(11) bond (1.425(3) Å) and considerably shorter than that expected for a C(sp) C(sp^2) bond (1.431 Å [15]). Conversely, C6 C7 is longer than C11 C12. These are in accord with expectations based on the bonding model depicted in Scheme 10. In **9a** the C9 C10 distance is longer (1.347(4) Å) than that usually observed for *trans*-substituted (H)C=C(H) bonds (1.312 Å [15]) and the C8 C9 single bond (1.469(3) Å) is in between those observed for conjugated and unconjugated C(sp^2) C(sp^2) single bonds [15] indicating interaction of the C_5H_4 unit and the allenylidene ligand.

The conclusions drawn from the solid-state structures are supported by the spectroscopic data. The ν(CO) absorptions in the IR spectra of all allenylidene complexes (Table 2) show the pattern expected for a local C_{4v} symme-



Scheme 10.

Table 2
Infrared data (ν(CO) and ν(CCC)) for **1a c**, **2a**, **5a**, **7a**, **9a**, and **11a c**

	M	R^1	R^2	Solv.[a]	ν(CO)	ν(CCC)	Ref.[b]
	Cr	Ph	Ph	P	2067, 1995, 1974	1930	4b
1a	Cr	Fc	Fc	P	2062, 1949, 1933	1964	t.w.
1a	Cr	Fc	Fc	T	2062, 1937, 1918	1961	t.w.
1b	W	Fc	Fc	P	2072, 1927, 1941	1957	t.w.
1c	Mo	Fc	Fc	P	2071, 1930, 1948	1964	t.w.
2a	Cr	Fc	Ph	P	2061, 1933, 1960	1975	t.w.
5a	Cr	Fc	NMe_2	H	2071, 1944, 1934		t.w.
5a	Cr	Fc	NMe_2	T	2079, 1932, 1915	2006	t.w.
7a	Cr	NMe_2	C≡C Fc	T	2078, 1935, 1913	2007	t.w.
9a	Cr	NMe_2	CH=C(H)Fc	T	2076, 1929, 1903	2005	t.w.
11a	Cr	NEt_2	CMe=CFc_2	P	1940, 1931	1978	t.w.
11b	W	NEt_2	CMe=CFc_2	P	1935, 1925	1978	t.w.
11c	Mo	NEt_2	CMe=CFc_2	P	1941, 1930	1978	t.w.
	Cr	NMe_2	NMe_2	T	2078, 1929, 1903	2014	5

[a] P = pentane, T = THF, H = hexane.
[b] This work.

try of the $(CO)_5M$ fragment. The positions of the ν(CO) absorptions as well as of the ν(CCC) vibration are dependant on the substituents at C_γ indicating electronic communication between the terminal groups. The positions of the ν(CCC) absorption are in the range 1960 2006 cm^{-1} depending on the π-donor properties of the substituents. The ν(CCC) absorption is in between that of the complexes $[(CO)_5Cr{=}C{=}C{=}C(R^1)R^2]$ with $C(R^1)R^2 = CPh_2$ (1930 cm^{-1} [4b]) and $C(NMe_2)_2$ (2014 cm^{-1} [5]) and roughly shifts towards higher energy in the series $CPh_2 < CFc_2 < C(Fc)Ph < C(NMe_2)C{\equiv}CFc \approx C(NMe_2)CH{=}CFc_2 < C(NMe_2)Fc < C(NMe_2)_2$. From the series an increasing triple bond character of the C_α C_β bond and an increasing contribution of the resonance forms II and III (see Scheme 10) to the overall bonding can be deduced. In accord with these conclusions is the shift of the resonance of the C_α atom in the ^{13}C NMR spectrum towards higher field in the same series and the approximate inverse correlation of the force constant of the *trans*-CO vibration.

In summary, we have developed several independent synthetic pathways to ferrocene-substituted allenylidene complexes. These routes should also be applicable to the synthesis of bi- and trinuclear allenylidene complexes with other metal combinations. The spectroscopic data suggest that the carbon-rich bridging groups in these complexes are able to mediate electronic communication between the metal centres and that there is considerable interaction of the terminal metal ligand fragments [16].

3. Experimental

All operations were performed in an inert gas atmosphere (argon or nitrogen) using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (petrol ether), and sodium/benzophenone ketyl (THF, Et_2O). The stationary phases used for chromatography [silica gel (Baker, silica gel for flash chromatography), neutral Al_2O_3 (Fluka, activity I), basic Al_2O_3 90 (Fluka, activity I)] was nitrogen-saturated. The yields refer to analytically pure compounds and are not optimized. Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer or on a Varian Inova 400 spectrometer at room temperature. Chemical shifts are reported relative to the residual solvent peaks. IR spectra were recorded on a Biorad FTS 60. MS measurements were carried out on a Finnigan MAT 312 instrument. The UV Vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. The following compounds were prepared according to literature procedures: di(ferrocenyl)ketone [17], 1,1-diferrocenyl-3-(trimethylsilyl)-prop-2-in-ol [18], 1,1-diferrocenyl-3-prop-2-in-ol [18], 1-ferrocenyl-1-phenyl-prop-2-in-1-ol [19] and the complexes $[(CO)_5M(THF)]$ [11], **3a** [20], **6a** [6], **8a** [21] and formylferrocene [22] were prepared according to published methods. All other chemicals were used as obtained from commercial suppliers.

3.1. Pentacarbonyl(3,3-bis[ferrocenyl]-1,2-propadienylidene)chromium (*1a*)

At −80 °C, a solution of 1.64 ml (2.6 mmol) of *n*-BuLi (1.6 M solution in hexane) was added to a solution of 0.5 g (1.2 mmol) of 1,1-diferrocenylprop-2-in-1-ol in 14 ml of THF. After 5 min, cooling was removed and the orange solution was stirred for 30 min. Then, 12 ml (1.2 mmol) of a 0.1 M solution of $[(CO)_5Cr(THF)]$ in THF was added. Stirring was continued for 1 h at room temperature. The colour of the solution changed from orange to red-brown. The solvent was removed in vacuo. The resulting brown residue was dissolved at −100 °C in 18 ml of toluene/CH_2Cl_2 (1:5) and 0.62 ml (1.2 mmol) of phosgene (1.92 M solution in toluene) (*Caution*: Phosgene is highly toxic and should only be handled with care in a well-vented fume hood!) was added. The solution was stirred for 1 h at −80 °C to −60 °C (temperature slowly increasing) and for 30 min at room temperature At −40 °C the solution turned dark blue. The solvent was again removed and the residue was chromatographed at −20 °C on silica or neutral Al_2O_3. With pentane/CH_2Cl_2/Et_2O (7:2:1) first a yellow band ($[Cr(CO)_6]$) and then a blue band containing the allenylidene complex was eluted. Blue-violet solid. Yield: 0.25 g (0.47 mmol, 39%). Mp 130 °C (dec). IR (petrol ether, cm^{-1}): ν(CO) 2062 w, 1949 m, 1933 m; ν(CCC) 1964 m; IR (THF, cm^{-1}): ν(CO) 2062 vw, 1937 s, 1918 vs, ν(CCC) 1961 m. ^1H NMR (400 MHz, acetone-d_6): δ 4.23 (s, 10H, C_5H_5), 4.94 (s, 4H, C_5H_4), 5.13 (s, 4H, C_5H_4). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 73.0 (C_5H_5), 75.9, 76.5, 77.5, 87.0 (C_5H_4), 162.0 (C_β), 168.5 (C_γ), 217.1 (*cis*-CO), 230.9 (*trans*-CO), 265.5 (C_α). UV Vis (λ_{max}, nm ($\log\varepsilon$) [pentane]): 768 (4.40), 580 (3.96). MAS (FAB), *m*/*z*: 598 [M^+], 542 [$(M-2CO)^+$], 486 [$(M-4CO)^+$], 458 [$(M-5CO)^+$]. *Anal.* Calc. for $C_{28}H_{18}CrFe_2O_5$ (598.1): C, 56.23; H, 3.03. Found: C, 56.36; H, 3.19%.

Complex **1a** was also obtained from (a) **5a** and 5 equiv. of freshly prepared ferrocenyllithium in THF or (b) dimethylamino(methoxy)allenylidene complex **6a** and 5 equiv. of freshly prepared ferrocenyllithium in THF. After stirring these solutions overnight, the solvent was removed and the residue recrystallized from pentane/dichloromethane.

3.2. Pentacarbonyl(3,3-bis[ferrocenyl]-1,2-propadienylidene)molybdenum (*1b*)

The procedure for the synthesis of **1b** is essentially analogous to that of **1a**. Deviation: After addition of phosgene the solution was stirred for 30 min at −60 °C and for 1 5 min at room temperature. The colour turned deep blue. Removal of the solvent at −50 °C and chromatography at −40 °C on basic Al_2O_3 with pentane/CH_2Cl_2/Et_2O (10:3:1) afforded $[W(CO)_6]$ (first band) and then **1b** (blue band). Complex **1b** was stable only below −40 °C. Blue solid. Yield: ca. 0.1 g (0.24 mmol, 20%). IR (pentane, cm^{-1}): ν(CO) 2071 w, 1930 vs, 1948 m; ν(CCC) 1964

m. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.23 (s, 10H, C_5H_5), 4.44 (m, 4H, C_5H_4), 4.78 (m, 4H, C_5H_4). UV Vis (λ_{max}, nm ($\log\varepsilon$) [pentane]): 747 (4.52), 575 (4.20), 349 (4.46), 257 (4.82), 235 (4.89), 207 (4.96). MAS (FAB), *m/z* (rel. ^{98}Mo): 644 [M^+], 616 [$(M-CO)^+$], 588 [$(M-2CO)^+$], 504 [$(M-5CO)^+$]. $C_{28}H_{18}MoFe_2O_5$ (642.1).

*3.3. Pentacarbonyl(3,3-bis[ferrocenyl]-1,2-propadienylidene)tungsten (**1c**)*

The procedure for the synthesis of **1c** is analogous to that of **1b**. Blue solid stable only below −40 °C. Yield: ca. 0.22 g (0.3 mmol, 25%). IR (pentane, cm^{-1}): *v*(CO) 2072 w, 1927 vs, 1941 m; *v*(CCC) 1957 m. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.34 (s, 10H, C_5H_5), 5.09 (m, 4H, C_5H_4), 5.22 (m, 4H, C_5H_4). UV Vis (λ_{max}, nm ($\log\varepsilon$) [pentane]): 739 (5.09), 566 (4.67), 350 (5.01), 255 (5.37), 233 (5.43), 202 (5.58). MS (FAB), *m/z*: 730 [M^+], 702 [$(M-CO)^+$], 646 [$(M-3CO)^+$], 590 [$(M-5CO)^+$]. $C_{28}H_{18}WFe_2O_5$ (730.0).

*3.4. Pentacarbonyl[3-ferrocenyl-3-phenyl-1,2-propadienylidene]chromium (**2a**)*

Complex **2a** was synthesized analogously to **1b** starting from 0.38 g (1.2 mmol) of 1-ferrocenyl-1-phenyl-prop-2-in-1-ol. Instead of phosgene, neutral Al_2O_3 (5 g in 60 ml of CH_2Cl_2) was used at −40 °C in the desoxygenation step. The complex adsorbed on Al_2O_3 was then eluted (after filtration) at −35 °C with CH_2Cl_2. The complex thus obtained after removal of the solvent was contaminated with $[Cr(CO)_6]$. Subsequent chromatography on basic Al_2O_3 at −35 °C with pentane/CH_2Cl_2 (4:1) yielded ca. 0.23 g (0.45 mmol, 38%) of thermally labile complex **2a** stable only below −40 °C. IR (pentane, cm^{-1}): *v*(CO) 2061 w, 1933 vs, 1960 m; *v*(CCC) 1975 m. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.25 (s, 10H, C_5H_5), 5.10 (m, 4H, C_5H_4), 5.21 (m, 4H, C_5H_4), 7.83 (m, 1H, Ph), 7.80 (m, 1H, Ph), 7.51 (m, 1H, Ph), 7.40 (m, 2H, Ph). UV Vis (λ_{max}, nm ($\log\varepsilon$) [pentane]): 754 (5.50), 618 (5.30), 350 (5.30), 280 (5.92), 229 (6.52).

*3.5. Pentacarbonyl(3-dimethylamino-1-ethoxy-3-ferrocenyl-prop-2-en-ylidene)chromium (**4a**)*

At room temperature, an excess of dimethylamine (43% in aqueous solution) was slowly added to a solution of the ethoxy(ferrocenylethynyl)carbene complex **3a** in THF. The dark violet solution turned light orange. The progress of the reaction was followed by TLC. After completion of the reaction, the solvent was removed in vacuo and the residue was chromatographed at −20 °C on silica with dichloromethane/pentane mixtures. The yellow band containing **4a** was eluted. Yellow crystals. Yield: 0.39 g (0.77 mmol, 48%). M.p. 130 °C (dec.). IR (THF, cm^{-1}): *v*(CO) 2041 m, 1958 w, 1916 vs, 1899 m. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, *J* 7.1 Hz, 3H, CH_3), 3.08 (s, 6H, NCH_3), 4.28 (s, 5H, C_5H_5), 4.49 (t, *J* 1.9 Hz, 2H, C_5H_4), 4.56 (t, *J* 1.8 Hz, 2H, C_5H_4), 4.59 (q, *J* 7.1 Hz, 2H, CH_2), 6.84 (s, 1H, C=C*H*). ^{13}C NMR (400 MHz, $CDCl_3$): δ 16.1 (NCH_3), 45.3 (CH_3), 71.1 (C_5H_5), 71.3 (2C, C_5H_4), 72.7 (2C, C_5H_4), 73.2 (1C, C_5H_4), 79.7 (*C*H=C), 117.4 (*C* Fc), 162.1 (Cr=*C*), 220.3 (*cis*-CO), 224.7 (*trans*-CO). UV Vis λ_{max}, nm ($\log\varepsilon$) [solvent]: 497 (3.738) [CH_2Cl_2]; 520 (3.469) [DMF]; 515 (3.695) [THF]. MAS (FAB), *m/z*: 503 [M^+], 475 [$(M-CO)^+$], 447 [$(M-2CO)^+$], 419 [$(M-3CO)^+$], 391 [$(M-4CO)^+$], 363 [$(M-5CO)^+$]. *Anal.* Calc. for $C_{22}H_{21}CrFeNO_6$ (503.25): C, 52.51; H, 4.21; N, 2.78. Found: C, 52.57; H, 4.21; N, 2.92%.

*3.6. Pentacarbonyl(3-dimethylamino-3-ferrocenyl-1,2-propadienylidene)chromium (**5a**)*

At 0 °C, a solution of 0.15 mmol of BCl_3 (1 M in hexane) was added dropwise to a solution of 0.15 mmol of **4a** in 50 ml of diethyl ether. The orange solution slowly turned red. After stirring the solution for 30 min, the solvent was removed in vacuo. The remaining oily residue was recrystallized from pentane/dichloromethane, giving dark red crystals of **5a**. Yield: 0.15 g (0.11 mmol, 73%). M.p. 125 °C (dec.). IR (hexane, cm^{-1}): *v*(CO) 2071 w, 1944 s, 1934 vs; (THF, cm^{-1}): *v*(CO) 2079 vw, 1932 vs, 1915 m, *v*(CCC) 2006 m. ^{1}H NMR (400 MHz, acetone-d_6): δ 3.39 (s, 3H, NMe), 3.62 (s, 3H, NMe), 4.34 (s, 5H, C_5H_5), 4.65 (s, 2H, C_5H_4), 4.89 (s, 2H, C_5H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 38.7, 42.7 (NMe_2), 72.6 (Cp), 71.9 (Cp), 73.3 (Cp), 105.1 (C_β), 167.7 (C_γ), 196.2 (C_α), 218.2 (*cis*-CO), 223.7 (*trans*-CO). MS (FAB), *m/z*: 457 [M^+], 401 [$(M-2CO)^+$], 373 [$(M-3CO)^+$], 345 [$(M-4CO)^+$], 317 [$(M-5CO)^+$]. *Anal.* Calc. for $C_{20}H_{15}CrFeNO_5$ (457.2): C, 52.54, H, 3.31, N, 3.06. Found: C, 52.64, H, 3.84, N, 2.80%.

*3.7. Pentacarbonyl(3-dimethylamino-3-ferrocenylethynyl-1,2-propadienylidene)chromium (**7a**)*

At −80 °C, *n*-BuLi (1.65 mmol, 1.04 ml of a 1.6 M solution in hexane) was added within ca. 1 min to 0.35 g (1.65 mmol) of ethynylferrocene in 50 ml of THF. The solution was stirred for 1 h at −80 °C and then added at −80 °C to a solution of 0.5 g (1.65 mmol) of **6a** in 50 ml of THF. Immediately afterwards, 0.21 ml (1.65 mmol) of trimethylchlorosilane was added. After 5 min at −80 °C, the solution was filtered over silica gel at −20 °C. With ca. 500 ml of CH_2Cl_2 a dark blue solution was eluted. The solvent was removed in vacuo and the residue was chromatographed at −20 °C on silica using pentane/dichloromethane mixtures (ratio decreasing from 4:1 to 1:1) as eluants. The product was isolated as a violet band. Removal of the solvent yielded 0.41 g (0.85 mmol; 52%) of **7a** as a red solid. M.p. 98 °C (dec.). IR (THF, cm^{-1}): *v*(CO) 2078 vw, 1935 vs, 1913 s; *v*(CCC) 2007 s. ^{1}H NMR (400 MHz, acetone-d_6): δ 3.46 (s, 3H, NCH_3) 3.50 (s, 3H, NCH_3), 4.28 (s, 5H, C_5H_5), 4.46 (s, 2H, C_5H_4),

4.62 (s, 2H, C_5H_4). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 41.9, 42.4 (NCH_3), 71.3 (C_5H_5), 71.8 (2C, C_5H_4), 72.7 (2C, C_5H_4), 73.2 (1C, C_5H_4), 82.4 (*C*≡CFc), 102.2 (C≡*C*Fc), 105.5 (C_β), 148.6 (C_γ), 209.5 (C_α), 217.8 (*cis*-CO), 224.0 (*trans*-CO). UV Vis (λ_{max}, nm ($\log\varepsilon$) [solvent]): 571 (4.178) [$CHCl_3$]; 555 (4.169) [CH_2Cl_2]; 513 (4.152) [DMF]. MS (FAB) *m*/*z*: 481 [M^+], 369 [$(M-4CO)^+$], 341 [$(M-5CO)^+$], 289 [$(M-5CO-Cr)^+$]. *Anal.* Calc. for $C_{22}H_{15}CrFeNO_5$ (481.2): C, 54.91; H, 3.14; N, 2.91. Found: C, 54.80; H, 3.28; N 2.97%.

*3.8. Pentacarbonyl(3-dimethylamino-5-E-ferrocenyl-1,2,4-pentatrienylidene)chromium (**9a**)*

At room temperature, 1 mmol of formylferrocene was added to a solution of 0.28 g (1 mmol) of **8a** in 10 ml of Et_3N/THF (1:1). The solution was stirred for 30 min. Then, 0.26 ml (3 mmol) of TMSCl was added. Stirring was continued. The solution slowly turned dark red. After 17 h, the reaction mixture was chromatographed at −20 °C on silica with pentane/THF mixtures (polarity increasing). With THF a red band was eluted containing **9a**. Removal of the solvent in vacuo afforded 0.20 g (0.41 mmol, 41%) of **9a**. Dark red crystals. M.p. 115 °C (dec.). IR (THF, cm^{-1}): *ν*(CO) 2076 vw, 1929 vs, 1903 m; *ν*(CCC) 2005 m. ^1H NMR (400 MHz, acetone-d_6): δ 3.50 (s, 3H, NCH_3), 3.66 (s, 3H, NCH_3), 4.24 (s, 5H, C_5H_5), 4.66 (t, *J* 1.8 Hz, 2H, C_5H_4), 4.78 (t, *J* 1.8 Hz, 2H, C_5H_4), 6.94 (d, *J* 14.6 Hz, 1H, C*H*=CHFc), 8.16 (d, *J* 14.6 Hz, 1H, CH=C*H*Fc). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 41.6 (NCH_3), 46.4 (NCH_3), 71.6 (C_5H_5), 71.8 (C_5H_4), 74.6 (C_5H_4), 80.8 (C_5H_4), 113.9 (C_β), 117.1 (*C*H=CHFc), 139.1 (CH=*C*HFc), 154.2 (C_γ), 197.0 (C_α), 220.5 (CO_{cis}), 225.1 (CO_{trans}). UV Vis (λ_{max}, nm ($\log\varepsilon$) [solvent]): 562 (3.891) [$CHCl_3$]; 527 (3.864) [CH_2Cl_2]; 492 (4.260) [DMF]. MS (FAB) *m*/*z*: 482 [$(M-H)^+$], 427 [$(M-2CO)^+$], 399 [$(M-3CO)^+$], 371 [$(M-4CO)^+$], 343 [$(M-5CO)^+$]. $C_{22}H_{17}CrFeNO_5$ (483.2).

*3.9. Pentacarbonyl[3,3-diferrocenyl-1-(N,N-dimethylamino)prop-2-enylidene]chromium (**10a**)*

At −45 °C, 10 equiv. of $HNMe_2$ (0.5 ml, ~12 mmol) was added to a solution of 0.35 g (0.6 mmol) of **1a** in 20 ml of CH_2Cl_2. The deep blue solution turned green and then yellow. The reaction was complete within 10 min. The solvent was removed in vacuo. The residue was chromatographed at −20 °C on neutral alumina. With pentane/CH_2Cl_2 (9:2) a yellow band was eluted. Removal of the solvent afforded 0.38 g (0.59 mmol, 98%) of **10a** as a yellow powder. IR (pentane, cm^{-1}): *ν*(CO) 2052 w, 1967 w, 1933 s, 1928 s, sh. ^1H NMR (250 MHz, $CDCl_3$): δ 3.07 (s, 3H, Me), 3.77 (s, 3H, Me), 4.12 (s, 5H, C_5H_5), 4.22 (s, 5H, C_5H_5), 4.31 (m, 6H, C_5H_4), 4.73 (s, 1H, C_5H_4), 4.83 (s, 1H, C_5H_4), 7.07 (s, 1H, =CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ 45.3, 50.4 (Me), 67.8, 68.0, 68.1, 68.4, 68.7, 68.8, 69.0, 69.6, 83.5, 87.6 (C_5H_4), 68.9, 69.3 (C_5H_5), 124.4 (C_γ), 135.4 (C_β), 217.4 (CO_{cis}), 223.2 (CO_{trans}), 267.7 (C_α). MS (EI, 70 EV) *m*/*z*: 643 [M^+], 615 [$(M-CO)^+$], 587 [$(M-2CO)^+$], 559 [$(M-3CO)^+$], 503 [$(M-5CO)^+$]. $C_{30}H_{25}CrFe_2NO_5$ (643.2).

*3.10. Pentacarbonyl[3,3-diferrocenyl-1-(N,N-dimethylamino)prop-2-enylidene]molybdenum (**10b**)*

The reaction of 0.39 g (0.6 mmol) of **1b** with $HNMe_2$ was carried out analogously to that of **1a**. After addition of the amine the solution was stirred for approx. 4 h at −10 °C to −5 °C. For the purification of **10b** see **10a**. Yield 0.25 g (0.36 mmol, 60%). IR (pentane, cm^{-1}): *ν*(CO) 2061 w, 1972 w, 1939 s,sh. IR (pentane, cm^{-1}): *ν*(CO) 1940 vs, 1931 s; *ν*(CCC) 1978 w. 1933 vs. ^1H NMR (250 MHz, $CDCl_3$): δ 3.06 (d, 3.70 Hz, 3H, Me), 3.72 (dd, 7.65 Hz, 1.17 Hz, 3H, Me), 4.11 (s, 5H, C_5H_5), 4.22 (s, 5H, C_5H_5), 4.39 4.27 (m, 6H, C_5H_4), 4.74 (m, 1H, C_5H_4), 4.82 (m, 1H, C_5H_4), 6.98 (m, 1H, =CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ 44.1, 51.9 (Me), 68.9, 69.3 (C_5H_5), 68.0, 68.1, 68.2, 68.4, 68.7, 68.8, 69.0, 69.7, 83.7, 87.6 (C_5H_4), 125.2 (C_γ), 135.1 (C_β), 206.3(CO_{cis}), 213.4 (CO_{trans}), 261.9 (C_α). MAS (FAB), *m*/*z* (rel. ^{98}Mo): 689 [M^+], 605 [$(M-3CO)^+$], 549 [$(M-5CO)^+$], 504 [$(M-5CO-HNMe_2)^+$]. $C_{30}H_{25}MoFe_2NO_5$ (687.2).

*3.11. Pentacarbonyl[3,3-diferrocenyl-1-(N,N-dimethylamino)prop-2-enylidene]tungsten (**10c**)*

The reaction of 0.44 g (0.6 mmol) of **1c** with $HNMe_2$ was carried out analogously to that of **1a**. After addition of the amine the solution was stirred for approx. 4 h at −10 °C to −5 °C. For the purification of **10c** see **10a**. Yield: 0.37 g (0.48 mmol, 80%). IR (pentane, cm^{-1}): *ν*(CO) 2060 w, 1965 w, 1932 s, sh, 1925 vs. ^1H NMR (250 MHz, $CDCl_3$): δ 3.05 (s, 3H, Me), 3.70 (s, 3H, Me), 4.11 (s, 5H, C_5H_5), 4.21 (s, 5H, C_5H_5), 4.36 4.25 (m, 6H, C_5H_4), 4.73 (m, 1H, C_5H_4), 4.82 (m, 1H, C_5H_4), 6.95 (m, 1H, =CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ 43.9, 52.1 (Me), 68.0, 68.2, 68.4, 68.8, 69.5, 83.2, 87.1 (C_5H_4), 68.9, 69.3 (C_5H_5), 126.8 (C_γ), 135.9 (C_β), 198.2 (J_{WC} 126.5 Hz, CO_{cis}), 203.1 (J_{WC} 124.0 Hz, CO_{trans}), 250.0 (C_α). MS (EI, 70 eV) *m*/*z*: 775 [M^+], 691 [$(M-3CO)^+$], 663 [$(M-4CO)^+$], 635 [$(M-5CO)^+$]. $C_{30}H_{25}WFe_2NO_5$ (775.1).

*3.12. Pentacarbonyl[5,5-diferrocenyl-3-diethylamino-4-methyl-pentatrien-1,2,4-ylidene]chromium (**11a**)*

At −45 °C, 1 ml of *N*,*N*-dimethylamino-1-propyne was added to a solution of 0.35 g (0.6 mmol) of **1a** in 20 ml of CH_2Cl_2. The solution was stirred for a total of 15 min at −20 °C. After 1 min the deep blue solution started to turn violet. After 15 min the reaction was complete and the colour of the solution was red. The solvent was removed in vacuo and the residue was chromatographed at −35 °C on basic alumina. With pentane/CH_2Cl_2 (6:1) red **11a** was eluted. Yield: 0.34 g (0.48 mmol, 80%). IR (pentane,

cm^{-1}): ν(CO) 1940 vs, 1931 s; ν(CCC) 1978 w. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.97 (t, 7.26 Hz, 3H, CH_2CH_3), 1.28 (t, 7.20 Hz, 3H, CH_2CH_3), 2.48 (s, 3H, Me), 2.98 (m, 1H, CH_2CH_3), 3.42 (m, 2H, CH_2CH_3), 3.54 (m, 1H, CH_2CH_3), 4.10 4.30 (m, 2H, C_5H_4), 4.15 (s, 5H, C_5H_5), 4.24 (s, 5H, C_5H_5), 4.43 (m, 3H, C_5H_4), 4.81 (m, 2H, C_5H_4), 5.08 (m, 1H, C_5H_4). ^{13}C NMR (62 MHz, $CDCl_3$): δ 11.4, 12.8 (CH_2CH_3), 22.5 (Me), 45.3, 48.1 (CH_2CH_3), 67.9, 68.2, 68.35, 68.6, 69.1, 69.7, 70.7, 71.6, 83.6, 88.9 (C_5H_4), 69.4, 70.0 (C_5H_5), 119.4 (C_δ), 127.0 (C_β), 136.7 (C_ε), 158.7 (C_γ), 218.0 (CO_{cis}), 218.7 (C_α), 223.9 (CO_{trans}). MS (EI, 70 eV) m/z: 709 [M^+], 597 [$(M-4CO)^+$], 569 [$(M-5CO)^+$], 539 [$(M-5CO-C_2H_6)^+$]. $C_{35}H_{31}CrFe_2NO_5$ (709.3).

3.13. Pentacarbonyl[5,5-diferrocenyl-3-diethylamino-4-methyl-pentatrien-1,2,4-ylidene]molybdenum (*11b*)

The synthesis of **11b** from 0.39 g (0.6 mmol) of **1c** and 1 ml of *N*,*N*-dimethylamino-1-propyne and the purification of **11b** was carried out analogously to **11a**. Exception: After addition of the alkyne the solution was stirred for 4 h at 10 °C. Yield: 0.18 g (0.24 mmol, 60%). IR (pentane, cm^{-1}): ν(CO) 1941 vs, 1930 s; ν(CCC) 1978 w. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.97 (t, 7.26 Hz, 3H, CH_2CH_3), 1.27 (t, 7.19 Hz, 3H, CH_2CH_3), 2.47 (s, 3H, Me), 2.95 (m, 1H, CH_2CH_3), 3.43 (m, 2H, CH_2CH_3), 3.51 (m, 1H, CH_2CH_3), 4.17 (s, 5H, C_5H_5), 4.22 (s, 5H, C_5H_5), 4.30 4.15 (m, 2H, C_5H_4), 4.43 (m, 3H, C_5H_4), 4.78 (m, 2H, C_5H_4), 5.05 (m, 1H, C_5H_4). ^{13}C NMR (62 MHz, $CDCl_3$): δ 11.4, 12.7 (CH_2CH_3), 22.6 (Me), 48.3, 45.4 (CH_2CH_3), 69.4, 70.1 (C_5H_5), 68.0, 68.2, 68.7, 68.8, 68.9, 69.8, 70.7, 71.5, 83.7, 86.0 (C_5H_4), 118.0 (C_δ), 127.0 (C_β), 137.1 (C_ε), 159.7 (C_γ), 206.0 (CO_{cis}), 211.6 (C_α), 213.0 (CO_{trans}). MS (FAB), m/z (rel. ^{98}Mo): 755 [M^+], 671 [$(M-3CO)^+$], 615 [$(M-5CO)^+$], 542 [$(M-5CO-HNEt_2)^+$]. $C_{35}H_{31}MoFe_2NO_5$ (753.3).

3.14. Pentacarbonyl[5,5-diferrocenyl-3-diethylamino-4-methyl-pentatrien-1,2,4-ylidene]tungsten (*11c*)

The synthesis of **11c** from 0.44 g (0.6 mmol) of **1c** and 1 ml of *N*,*N*-dimethylamino-1-propyne and the purification of **11c** was carried out analogously to **11b**. Yield: 0.33 g (0.39 mmol, 65%) of **11c**. IR (pentane, cm^{-1}): ν(CO) 1935 vs, 1925 s; ν(CCC) 1978 w. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.98 (t, 7.25 Hz, 3H, CH_2CH_3), 1.27 (t, 7.19 Hz, 3H, CH_2CH_3), 2.46 (s, 3H, Me), 2.94 (m, 1H, CH_2CH_3), 3.42 (m, 2H, CH_2CH_3), 3.51 (m, 1H, CH_2CH_3), 4.17 (s, 5H, C_5H_5), 4.22 (s, 5H, C_5H_5), 4.10 4.30 (m, 2H, C_5H_4), 4.43 (m, 3H, C_5H_4), 4.80 (m, 2H, C_5H_4), 5.05 (m, 1H, C_5H_4). ^{13}C NMR (62 MHz, $CDCl_3$): δ 11.4, 12.7 (CH_2CH_3), 22.5 (Me), 45.5, 48.3 (CH_2CH_3), 69.4, 70.0 (C_5H_5), 68.0, 68.2, 68.7, 68.8, 68.9, 69.2, 70.7, 71.5, 83.6, 85.9 (C_5H_4), 117.5 (C_δ), 126.9 (C_β), 136.3 (C_ε), 160.3 (C_γ), 196.2 (C_α), 197.3 (J_{WC} 125 Hz, CO_{cis}), 203.7 (J_{WC}

Table 3
Crystallographic data and refinement methods for **5a**, **7a**, and **9a**

	5a	**7a**	**9a**
Empirical formula	$C_{20}H_{15}CrFeNO_5$	$C_{22}H_{15}CrFeNO_5$	$C_{22}H_{17}CrFeNO_5$
M_r	457.18	481.20	483.22
Crystal system	monoclinic	triclinic	triclinic
0 Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.7348(17)	7.0311(14)	7.033(3)
b (Å)	10.112(2)	11.306(2)	11.182(6)
c (Å)	22.032(4)	13.648(3)	13.806(9)
α (°)	90	95.58(3)	80.57(6)
β (°)	99.61(3)	97.67(3)	83.44(3)
γ (°)	90	107.17(3)	74.875(2)
V (Å^3)	1918.6(7)	1016.6(4)	1031.1(10)
Z	4	2	2
Crystal size (mm)	0.30 × 0.157 × 0.10	0.50 × 0.367 × 0.20	0.5 × 0.4 × 0.3
ρ_{calc} (g cm^{-3})	1.583	1.572	1.556
μ (mm^{-1})	1.353	1.282	1.264
F(000)	928	488	492
T (K)	100(2)	100(2)	188(2)
Maximum 2θ (°)	50.4	53.4	54.0
Index range	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-26 \leqslant l \leqslant 25$	$-8 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 17$	$-8 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 17$
Number of data	20876	14995	4756
Number of unique data	3422	4304	4453
R_{int}	0.2012	0.0720	0.0526
Parameters	253	271	271
Goodness of fit on F^2	1.076	1.034	1.038
R_1, wR_2 ($I > 2\sigma > (I)$)	0.0806, 0.1126	0.0363, 0.0936	0.0410, 0.0949

123.9 Hz, CO_{trans}). MS (EI, 70 eV), *m/z*: 841 [M^+], 757 [$(M-3CO)^+$], 701 [$(M-5CO)^+$], 628 [$(M-5CO-HNEt_2)^+$]. $C_{35}H_{31}WFe_2NO_5$ (841.2).

3.15. X-ray structure analysis of **5a**, **7a**, and **9a**

Single crystals of **5a**, **7a**, and **9a** suitable for X-ray structure analysis were obtained by slow diffusion of petrol ether into solutions of **5a**, **7a**, and **9a** in CH_2Cl_2 at 4 °C. The measurements were performed with a crystal mounted on a glass fibre on a Stoe IPDS II diffractometer (graphite monochromator, Mo Kα, radiation, λ 0.71073 Å, scan rate 3 30° min^{-1} in ω). The structures were solved by direct methods using the SHELX-97 program package [23]. The position of the hydrogen atoms were calculated by assuming ideal geometry and their coordinates were refined together with those of the attached carbon atoms as riding-model. All other atoms were refined anisotropically. For the crystallographic data and the refinement details see Table 3.

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Appendix A. Supplementary material

CCDC 667920, 667921 and 667922 contain the supplementary crystallographic data for **5a**, **7a** and **9a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.02.024.

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