

Heterobimetallic carbene and allenylidene complexes; syntheses and crystal structures of iron(II)–chromium(0) cycloheptatrienylydene and (cycloheptatrienylydene)ethenylydene complexes †

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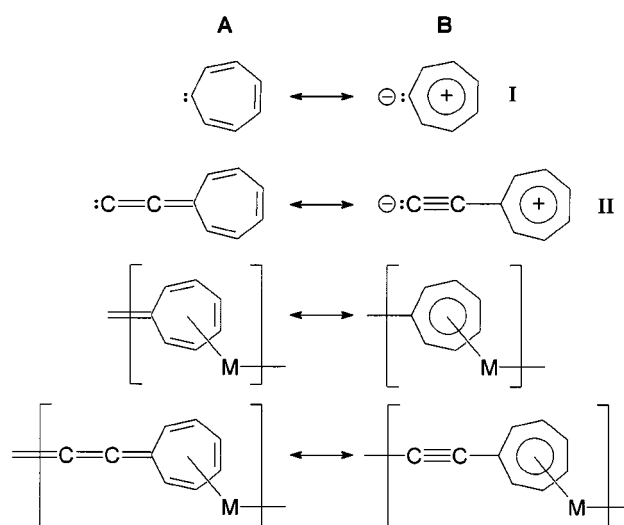
The heterobimetallic iron(II)–chromium(0) complexes $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_7H_6)Cr(CO)_3]^+$ and $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_2C_7H_6)Cr(CO)_3]^+$ containing the bridging carbene ligand cycloheptatrienylydene C_7H_6 and the cumulous allenylidene ligand (cycloheptatrienylydene)ethenylydene $C_2C_7H_6$ have been prepared and their properties studied. The former has been prepared by hydride abstraction from the heterobimetallic $\mu-\eta^1:\eta^6$ -cyclohepta-1,3,5-trien-2-yl complex obtained by lithiation of 2-trimethylstannyl-cyclohepta-1,3,5-triene followed by reaction with $[FeCp(CO)_2-Br]$ and $[Cr(CO)_3(NCet)_3]$. Treatment of 7-ethynyl-cyclohepta-1,3,5-triene with $LiBu^u$ and consecutive reaction with $[FeCp(CO)_2Br]$ and $[Cr(CO)_3(NCet)_3]$ led to the formation of *endo*- $[(OC)_2CpFe(\mu-\eta^1:\eta^6-C\equiv C-C_7H_7)Cr(CO)_3]$ which was treated with $[Ph_3C][BF_4]$ to give $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_2C_7H_6)Cr(CO)_3][BF_4]$. The crystal structures of $[(OC)_2CpFe(\mu-\eta^1:\eta^6-C_7H_7)Cr(CO)_3]$, $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_7H_6)Cr(CO)_3][PF_6]\cdot 0.25CH_2Cl_2$ and $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_2C_7H_6)Cr(CO)_3]^+[BF_4]\cdot CH_2Cl_2$ have been determined.

Introduction

Over recent years considerable efforts have been devoted to exploring the organometallic chemistry of η -cycloheptatrienyl ligands and significant progress has been made in the development of new synthetic routes.¹ However, η -cycloheptatrienyl–transition metal complexes, $M(\eta-C_7H_7)$, still remain neglected in comparison with the η -cyclopentadienyl, $M(\eta-C_5H_5)$, and benzene systems, $M(\eta-C_6H_6)$. This also holds for the area of bimetallic complexes with conjugated hydrocarbon-bridged transition metal fragments which is dominated by ligands containing five- and six-membered rings, e.g. fulvalene and biphenyl.² On the other hand, related complexes with *bicyclic* hydrocarbons incorporating cycloheptatrienyl units such as heptafulvalene,³ bicycloheptatrienyl⁴ and sesquifulvalene^{5–8} are rare and have attracted considerable attention only recently due to their potential use in material science.^{6–8}

Even less is known about bimetallic complexes of *monocyclic* cycloheptatrienyl derivatives like cycloheptatrienylydene **I** and (cycloheptatrienylydene)ethenylydene **II** which are suitable for linking two metal centers in a conjugated $\mu-\eta^1:\eta^7$ -fashion as outlined for hypothetical organometallic polymers. In **I** and **II** the well known ability of the tropylium system effectively to stabilize a positive charge should lead to polarizable compounds with strong dipolar characteristics (canonical forms **B**), possibly resulting in interesting physicochemical properties.

Accordingly, interesting linear and non-linear optical properties have been observed only recently for monometallic allenylidene complexes such as $[RuCp(PPh_3)_2(\eta^1-C_2C_7H_6)]^+$ and derivatives thereof.⁹ In contrast, corresponding monometallic η^1 -cycloheptatrienylydene complexes have been reported much earlier by Jones and co-workers¹⁰ comprising cationic $[FeCp(CO)_2(\eta^1-C_7H_6)]^+$ and $[RuCp(CO)_2(\eta^1-C_7H_6)]^+$ as well as neutrally charged $[W(CO)_5(\eta^1-C_7H_6)]$. The seven-membered ring can subsequently be co-ordinated to a second metal fragment,



and we have recently communicated the synthesis of $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_7H_6)Cr(CO)_3][BF_4]$ representing the first heterobimetallic cycloheptatrienylydene complex.¹¹ With this contribution we wish to give a detailed account of the synthesis and properties of $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_7H_6)Cr(CO)_3]^+$ including crystal structure determination of its $[PF_6]^-$ salt. Furthermore, the preparation and molecular structure of the corresponding allenylidene complex $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_2C_7H_6)Cr(CO)_3][BF_4]$ will be presented. Ultimately, we hope that investigating discrete bimetallic model complexes of that kind will eventually allow the preparation of conducting organometallic polymers,^{1,2,12} in which **I** and **II** build the conjugated backbones.

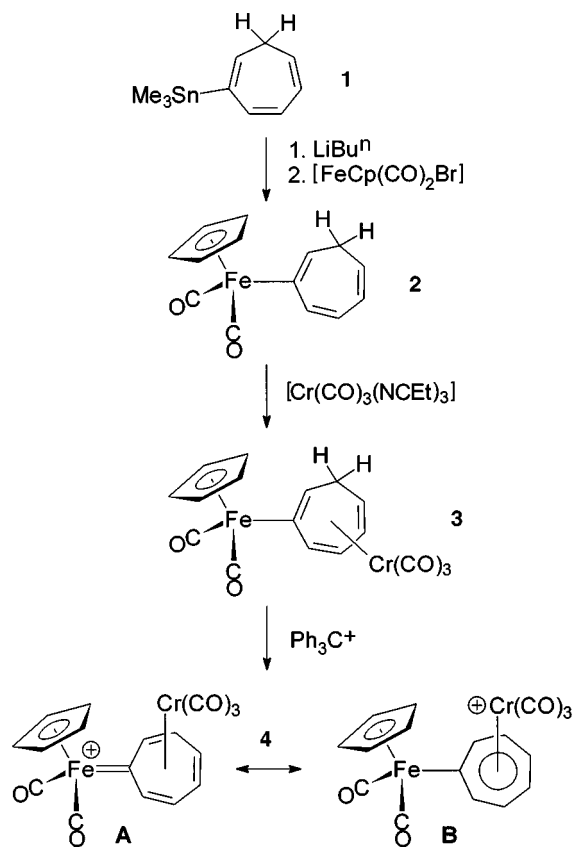
Results and discussion

Synthesis and spectroscopic characterization of $[(OC)_2CpFe(\mu-\eta^1:\eta^7-C_7H_6)Cr(CO)_3]^+$ **4**

2-Trimethylstannylcyclohepta-1,3,5-triene **1** can be obtained

† Dedicated to Professor Dr Bernt Krebs on the occasion of his 60th birthday.

by selective metallation of cyclohepta-1,3,5-triene in the 2 position followed by quenching of the generated anion with SnMe_3Cl .^{8,13} In our hands **1** has been successfully employed in Stille coupling reactions leading to isomerically pure cycloheptatrienyl derivatives.⁸ Alternatively, it can also be used for the formation of transition metal–carbon bonds, and complex **2** can be prepared by lithiation of **1** with LiBu^n and reaction with $[\text{FeCp}(\text{CO})_2\text{Br}]$ (Scheme 1). The ^1H NMR spectrum



Scheme 1

exclusively shows the presence of a cyclohepta-1,3,5-triene-2-yl derivative exhibiting a doublet of doublets for the allylic protons and five resonances for the vinylic protons in a 2:1:1:1:1 ratio. Complex **2** had been obtained previously by Jones and co-workers,^{10a} albeit in a mixture of three isomeric iron complexes.

Complex **2** was treated with $[\text{Cr}(\text{CO})_3(\text{NCEt})_3]$ at room temperature to give heterobimetallic **3** as stable red-orange crystals. The ^1H NMR spectrum exhibits five resonances due to the vinylic protons and two resonances due to the allylic *exo*- and *endo*-protons. As **3** is a racemic mixture of two enantiomers, two ^{13}C NMR resonances are observed for the diastereotopic FeCO carbon atoms. In order unambiguously to confirm the substitution pattern in **3**, its molecular structure was determined by X-ray diffraction (Fig. 1).¹¹ The bond lengths and angles about the iron atom fall in the range observed for other alkenyl complexes,¹⁴ and the structural parameters of the $[(\text{C}_7\text{H}_7)\text{Cr}(\text{CO})_3]$ units are similar to those reported for a manganese–chromium hydrosesquivalvalenyl complex (Table 1).⁸

The cyclohepta-1,3,5-triene-2-yl ring is indeed co-ordinated in a $\mu\text{-}\eta^1:\eta^6$ fashion, which represents a new bonding type for the bridging of two metal centers by the cycloheptatrienyl ligand.¹⁶ Related complexes incorporating $\mu\text{-}\eta^1:\eta^6\text{-C}_7\text{H}_7$ rings have been obtained by Beck and co-workers¹⁷ and Whiteley and co-workers^{16,18} through the addition of nucleophilic anions such as $[\text{Re}(\text{CO})_5]^-$ or $[\text{RuCp}(\text{CO})_2]^-$ to electrophilic cations of the type $[\text{M}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$ ($\text{M} = \text{Cr}$ or Mo). Contrary to **3** these bimetallic complexes are not vinyl complexes, as the

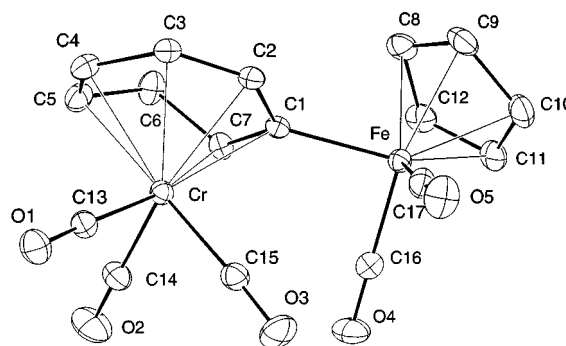


Fig. 1 An ORTEP¹⁵ drawing of complex **3**.

η^1 -co-ordinated metal fragments adopt the allylic *exo* position of the respective cycloheptatrienyl ring.

In complex **3** the 7-*exo*-hydrogen atom is easily accessible for hydride abstraction, and the carbene complexes **4** $[\text{BF}_4]$ and **4** $[\text{PF}_6]$ with cationic $[(\text{OC})_2\text{CpFe}(\mu\text{-}\eta^1:\eta^7\text{-C}_7\text{H}_6)\text{Cr}(\text{CO})_3]^+$ **4** were formed quantitatively upon reaction with $[\text{Ph}_3\text{C}][\text{BF}_4]$ or $[\text{Ph}_3\text{C}][\text{PF}_6]$, respectively. The carbene carbon resonance (δ 159.1, CD_3CN) is observed at much higher field than for the corresponding monometallic complex $[\text{FeCp}(\text{CO})_2(\eta^1\text{-C}_7\text{H}_6)]^+$ [δ 242.3, $(\text{CD}_3)_2\text{CO}$] due to co-ordination of the $\text{Cr}(\text{CO})_3$ unit to the $\mu\text{-}\eta^1:\eta^7$ -cycloheptatrienyldiene ligand (see below). A direct relationship between the chemical shift of the cyclopentadienyl group and the degree of electron richness at the metal site has been suggested.¹⁹ Consequently, the ^1H cyclopentadienyl resonance of **4** is observed at substantially higher field (δ 5.14) than that of $[\text{FeCp}(\text{CO})_2(\eta^1\text{-C}_7\text{H}_6)][\text{PF}_6]$ (δ 5.50),^{10a} thus indicating that $[(\eta^7\text{-C}_7\text{H}_6)\text{Cr}(\text{CO})_3]$ is a weaker π acceptor than cycloheptatrienyldiene **1** and that the canonical form **B** contributes more strongly to the ground-state electronic structure of **4** (Scheme 1).

Synthesis and spectroscopic characterization of $[(\text{OC})_2\text{CpFe}(\mu\text{-}\eta^1:\eta^7\text{-C}_2\text{C}_7\text{H}_6)\text{Cr}(\text{CO})_3]^+ 7$

We have previously used 7-ethynylcyclohepta-1,3,5-triene **III** as a starting material for the preparation of ruthenium(II) allenylidene complexes.⁹ Accordingly, the cycloheptatrienyl-acetylide complex **5** was prepared by the reaction of lithiated **III** with $[\text{FeCp}(\text{CO})_2\text{Br}]$ (Scheme 2). The molecular structure of **5** was established by X-ray diffraction analysis.²⁰

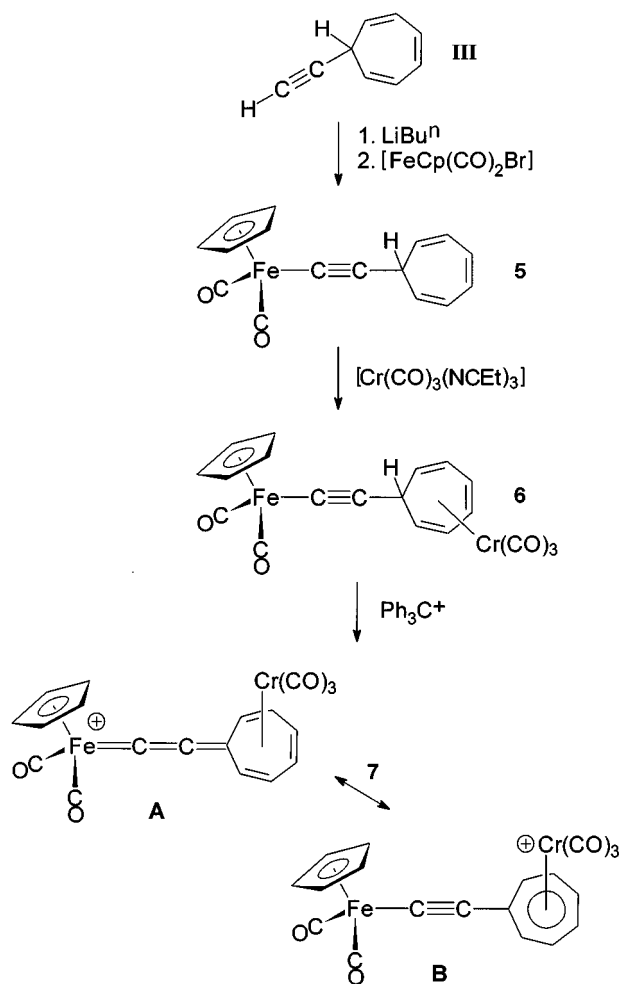
7-substituted cycloheptatriene complexes of the type $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_7\text{R})]$ can form, in principle, two different stereoisomers having either *endo* or *exo* configuration, and it has been shown that only the *endo*-substituted complexes are accessible to hydride abstraction with formation of cationic tropylium complexes $[\text{Cr}(\text{CO})_3(\eta^7\text{-C}_7\text{H}_7\text{R})]^+$.²¹ Fortunately, treatment of **5** with $[\text{Cr}(\text{CO})_3(\text{NCEt})_3]$ resulted exclusively in the formation of the *endo*-configured complex **6**. The ^1H NMR spectrum of **6** exhibits the resonance for the allylic $\text{C}\equiv\text{CCH}$ proton at δ 2.52 which clearly falls in the range expected for an *exo*-hydrogen atom.⁸ Consequently, hydride abstraction in **6** can be achieved in good yield with $[\text{Ph}_3\text{C}][\text{BF}_4]$ giving red-orange $[(\text{OC})_2\text{CpFe}(\mu\text{-}\eta^1:\eta^7\text{-C}_2\text{C}_7\text{H}_6)\text{Cr}(\text{CO})_3][\text{BF}_4]$ **7** $[\text{BF}_4]$ (Scheme 2).

The ^{13}C NMR resonance of the $\text{Fe}\text{-C}_\alpha$ carbon atom is found at substantially higher field (δ 149.5) than the resonances in "typical" diaryl- or dialkyl-allenylidene carbonyl complexes of the type $\text{M}=\text{C}=\text{C}=\text{CR}_2$.²² Similar high-field shifts are observed for amino-substituted allenylidene complexes indicating a much stronger contribution from the dipolar mesomeric structure $\text{M}^--\text{C}\equiv\text{C}=\text{CR}_2^+$ due to stabilization of the positive charge on C_γ by (p-p) π donation from the nitrogen atoms.^{23,24} For instance, Fischer and co-workers have recently reported strongly polarized allenylidene complexes of the type $[(\text{OC})_3\text{M}=\text{C}=\text{C}=\text{C}(\text{NMe}_2)_2 \longleftrightarrow (\text{OC})_3\text{M}^--\text{C}\equiv\text{C}-\text{C}^+(\text{NMe}_2)_2]$ exhibiting

Table 1 Selected bond distances (Å), bond angles (°) and dihedral angles (°) for complexes **3**, **4**[PF₆]⁻·0.25CH₂Cl₂ and **7**[BF₄]⁻·CH₂Cl₂

	3	4	7
Fe–Cl	2.014(4)	1.993(5)	1.896(4)
Cl–C2	1.446(5)	1.412(7)	1.210(5)
C1–C7	1.397(7)	1.437(8)	—
C2–C3	1.406(5)	1.424(8)	1.428(6)
C3–C4	1.449(7)	1.413(8)	1.432(6)
C3–C9	—	—	1.433(7)
C4–C5	1.385(7)	1.421(9)	1.406(5)
C5–C6	1.514(5)	1.410(9)	1.413(7)
C6–C7	1.516(7)	1.407(8)	1.416(7)
C7–C8	—	—	1.419(6)
C8–C9	—	—	1.409(6)
Fe–C (C ₅ H ₅)	2.110(6)–2.139(6)	2.091(6)–2.128(7)	2.093(4)–2.120(6)
(average)	2.121	2.107	2.104
Cr–C (η ⁶ -C ₇ H ₇)	2.220(5)–2.386(6)	—	—
(average)	2.275	—	—
Cr–C (η ⁷ -C ₇ H ₆)	—	2.232(7)–2.325(5)	2.229(4)–2.309(4)
(average)	—	2.258	2.254
Fe–C(CO)	1.761(5), 1.767(5)	1.767(6), 1.769(6)	1.770(4)–1.774(6)
Cr–C(CO)	1.847(4)–1.859(5)	1.879(6)–1.895(7)	1.905(5)–1.924(5)
O–C(Fe)	1.132(6)–1.140(7)	1.139(7)–1.147(8)	1.142(7), 1.145(5)
O–C(Cr)	1.138(7)–1.151(5)	1.144(7)–1.145(8)	1.129(6)–1.140(7)
Fe–C1–C2	119.3(3)	116.7(4)	178.6(4)
C1–C2–C3	129.6(4)	131.3(5)	172.2(2)
Fe–C–O	178.5(4), 176.2(4)	177.8(5), 179.0(5)	178.1(5), 179.3(4)
Cr–C–O	175.7(4)–178.5(3)	176.4(6)–178.9(5)	177.0(3)–178.6(3)
DA	—	98.2(2) ^a	16.2(2) ^b

^a DA (dihedral angle) = angle between normals to least-squares planes defined by C* (centroid of the C₅H₅ ring), Fe, C1 and C1, C2, C3, C4, C5, C6, C7. ^b DA (dihedral angle) = angle between normals to least-squares planes defined by C* (centroid of the C₅H₅ ring), Fe, C1 and C3, C4, C5, C6, C7, C8, C9.

**Scheme 2**

C_α carbon resonances at δ 185.9 (M = Cr) and 173.0 (M = W)²⁴ as well as heterobimetallic ethynylcarbene complexes such as [(OC)₅M=C(NMe₂)-C≡C-FeCp(CO)₂ ↔ (OC)₅M⁻-C(NMe₂)=C=C=Fe⁺Cp(CO)₂] of which the Fe-C_α and C_β carbon resonances are almost identical with those of **7**.²⁵ In **7** the ability of the (C₇H₆R)Cr(CO)₃ moiety effectively to stabilize a positive charge and the relatively weak π-electron release ability of the CpFe(CO)₂ metal fragment obviously lead to a very strong contribution of the “tropylium acetylide” structure **B** (Scheme 2). In contrast, co-ordination of **II** to an electron-rich metal center as in [RuCp(PPh₃)₂(η¹-C₂C₇H₆)]⁺ gives rise to a low field C_α resonance at δ 235.4 due to much stronger metal-to-ligand back donation.⁹

Complex **7**[BF₄]⁻ is intensely red-orange. It shows moderate solvatochromic behaviour, and in its UV/VIS spectrum the lowest energy band λ_{max} is hypsochromically shifted (Δν̄ = -900 cm⁻¹) upon changing the solvent from dichloromethane (λ_{max} = 528 nm) to acetonitrile (λ_{max} = 504 nm). Similarly to related sesquifulvalene complexes,^{6–8} the lowest energy transition can be assigned to the π to π* charge transfer excitation,²⁶ which is *approximately* (!) represented by the canonical forms **B** (ground state) and **A** (excited state) shown in Scheme 2.

Structural characterization of [(OC)₂CpFe(μ-η¹:η⁷-C₇H₆)-Cr(CO)₃]⁺ **4** and [(OC)₂CpFe(μ-η¹:η⁷-C₂C₇H₆)Cr(CO)₃]⁺ **7**

The molecular structures of the cations in **4**[PF₆]⁻·0.25CH₂Cl₂ (top) and **7**[BF₄]⁻·CH₂Cl₂ (bottom) are depicted in Fig. 2. The most striking features are the different orientations of the seven-membered rings in **4** and **7** toward the pseudo mirror plane including C1, Fe and the centroid of the cyclopentadienyl ring. According to the model developed by Hoffmann and co-workers,²⁷ the preferred orientation in complexes of the type [(OC)₂CpFe=CR₂]⁺ and [(OC)₂CpFe=C=C-CR₂]⁺ will align an empty p orbital (or a symmetry-related π* orbital) anti-symmetric with respect to the mirror plane to interact optimally with the metal *a*'' HOMO. Steric requirements may force the

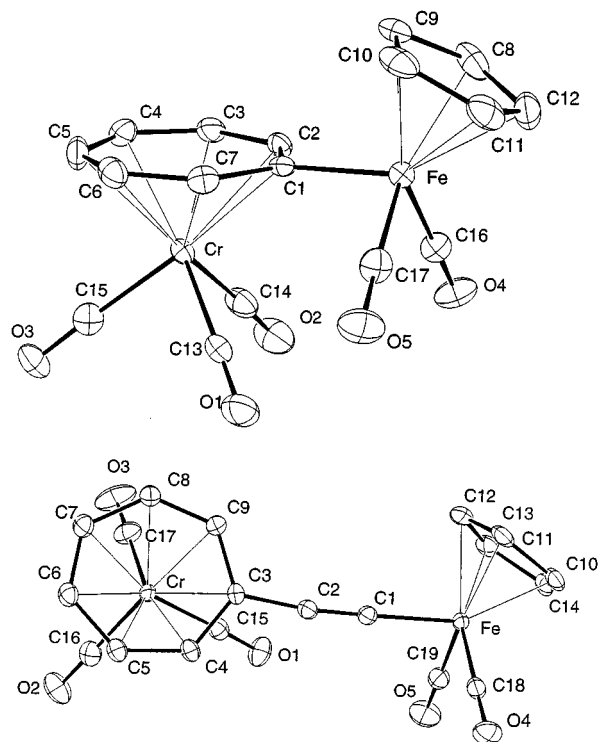
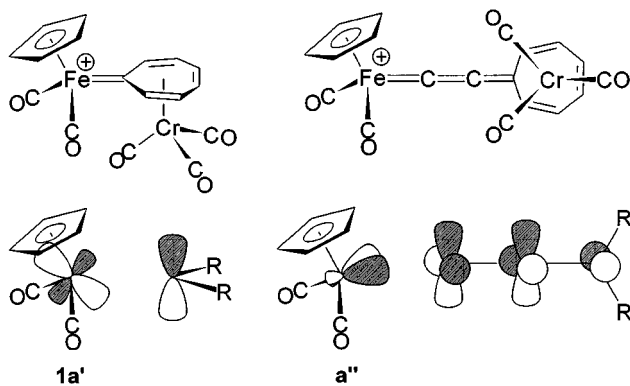


Fig. 2 The ORTEP¹⁵ drawings of the cations of complexes **4**[PF₆] \cdot 0.25 CH₂Cl₂ (top) and **7**[BF₄] \cdot CH₂Cl₂ (bottom).

ligand into the electronically less favourable horizontal conformation only allowing π interaction with the lower lying metal $1a'$ orbital. Whereas the allenylidene ligand in **7** adopts the expected vertical conformation [dihedral angle = 16.2(2) $^\circ$, Table 1], the perpendicular orientation of the carbene ligand in **4** [dihedral angle = 98.2(2) $^\circ$, Table 1] deviates from the theoretically predicted coplanarity. This is probably due to steric hindrance between the *ortho*-C₇H₆ and the cyclopentadienyl hydrogen atoms. The same conformation is also found in related monometallic cycloheptatrienylidene complexes,^{10b} in heterocyclic carbene complexes²⁸ and in bimetallic π -arene complexes,^{12,29} whereas the solid state structures of carbene complexes with sterically less demanding and stronger π -accepting ligands such as dichlorocarbene are in accordance with the Hoffmann model.³⁰ Acyclic thiocarbene³¹ and aminocarbene complexes³² may exhibit the vertical as well as the horizontal conformation indicating that even packing forces might control the orientation of the carbene ligand.



In complex **4** the Fe–C (carbene) bond length, 1.993(5) Å, falls in the range of Fe–C(sp²) bonds with only little multiple character.³³ It is only slightly longer than the Fe–C bond in the corresponding monometallic cycloheptatrienylidene complex [FeCp(CO)₂(η^1 -C₇H₆)] [PF₆]^{10b} and similar to bimetallic π -arene

complexes, e.g. [(OC)₂CpFe(μ - η^1 : η^6 -1,4-C₆H₄Me)Cr(CO)₃].¹² As expected for a Fe–C(sp) bond the Fe–C _{α} distance in **7** [1.896(4) Å] is significantly shorter. Nevertheless, the structural parameters of the Fe–C _{α} –C _{β} –C _{γ} chain (Table 1) differ only marginally from the bond distances in iron acetylide complexes³⁴ and are virtually identical with those in the heterobimetallic ethynylcarbene complex [(OC)₅M=C(NMe₂)C \equiv CFcCp(CO)₂] (see above).²⁵ These observations together with only little variation in the C₇ ring C–C distances indicate that the solid-state structures of **4** and **7** are best described as substituted tropylium salts by the canonical form **B** as shown in Scheme 1 for **4** and in Scheme 2 for **7**.

Conclusion

In this work we have introduced heterobimetallic cycloheptatrienylidene and (cycloheptatrienylidene)ethynylidene complexes which represent the first members of a series of metal-lacumulenes with (:C=C) _{n} =C₇H₆ ligands ($n=0$ or 1). The experimental procedures described in this contribution will allow the syntheses of various heterobimetallic carbene and allenylidene complexes with a wide range of different electronic and optical properties. In addition, we believe that the preparation of higher members of this family ($n > 1$) is a feasible goal taking into account the similarity to cumulenes of the type (:C=C) _{n} =C(NMe₂)₂ which form stable Group 6 allenylidene ($n=1$) and pentatetraenylidene complexes³⁵ ($n=2$).²⁴ Even generation and trapping of a metallaoctaheptene [M=C=C=C=C=C=C=C(NMe₂)₂] could be demonstrated.³⁶ Extension of the carbon chain will certainly lead to compounds with interesting physical and chemical properties and, in particular, with increased non-linear optical efficiencies.^{9,37}

Experimental

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. The NMR spectra were recorded on a Bruker AM 250 (250 MHz) instrument, infrared spectra on a Perkin-Elmer 983 instrument. Elemental analyses (C,H,N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra were recorded on a Varian MAT 711 instrument and UV/VIS spectra on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer using 10⁻⁴ solutions. 2-Trimethylstannylcyclohepta-1,3,5-triene **1**,⁸ 7-ethynylcyclohepta-1,3,5-triene **III**,³⁸ [FeCp(CO)₂Br]³⁹ and [Cr(CO)₃(NCEt)₃]⁴⁰ were prepared according to published procedures; [Ph₃C][BF₄] and [Ph₃C][PF₆] were synthesized as described in ref. 41.

Preparations

Complex 2. A solution of complex **1** (2.01 g, 7.9 mmol) in 30 ml of thf was treated with LiBuⁿ (3.2 ml of a 2.5 M solution in hexane, 8.0 mmol) at –70 $^\circ$ C. After stirring for 60 min the reaction mixture was slowly transferred to a solution of [FeCp(CO)₂Br] (2.00 g, 7.8 mmol) in 50 ml of thf at –70 $^\circ$ C. Stirring was continued for 60 min at –70 $^\circ$ C and, after warming, for 45 min at room temperature. The reaction mixture was evaporated to dryness and purified by column chromatography on silica using hexane–diethyl ether (2:1). Complex **2** was eluted as a yellow fraction followed by a red fraction containing 400 mg of unchanged [FeCp(CO)₂Br]. After removal of the solvent **2** was isolated as a dark yellow oil which was crystallized by cooling to –78 $^\circ$ C for a short period of time (1.50 g, 72%) (Found: C, 62.53; H, 4.60%; m/z 268. C₁₄H₁₂FeO₂ requires C, 62.72; H, 4.51%; M 268). IR (CH₂Cl₂); $\tilde{\nu}_{\max}$ /cm⁻¹ 2013 and 1956 (CO). ¹H NMR (400 MHz, CDCl₃); δ 6.70 (d, 1 H, 3-CH), 6.12 (dd, 1 H, 4-CH), 6.05 (dd, 1 H, 5-CH), 5.30 (td, 1 H, 6-CH), 5.14

Table 2 Crystallographic data for complexes **3**, **4**[PF₆]₂·0.25CH₂Cl₂ and **7**[BF₄]₂·CH₂Cl₂

	3	4 [PF ₆] ₂ ·0.25 CH ₂ Cl ₂	7 [BF ₄] ₂ ·CH ₂ Cl ₂
Formula	C ₁₇ H ₁₂ CrFeO ₅	C ₁₇ H ₁₁ CrF ₆ FeO ₅ P·0.25 CH ₂ Cl ₂	C ₂₀ H ₁₃ BCl ₂ CrF ₄ FeO ₅
<i>M</i>	404.12	569.31	598.87
Crystal system	Triclinic	Orthorhombic	Triclinic
<i>a</i> /Å	7.859(2)	13.795(7)	10.382(7)
<i>b</i> /Å	9.320(2)	14.156(8)	10.500(8)
<i>c</i> /Å	12.403(4)	20.742(7)	12.258(7)
<i>α</i> /°	99.94(4)		69.843(5)
<i>β</i> /°	102.55(4)		65.149(5)
<i>γ</i> /°	109.13(4)		70.838(6)
<i>U</i> /Å ³	807.98	4050.54	1111.58
<i>T</i> /K	293	113	113
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>I</i> 222 (no. 23)	<i>P</i> $\bar{1}$ (no. 2)
<i>Z</i>	2	8	2
<i>D</i> _c /g cm ⁻³	1.66	1.87	1.79
Reflections collected	4968	3248	4112
Independent reflections	4652	3244	3912
Observed reflections [<i>F</i> _o ≥ 2σ(<i>F</i> _o)]	3879	2848	3476
No. parameters	217	297	307
<i>R</i>	0.053	0.046	0.038
<i>R</i> '	0.066	0.050	0.048

Weighting scheme $w = 1/[\sigma(F)]^2$.

(t, 1 H, 1-CH), 4.64 (s, 5 H, C₅H₅) and 2.23 (dd, 2 H 7-CH₂).[‡] ¹³C NMR (62.9 MHz, CDCl₃): δ 216.3 (Fe–CO), 146.2 (C-3), 133.0 (C-2), 126.7 (C-1), 124.8 (C-5), 122.8 (C-4), 120.7 (C-6), 85.8 (C₅H₅) and 32.2 (C-7).[‡] Mass spectrum (EI): *m/z* 268 (*M*⁺, 17), 240 (19, *M* – CO), 212 (100, *M* – 2CO) and 121 (48%, C₅H₅Fe).

Complex 3. The complex [Cr(CO)₃(NCEt)₃] (3.00 g, 10.0 mmol) and **2** (2.22 g, 8.3 mmol) were dissolved in 35 ml of thf and stirred for 40 h. The reaction mixture was evaporated to dryness, and the residue extracted with diethyl ether (approximately 700 ml). Removal of the solvent afforded **3** as a red solid (1.1 g, 33%) (Found: C, 50.32; H, 3.31%; *m/z* 404. C₁₇H₁₂CrFeO₅ requires C, 50.53; H, 2.99%; *M* 404). IR (CH₂Cl₂): $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2025, 1972, 1958, 1893 and 1860 (CO). ¹H NMR (400 MHz, CDCl₃): δ 6.08 (d, 1 H, 3-CH), 5.63 (dd, 1 H, 4-CH), 4.88 (s, 5 H, C₅H₅), 4.78 (dd, 1 H, 5-CH), 3.25 (dd, 1 H, 1-CH), 3.16 (m, 1 H, 6-CH), 2.90 (m, 1 H, 7-endo-CH) and 1.46 (m, 1 H, 7-exo-CH). ¹³C NMR (62.9 MHz, CD₃CN): δ 235.1 (Cr–CO), 217.5, 216.7 (Fe–CO), 128.4 (C-2), 115.3, 100.7, 97.1 (C₇ ring: CH), 87.7 (C₅H₅), 64.6, 56.1 (C₇ ring: CH) and 26.9 (C-7). Mass spectrum (EI): *m/z* 404 (*M*⁺, 20), 348 (22, *M* – 2CO), 320 (25, *M* – 3CO), 292 (30, *M* – 4CO), 264 (100, *M* – 5CO) and 208 [72%, (C₅H₅)Cr(C₇H₇)].

Complex 4[BF₄]. A solution of complex **3** (300 mg, 0.74 mmol) in 40 ml of dichloromethane was treated with a solution of triphenylmethyl tetrafluoroborate (250 mg, 0.74 mmol) in 10 ml of dichloromethane at –78 °C. Stirring was continued at low temperature for 15 min. The reaction mixture was allowed to warm to room temperature whereupon an orange precipitate formed. About 20 ml of the solvent were removed and 80 ml of diethyl ether were added. The precipitate was filtered off and washed with diethyl ether to give red-orange crystals of **4**[BF₄] (320 mg, 89%) (Found: C, 39.89; H, 2.69. C₁₇H₁₁BCrF₄FeO₅ requires C, 41.68; H, 2.26%). IR (CH₃CN): $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2052, 2025 and 1999 (CO). ¹H NMR (250 MHz, CD₃CN): δ 6.69 (d, 2 H, C₇ ring: CH), 6.35 (m, 2 H, C₇ ring: CH), 6.05 (m, 2 H, C₇ ring: CH) and 5.14 (s, 5 H, C₅H₅). ¹³C NMR (62.9 MHz, CD₃CN): δ 225.2 (Cr–CO), 214.8 (Fe–CO), 159.1 (C-1), 119.0, 105.6, 104.0 (C₇ ring: CH) and 89.0 (C₅H₅). Mass spectrum (FAB): *m/z* 403 (*M*⁺, 100), 375 (38, *M* – CO), 347 (34, *M* – 2CO), 319 (19, *M* – 3CO), 291 (13, *M* – 4CO) and 263

(17%, *M* – 5CO). UV/VIS: λ_{\max}/nm (ε/dm³ mol⁻¹ cm⁻¹) (CH₂Cl₂): 241 (9200), 273 (7200), 307 (8700) and 423 (1140); (CH₃CN): 236 (9515), 272 (7300), 308 (8700) and 429 (1100).

Complex 5. A solution of compound **III** (2.49 g, 21.4 mmol) in 30 ml of thf was treated with LiBuⁿ (9.0 ml of a 2.5 M solution in hexane, 22.5 mmol) at –60 °C. After stirring for 90 min the reaction mixture was slowly transferred to a solution of [FeCp(CO)₂Br] (6.06 g, 23.6 mmol) in 100 ml of thf at –60 °C. The reaction mixture was allowed to warm to room temperature and stirring was continued for 45 min. The solvent was removed *in vacuo* and the residue purified by column chromatography on alumina using hexane–diethyl ether (2:1). After removal of the solvent complex **5** was isolated as yellow crystals (2.86 g, 46%) (Found: C, 65.79; H, 4.46%; *m/z* 292. C₁₆H₁₂FeO₂ requires C, 65.79; H, 4.14%; *M* 292). IR: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CH₂Cl₂) 2040 and 1990 (CO); (KBr) 2114 (C≡C), 2033 and 1972 (CO). ¹H NMR (250 MHz, CDCl₃): δ 6.60 (m, 2 H, C₇ ring: CH), 6.09 (m, 2 H, C₇ ring: CH), 5.35 (dd, 2 H, C₇ ring: CH), 5.00 (s, 5 H, C₅H₅) and 2.50 (t, 1 H, C₇ ring: CH). ¹³C NMR (100.4 MHz, CDCl₃): δ 212.7 (Fe–CO), 130.6, 127.0, 123.3 (C₇ ring: CH), 116.5 (C≡C), 85.0 (C₅H₅), 70.4 (C≡C) and 34.8 (C-7). Mass spectrum (EI): *m/z* 292 (*M*⁺, 2), 264 (*M* – CO, 9), 236 (*M* – 2CO, 88) and 56 (Fe, 100%).

Complex 6. The complex [Cr(CO)₃(NCEt)₃] (750 mg, 2.5 mmol) and **5** (600 mg, 2.1 mmol) were dissolved in 15 ml of thf and stirred for 17 h. The reaction mixture was evaporated to dryness, and the residue extracted with diethyl ether (approximately 250 ml). Removal of the solvent afforded **6** as a red solid (330 mg, 37%). IR (CH₂Cl₂): $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2041, 1990, 1977, 1911 and 1878 (CO). ¹H NMR (400 MHz, CDCl₃): δ 5.92 (m, 2 H, C₇ ring: CH), 5.02 (s, 5 H, C₅H₅), 4.70 (m, 2 H, C₇ ring: CH), 3.36 (m, 2 H, C₇ ring: CH) and 2.52 (m, 1 H, C₇ ring: CH). Mass spectrum (EI): *m/z* 428 (*M*⁺, 5), 372 (13, *M* – 2CO), 344 (43, *M* – 3CO), 316 (29, *M* – 4CO), 288 (100, *M* – 5CO) and 236 (99%, *M* – 5CO – Cr).

Complex 7[BF₄]. A solution of complex **6** (300 mg, 0.70 mmol) in 15 ml of dichloromethane was treated with a solution of triphenylmethyl tetrafluoroborate (210 mg, 0.63 mmol) in 10 ml of dichloromethane at –78 °C. Stirring was continued at low temperature for 15 min. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The product was precipitated by addition of 100 ml of diethyl ether. The precipitate was filtered off and washed with diethyl ether to

[‡] The assignment of all cycloheptatrienyl resonances is supported by two-dimensional NMR spectroscopy (COSY experiments).

afford **7**[BF₄] as a red-brown solid (280 mg, 86%) (Found: C, 43.46; H, 2.51. C₁₉H₁₁BCrF₄FeO₅ requires C, 44.40; H, 2.16%). IR (CH₂Cl₂): $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2092 (CCC), 2060, 2035 and 2010 cm⁻¹ (CO). ¹H NMR (250 MHz, CD₃CN): δ 6.56 (m, 2 H, C₇ ring: CH), 6.30 (m, 2 H, C₇ ring: CH), 6.12 (m, 2 H, C₇ ring: CH) and 5.24 (s, 5 H, C₅H₅). ¹³C NMR (100.4 MHz, CD₃CN): δ 223.4 (Cr–CO), 212.7 (Fe–CO), 149.5 (FeCC), 131.1 (FeCC), 117.1 (FeCCC), 105.3 (2 × C₇ ring: CH), 104.1 (C₇ ring: CH) and 87.7 (C₅H₅). Mass spectrum (FAB): m/z 427 (M⁺, 56), 399 (25, M – CO), 371 (20, M – 2CO), 343 (17, M – 3CO) and 235 (17%, M – 5CO – Cr). UV/VIS: λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂) 243 (11800), 260 (11200), 309 (11400), 355 (6200) and 528 (2500); (CH₃CN) 227 (14400), 252 (14900), 309 (8000), 346 (9300) and 504 (3800).

Crystallography

Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using the ω - 2θ scan mode. Unit cell dimensions were determined from the angular setting of 25 reflections. Crystal data and details of data collection are given in Table 2. A semiempirical absorption correction (Ψ scan) was applied for all complexes. Structures were solved with direct methods (SHELXS 86)⁴² and refined with standard methods (refinement against F values with XTAL 3.4).⁴³

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