First Hyperpolarizabilities of Manganese(I)−Chromium(0) Sesquifulvalene Complexes

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Dedicated to Hedda Meyer on the occasion of her 60th birthday

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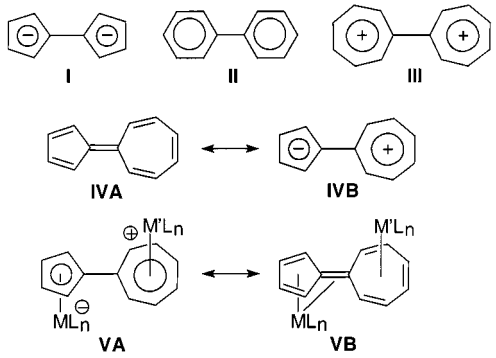
The synthesis of monometallic manganese and bimetallic manganese–chromium complexes incorporating the sesquifulvalene derivatives 2-(2,4,6-cycloheptatrien-1-ylidene)indene (**VI**) and [(2,4,6-cycloheptatrien-1-ylidene)ethenylidene]cyclopentadiene (**VII**) is reported. Charge separation is observed upon complexation and stabilization of **VI** and **VII** by metal centers, and the spectroscopic and structural properties of [(**VI**)$Mn(CO)_3$]BF_4 (**6**), [$(OC)_3$Mn(μ-**VI**)$Cr(CO)_3$]BF_4 (**8**), [(**VII**)$Mn(CO)_3$]BF_4 (**13**), and [$(OC)_3$Mn(μ-**VII**)$Mn(CO)_3$]BF_4 (**15**) are clearly indicative of sesquifulvalene ligands coordinated in a dipolar η^5 or μ-η^5:η^7 fashion, respectively. The coplanar cyclopentadienyl and cycloheptatrienyl fragments act as strongly coupled electron-donating and -accepting groups and strong negative solvatochromism is observed for complexes **6**, **8**, **13**, and **15**. Accordingly, exceptionally large first molecular hyperpolarizabilities β have been determined by means of hyper Raleigh scattering for the bimetallic species **8** and **15**, as well as for some related compounds. The X-ray crystal structures of *anti*-[$(OC)_3$Mn(μ-η^5:η^7-**VI**)$Cr(CO)_3$] (**8**) and *syn*-[$(OC)_3$Mn(μ-η^5:η^7-**VII**)$Cr(CO)_3$] (**15**) are reported.

Introduction

In recent years, considerable effort has been devoted to exploring the organometallic chemistry of η-cycloheptatrienyl ligands and significant progress has been made in the development of new synthetic routes to their metal complexes.[1] However, η-cycloheptatrienyl transition metal complexes, M(η-C_7H_7), still remain poorly explored in comparison with the analogous η-cyclopentadienyl, M(η-C_5H_5), and benzene systems, M(η-C_6H_6). This also holds true in the area of bimetallic complexes with conjugated hydrocarbon-bridged transition metal fragments, which is dominated by ligands containing five- and six-membered rings,[2] e.g. bicyclopentadienyl (**I**)[3,4] and biphenyl (**II**)[5] (Scheme 1). On the other hand, related complexes with the iso-π-electronic hydrocarbon bicycloheptatrienyl (**III**) have been reported only recently by Whiteley and co-workers.[6] Direct linkage of an anionic cyclopentadienyl unit and a cationic cycloheptatrienylium unit gives the cross-conjugated hydrocarbon sesquifulvalene (**IV**), which constitutes a dipolar structural isomer of biphenyl (**II**). Despite the fact that **IV** can be described by resonance structure **IVB** containing two aromatic subunits, it is quite unstable and behaves like a polyene with alternating bond lengths;[7] its ground state electronic structure is best represented by the apolar canonical form **IVA**.



Scheme 1

In contrast, charge separation is observed upon complexation and stabilization of **I** and its derivatives by transition metal fragments,[8−10] and heterobimetallic iron−chromium[9] and manganese−chromium[10] complexes of type **V** have been obtained. The spectroscopic and structural properties of the latter are clearly indicative of sesquifulvalene ligands coordinated in a dipolar μ-η^5:η^7 fashion (resonance structure **VA**, Scheme 1). In these complexes, the cyclopentadienyl and cycloheptatrienyl frag-

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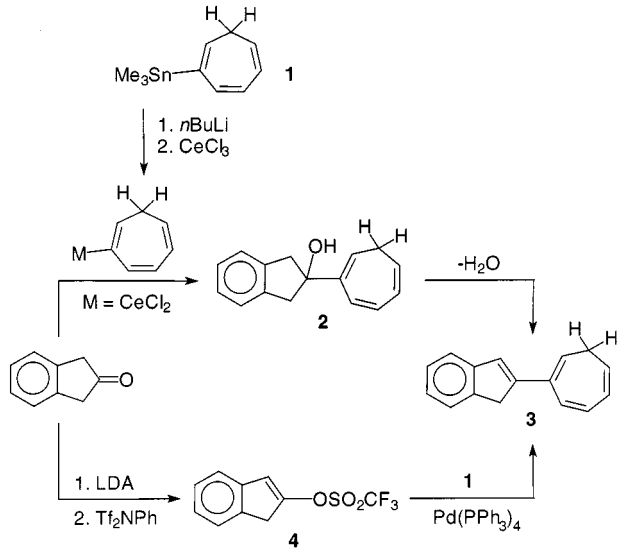
ments act as strongly coupled electron-donating and -accepting groups, respectively, and thus together meet the requirements for the classical construction of compounds with large SHG (second harmonic generation) efficiencies.[11] Accordingly, it has been observed that sesquifulvalene complexes exhibit unusually pronounced nonlinear optical (NLO) properties, and their first molecular hyperpolarizabilities β are among the highest ever measured for organometallic NLO chromophores.[12]

In continuation of our work on transition metal complexes with dipolar cycloheptatrienyl ligands,[8−10,13] we report herein on the syntheses and properties of mono- and bimetallic complexes incorporating either the benzanellated sesquifulvalene derivative 2-(2,4,6-cycloheptatrien-1-ylidene)indene (**VI**) (complexes **6**, **8**) or the "cumulogous" sesquifulvalene [(2,4,6-cycloheptatrien-1-ylidene)ethenylidene]-cyclopentadiene (**VII**) (complexes **13**, **15**). Furthermore, an investigation of the first molecular hyperpolarizabilities of various manganese sesquifulvalene complexes using the hyper Raleigh scattering technique is presented.

Results and Discussion

Synthesis of Complexes 6 and 8

The preparation of sesquifulvalene complexes has hitherto been accomplished by template syntheses, which usually involve a C−C coupling reaction between a cyclopentadienyl complex and a cycloheptatrienyl derivative, followed by complexation of the cycloheptatrienyl unit and/or hydride abstraction.[8]−[10] This synthetic procedure is limited to cyclopentadienyl complexes that can readily be functionalized at the five-membered ring, e.g. by metallation and halogenation reactions.[14] In order to develop methods more widely applicable to the preparation of sesquifulvalene complexes, we became interested in employing dihydrosesquifulvalenes such as **3** (Scheme 2), which can be deprotonated and transferred to metal centers in the same way as ordinary cyclopentadiene derivatives.[15] In principle, dihydrosesquifulvalenes can be prepared by addition of a nucleophilic cyclopentadienyl anion to an electrophilic tropylium cation yielding 1,3,5-cycloheptatrienes bearing the Cp residue in the allylic 7-position.[16] These hydrocarbons are of limited use, however, as complexation of the seven-membered ring can lead to two different stereoisomers with *exo* and *endo* configurations, and this may hamper the ensuing hydride abstraction.[10,17] Therefore, as a suitable starting material we chose 2-trimethylstannyl-1,3,5-cycloheptatriene (**1**), which is functionalized in a vinylic rather than the allylic position, and which can be obtained directly from cycloheptatriene by metallation and subsequent reaction with Me_3SnCl.[10,18] The 1,3,5-cycloheptatrien-2-yl anion can easily be generated and used as a nucleophile by transmetallation of **1** with *n*BuLi.[13b,13c] Hence, its addition to cyclopentenones and subsequent dehydration of the resulting adducts by acidic workup should lead to appropriately substituted dihydrosesquifulvalenes.[15,19]

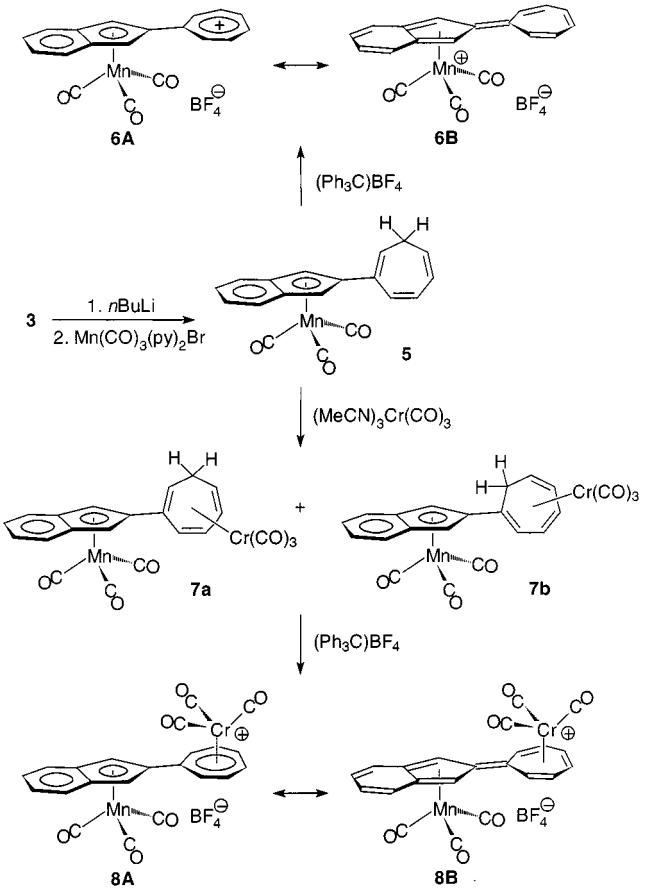


Scheme 2

To test the strategy outlined above, we started with 2-indanone, since the dihydrosesquifulvalene **3** was expected to be stable and isolable in isomerically pure form as a result of benzanellation in the 4,5-positions (Scheme 2). The alcohol **2**, however, could only be isolated in 26% yield from the reaction of 2-indanone with RLi (R = 1,3,5-cycloheptatrienyl-2-yl). Evidently, the lithium complex not only acts as a nucleophile towards the ketone, but the desired addition to the carbonyl group is accompanied by significant simple deprotonation.[20] As organocerium compounds generally exhibit higher nucleophilicity and reduced basicity compared to organolithium compounds,[21] the undesired formation of the enolate anion could be suppressed to some extent by employing $RCeCl_2$ (R = 1,3,5-cycloheptatrienyl-2-yl), although the yield still remained quite low (40%). Dehydration of **2** was then achieved by refluxing in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid using a water trap; subsequent chromatographic separation afforded **3** as a crystalline white solid.[22]

To improve the poor overall yield of **3** (10−20% based on 2-indanone), an alternative route involving a Stille coupling reaction[23] between the triflate **4** and the stannane **1** was used (Scheme 2).[24] Triflate **4** was prepared by deprotonation of 2-indanone with lithium diisopropylamide (LDA) and subsequent reaction of the intermediate enolate with bis(trifluoromethanesulfonato)phenylamine (Tf_2NPh).[25] Stille coupling with a catalytic amount of $Pd(PPh_3)_4$ afforded **3** in at least moderate yield (60% based on **1**, 45% based on 2-indanone). The dihydrosesquifulvalene **3** proved to be indefinitely stable at 0 °C under argon, but was found to slowly decompose in solution over a period of several hours with the deposition of a precipitate. All resonances in the ^1H and ^{13}C NMR spectra could unambiguously be assigned by means of correlated two-dimensional NMR spectroscopy ($^1H,^1H$ and $^1H,^{13}C$ COSY).

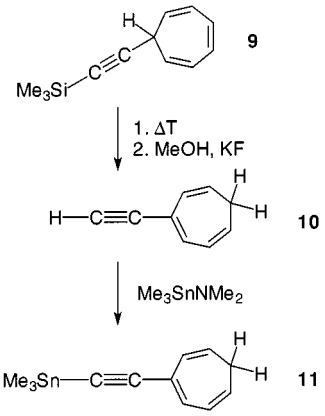
Compound **3** could then be used for the preparation of cycloheptatrienyl-substituted indenyl complexes. In order to assess the influence of benzanellation on the electronic and



Scheme 3

optical properties of sesquifulvalene complexes derived from **3**, complexes **6** and **8** were prepared and compared with the known parent compounds **16** and **17** (Figure 3, vide infra). Treatment of **3** with *n*BuLi followed by $Mn(CO)_3(pyridine)_2Br$[19b,26] produced the cymantrene derivative **5** (Scheme 3). Hydride abstraction at this stage using triphenylcarbenium tetrafluoroborate, $(Ph_3C)BF_4$, led to the monometallic benzosesquifulvalene complex **6**, which could be quantitatively isolated in the form of red-brown crystals. Alternatively, reaction of **5** with $(MeCN)_3Cr(CO)_3$ in refluxing THF gave a mixture of the two bimetallic isomers **7a** and **7b** (**7a**:**7b** ≈ 60:40, Scheme 3). Comparison with the spectroscopic data of related complexes[10] revealed that in **7a** the $Cr(CO)_3$ group is coordinated to a 1,3,5-cycloheptatrien-2-yl ring as expected, whereas **7b** contains a 1,3,5-cycloheptatrien-1-yl ring. The formation of **7b** must have resulted from thermal rearrangement of the coordinated cycloheptatrienyl ring in **7a** through a 1,5-sigmatropic hydrogen migration.[17,27] As both complexes are racemic mixtures of two enantiomers, six resonances are observed for the diastereotopic indenyl protons of each isomer.

Nevertheless, **7a** and **7b** are equally useful for the synthesis of the bimetallic sesquifulvalene complex **8** as the *exo* hydrogen atom in both isomers is easily accessible for hydride abstraction. Indeed, **8** was formed quantitatively upon treatment with $(Ph_3C)BF_4$ and could be isolated in the form of orange-brown crystals.



Scheme 4

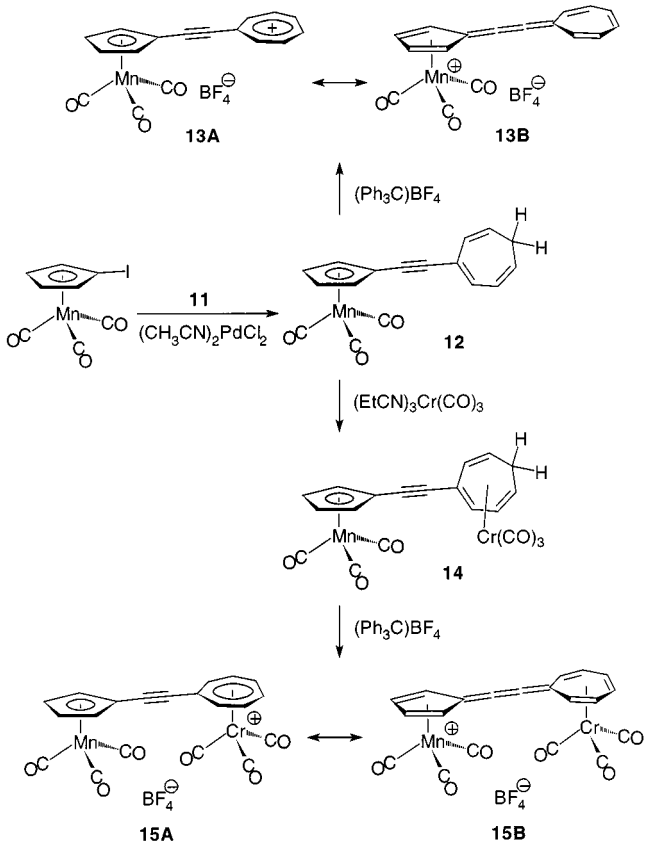
Synthesis of Complexes 13 and 15

The monometallic complex **13** has previously been obtained from the reaction of $[\eta^5\text{-}(LiC{\equiv}CC_5H_4)Mn(CO)_3]$ with tropylium salts, followed by hydride abstraction.[8a] However, the complexation of the intermediate 1,3,5-cycloheptatrien-7-yl derivative could again lead to an isomeric mixture of *exo* and *endo* isomers, which would hamper the required reaction with the trityl cation (vide supra). In order to obtain suitably functionalized ethynylcycloheptatriene derivatives that would allow a high-yielding synthesis of **15**, we followed a route involving the stannane **11** (Scheme 4). 7-Trimethylsilylethynyl-1,3,5-cycloheptatriene (**9**) was found to undergo thermal rearrangement in DMF at 135 °C.[28] Desilylation in methanol in the presence of a catalytic amount of KF[29] followed by distillation yielded a mixture of isomeric hydrocarbons composed almost entirely of 3-ethynyl-1,3,5-cycloheptatriene (**10**) formed by just one 1,5-hydrogen shift. Further hydrogen migrations led to the formation of cycloheptatrienes substituted in the 1- and 2-positions. Treatment of **10** with Me_3SnNMe_2 gave **11**, which could then be used in Stille coupling reactions.

Thus, the Pd-catalyzed reaction of **11** with iodocymantrene, $[\eta^5\text{-}(C_5H_4I)Mn(CO)_3]$,[14a,14b] in DMF afforded a yellow oil, which crystallized on standing at 4 °C for a couple of days (Scheme 5). At this stage, the 1,3,5-cycloheptatrien-3-yl derivative **12** was the only isomer detectable by NMR spectroscopy. As expected, hydride abstraction gave the known monometallic sesquifulvalene complex **13**,[8b] whereas reaction with $(EtCN)_3Cr(CO)_3$ at room temperature produced bimetallic **14**. As the two sides of the seven-membered ring in **13** are enantiotopic, **14** forms a racemic mixture of two enantiomers and its ^{13}C NMR spectrum features five cyclopentadienyl resonances due to the diastereotopic carbon atoms. The allylic *exo* hydrogen atom in **14** is again easily accessible to the trityl cation and **15** can be isolated in quantitative yield as yellow-orange crystals following treatment with $(Ph_3C)BF_4$.

Structural Characterization of Sesquifulvalene Complexes 8 and 15

The molecular structure of the cation in **8** is depicted in Figure 1. The five- and seven-membered rings are almost



Scheme 5

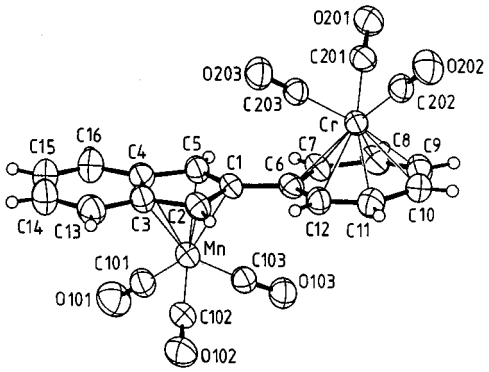


Figure 1. ORTEP drawing of the cation in **8**; selected bond lengths [Å] and angles [°]: Mn−C1 2.110(8), Mn−C2 2.125(11), Mn−C3 2.207(11), Mn−C4 2.236(10), Mn−C5 2.151(10), C1−C2 1.433(12), C2−C3 1.440(14), C3−C4 1.41(2), C4−C5 1.436(13), C5−C1 1.432(12), C1−C6 1.489(12), C6−C7 1.391(12), C7−C8 1.422(14), C8−C9 1.38(2), C9−C10 1.40(2), C10−C11 1.45(2), C11−C12 1.321(14), C12−C6 1.440(13), Cr−C6 2.277(9), Cr−C7 2.222(9), Cr−C8 2.210(10), Cr−C9 2.224(11), Cr−C10 2.206(11), Cr−C11 2.219(11), Cr−C12 2.215(10); (C1−5)(C6−12) 4.6(6)°

perfectly coplanar [dihedral angle of 4.6(6)°]. The ligand coordinates to the $Mn(CO)_3$ and $Cr(CO)_3$ fragments in η^5 and η^7 modes, respectively, and the fragments adopt an *anti*-facial arrangement. Unfortunately, due to the high absorption coefficient (see Experimental Section), the structure could only be refined with reduced accuracy, thus preventing a very detailed discussion of the bonding geometry. Nevertheless, the inter-ring bond length in **8** [C1−C6 = 1.489(12) Å] clearly corresponds to a $C(sp^2)-C(sp^2)$ single bond, and hence the solid-state structure of **8** is evidently that of an indenyl-cycloheptatrienyl complex and is best described by canonical form **8A** in Scheme 4. However, a minor contribution from resonance form **8B** could be deduced from the observation that the bonding between the seven-membered ring and the $Cr(CO)_3$ moiety is slightly distorted towards a fulvene-type coordination geometry, the Cr−C6 bond length [2.277(9) Å] being significantly longer than the remaining Cr−C distances [average 2.216(10) Å].

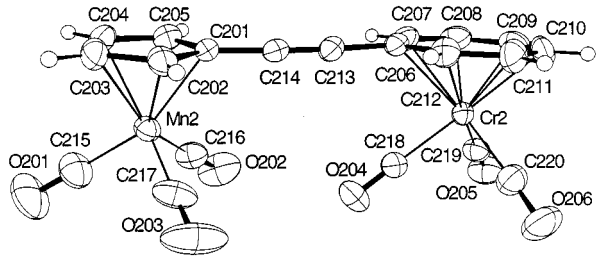


Figure 2. ORTEP drawing of one cation in **15**·CH_2Cl_2; the asymmetric unit contains two independent molecules of **15**; selected bond lengths [Å] and angles [°]: molecule 2 [molecule 1] Mn2−C201 2.122(3) [2.132(3)], Mn2−C202 2.124(3) [2.134(3)], Mn2−C203 2.139(3) [2.148(3)], Mn2−C204 2.150(3) [2.144(3)], Mn2−C205 2.134(3) [2.135(3)], C201−C202 1.422(5) [1.421(4)], C202−C203 1.400(5) [1.403(4)], C203−C204 1.403(6) [1.407(5)], C204−C205 1.403(5) [1.405(4)], C201−C214 1.424(4) [1.424(4)], C214−C213 1.186(4) [1.189(4)], C213−C206 1.434(4) [1.435(4)], C206−C207 1.416(4) [1.407(4)], C207−C208 1.382(4) [1.394(4)], C208−C209 1.400(5) [1.404(5)], C209−C210 1.377(6) [1.382(5)], C210−C211 1.416(6) [1.411(5)], C211−C212 1.395(5) [1.386(4)], C212−C206 1.411(4) [1.425(4)], Cr2−C206 2.261(3) [2.266(3)], Cr2−C207 2.234(3) [2.249(3)], Cr2−C208 2.223(3) [2.210(3)], Cr2−C209 2.221(3) [2.235(3)], Cr2−C210 2.222(3) [2.231(3)], Cr2−C211 2.213(4) [2.222(3)], Cr2−C212 2.251(3) [2.234(3)]; C201−C214−C213 177.8(3) [178.2(3)], C214−C213−C206 176.1(3) [177.5(3)]; (C201−205)(C206−212) 5.4(0)° [17.2(0)°]

In **15**, the asymmetric unit contains two independent molecules with both cations adopting a *syn*-facial conformation. The molecular structure of one cation is shown in Figure 2. The two cations differ slightly in the relative orientations of their *cyclo*-C_5 and *cyclo*-C_7 units, the relevant dihedral angles being 5.4(4)° and 17.2(4)°. Within experimental error, the bond lengths and angles in the two molecules are almost identical and correspond to a solid-state structure best described by canonical form **15A** in Scheme 5. For instance, the C(sp)−C(sp) bonds are clearly triple bonds [C113−C114 = 1.189(4) Å and C213−C214 = 1.186(4) Å]. Furthermore, the intra-ring bond lengths do not alternate significantly, as befits aromatic cyclopentadienyl and cycloheptatrienyl units.

Spectroscopic Properties of Sesquifulvalene Derivatives

The NMR spectroscopic data of the mono- and bimetallic complexes **6**, **8**, **13**, and **15** confirm that complexation of the sesquifulvalene derivatives leads to charge separation within the ligands and to dipolar coordination of the respective hydrocarbon. Accordingly, low-field resonances at $\delta \approx 9$ are observed for the cycloheptatrienyl protons in monometallic **6** and **13**, which fall in the expected range for tropylium cations of the type $(C_7H_6R)^+$.[30] As a result of coordination of the seven-membered rings to the $Cr(CO)_3$ moieties, these resonances are shifted to significantly higher

Table 1. UV/Vis data for complexes **6**, **8**, **13**, and **15**

Compound	λ_{max} [nm] CH_2Cl_2	CH_3CN	$\Delta\tilde{\nu}$ [cm^{-1}]
6	501	471	−1270
8	486	468	−790
13	537	491	−1740
15	449	429	−1040

field in bimetallic **8** and **15** (δ = 6.25−6.50) and are wholly consistent with the values expected for cycloheptatrienyl complexes of the type $[\eta^7\text{-}(C_7H_6R)Cr(CO)_3]$.[17,31]

As mentioned above, the four sesquifulvalene derivatives are intensely colored compounds. They show strong solvatochromic behaviour and their UV/Vis spectra are markedly solvent-dependent, which is usually a good indication of possible NLO activity.[32] The lowest-energy band λ_{max} (Table 1) is most strongly shifted upon changing the solvent from dichloromethane to acetonitrile ($\Delta\tilde{\nu}$ ranging from −790 cm^{-1} in **8** to −1740 cm^{-1} in **13**). On the basis of these hypsochromic shifts (negative solvatochromic behaviour), the lowest-energy transition in these systems can be assigned to a π to π^* CT transition,[33] which is APPROXIMATELY (!) represented by the canonical forms **A** (ground state) and **B** (excited state) shown in Scheme 3 for **6** and **8** and in Scheme 5 for **13** and **15**.

The bimetallic derivatives **8** and **15** absorb at higher energy than the corresponding monometallic complexes **6** and **13**, and λ_{max} is hypsochromically shifted upon complexation of the seven-membered ring. This observation implies that interaction of the $Cr(CO)_3$ group with the cycloheptatrienyl unit increases the HOMO/LUMO energy gap of the relevant π to π^* CT excitation. In other words, the $[(C_7H_6R)Cr(CO)_3]$ moiety has a stronger ability to effectively stabilize a positive charge than the "naked" tropylium system, which leads to an increase in the energy difference between the two limiting resonance structures **A** and **B** (Schemes 3 and 5).

Nonlinear Optical Properties of Sesquifulvalene Derivatives

It has been demonstrated that sesquifulvalene complexes are among the most promising organometallic candidates for nonlinear optical applications.[9] Consequently, we have measured the first molecular hyperpolarizabilities β of selected monometallic manganese and bimetallic manganese−chromium sesquifulvalene complexes (Figure 3) using the hyper Raleigh scattering technique (HRS), which allows determination of β in solution even for ionic compounds.[34] Here, HRS experiments were performed with an Nd:YAG laser (λ = 1064 nm). The intensity of the frequency-doubled scattered light ($\lambda/2$ = 532 nm) was measured as a function of the concentration of the NLO chromophore. The results are shown in Table 2.

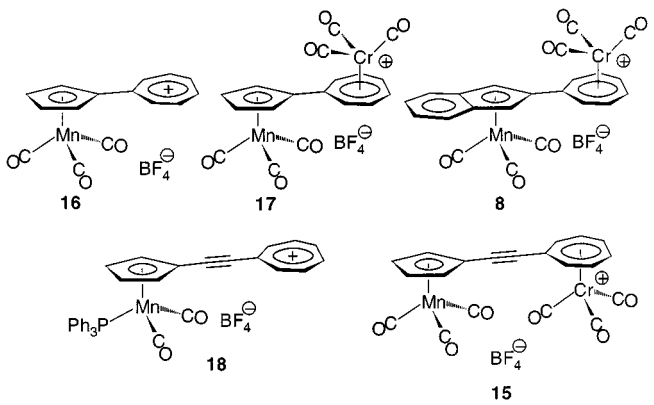


Figure 3. Sesquifulvalene complexes studied by hyper Raleigh scattering

Table 2. UV/Vis and NLO data for selected sesquifulvalene complexes

Compound	Solvent[a]	λ_{max}, nm	β, 10^{-30} esu[b]	β_0, 10^{-30} esu[b][c]
8	CH_3NO_2	435	112	31
15	CH_2Cl_2	449	244	58
16	CH_3NO_2	510	240	15
17	CH_3NO_2	445	77	19
18	CH_2Cl_2	751	226	113

[a] Solutions of *p*-nitroaniline as external reference [$\beta(CH_2Cl_2)$ = 21.6 × 10^{-30} esu, $\beta(CH_3NO_2)$ = 34.6 × 10^{-30} esu]. − [b] β-values in electrostatic units (esu) of the CGS systems (Gaussian system); $[\beta_{CGS}] = cm^4/statV = esu$; $[\beta_{SI}] = Cm^3/V^2 = C^3m^3/J^2$; $\beta_{SI} = (1/3)^3 \times 10^{-19}\ \beta_{CGS}$ (see ref.[12a]). − [c] $\beta_0 = \beta\,[(1 - 4\lambda_{max}^2/\lambda^2)\,(1 - \lambda_{max}^2/\lambda^2)]$ with λ = 1064 nm (Nd:YAG laser) (see refs.[34a,35]).

The β values in Table 2 are unusually large owing to resonance enhancement, which occurs when the frequency of the charge-transfer excitation is close to the frequency of the stimulating laser or close to the doubled frequency. Therefore, extrapolation of the dynamic hyperpolarizabilities β to their static counterparts β_0 was accomplished by means of the two-level model (Table 2).[34a,35] The first molecular hyperpolarizabilities presented here are very high compared to those of organic[11,36] or organometallic[12] compounds with chromophores of similar lengths. Comparison of the nonlinear optical efficiency of bimetallic **15** with that of the related ferrocene derivative $[(C_5H_5)Fe(\mu\text{-}\eta^5\text{:}\eta^7\text{-}C_5H_4\text{−}C{\equiv}C\text{−}C_7H_6)Cr(CO)_3]BF_4$ ($\beta_0 = 105 \times 10^{-30}$ esu)[9] shows that the ferrocene moiety is superior to the cymantrene unit, $(C_5H_4R)Mn(CO)_3$, probably due to its stronger electron-donating ability. However, the electronic and optical properties of these manganese complexes can be easily and efficiently tuned by ligand substitution reactions,[8b] and the introduction of a phosphane ligand to give monometallic **18** results in extraordinary frequency-doubling characteristics. Furthermore, this protocol could be extended to the introduction of readily available chiral phosphanes leading to optically active compounds that can be expected to crystallize in noncentrosymmetric space groups, thereby fulfilling a crucial requirement for the observation of macroscopic NLO effects.[11,12]

Conclusion

In summary, we have presented new methods for the syntheses of sesquifulvalene complexes that can be considered

as widely applicable for the preparation of various other bimetallic complexes. In particular, use of the appropriately substituted cycloheptatrienyl derivatives **3** and **11** circumvents the *exo*/*endo* problem encountered with the 1,3,5-cycloheptatrien-7-yl derivatives and facilitates high-yielding syntheses. Finally, the first hyperpolarizabilities determined for various manganese sesquifulvalene complexes confirm the suitability of such complexes for nonlinear optical applications.

Experimental Section

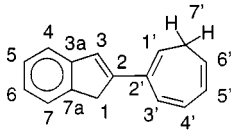
General: All operations were performed under an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. The following compounds were prepared as described in the literature: $Mn(CO)_3(pyridine)_2Br$,[26] $(C_5H_4I)Mn(CO)_3$,[14a] $(CH_3CN)_3Cr(CO)_3$,[37] $(CH_3CH_2CN)_3Cr(CO)_3$,[38] 2-trimethylstannyl-1,3,5-cycloheptatriene (**1**).[10] The synthesis of **13** has been published previously.[8a] Complete assignment of all resonances in **3** and **10** was achieved with the aid of two-dimensional NMR spectroscopy ($^1H,^1H$ and $^1H,^{13}C$ COSY experiments).

2-(1,3,5-Cycloheptatrien-2-yl)indan-2-ol (2). − Method A: A solution of **1** (1.59 g, 6.24 mmol) in THF (30 mL) was treated with *n*-butyllithium (2.5 mL of a 2.5 M solution in hexane, 6.3 mmol) at −78 °C. After stirring for 45 min, a solution of 2-indanone (0.79 g, 5.98 mmol) in THF (15 mL) was added. The reaction mixture was then allowed to warm to room temperature and stirring was continued for 12 h. Quenching with aqueous HCl (24%, 2 mL) and ice (6 g) resulted in the formation of **2**. After 30 min, the reaction mixture was made alkaline with aqueous ammonia solution (3.5%) and then diluted with brine (20 mL). It was then extracted with diethyl ether (3 × 20 mL) and the combined extracts were dried over Na_2SO_4 and concentrated. Chromatography of the residue on alumina (4% H_2O) eluting with dichloromethane gave **2** as a white solid. Yield: 0.35 g (26%).

Method B: At −78 °C, a suspension of $CeCl_3$ (2.88 g, 11.68 mmol) in THF (35 mL) was added to a solution containing the 1,3,5-cycloheptatrien-2-yl anion, which had been generated from a solution of **1** (2.54 g, 9.96 mmol) in THF (50 mL) and *n*-butyllithium (4.0 mL of a 2.5 M solution in hexane, 10.0 mmol) as described above (Method A). After stirring for 30 min, a solution of 2-indanone (1.19 g, 9.00 mmol) in THF (9 mL) was added dropwise and stirring was continued for 15 h at −74 °C. The reaction mixture was then allowed to warm to room temperature, whereupon TMEDA (ca. 2.6 mL) was added. After 30 min, the reaction mixture was quenched with aqueous $NaHCO_3$ and diluted with brine. Extraction with dichloromethane (3 × 100 mL), drying of the combined extracts with Na_2SO_4, and evaporation of the solvent afforded **2**, which could be purified chromatographically as described above. Yield: 0.81 g (40%). − ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.32−7.22 (m, 4 H, C_6H_4), 6.83 (d, 1 H, C_7 ring: CH), 6.65 (dd, 1 H, C_7 ring: CH), 6.15 (dd, 1 H, C_7 ring: CH), 5.63 (t, 1 H, C_7 ring: CH), 5.54 (dt, 1 H, C_7 ring: CH), 3.36 (d, 2 H, C_5 ring: CH_2), 3.06 (d, 2 H, C_5 ring: CH_2), 2.26 (t, 2 H, C_7 ring: CH_2); no OH resonance could be observed.

2-(1,3,5-Cycloheptatrien-2-yl)indene (3). − Method A: A solution of **2** (1.75 g, 7.80 mmol) in benzene (30 mL) was treated with a catalytic amount of *p*-toluenesulfonic acid and refluxed for 12 h in an apparatus fitted with a water trap. After removal of the solvent in vacuo, the crude product was purified by chromatography on silica (4% H_2O) using petroleum ether/dichloromethane (3:1) as eluent to afford **3** as a white crystalline solid. Yield: 0.60 g (37%).

Method B: At room temperature, a suspension of lithium chloride (2.41 g, 56.85 mmol) and $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol) in THF (20 mL) was treated with a solution of **4** (2.05 g, 7.76 mmol) in THF (20 mL). After stirring for 15 min, a solution of stannane **1** (1.97 g, 7.73 mmol) in THF (20 mL) was added and the resulting mixture was refluxed for 16 h. The dark-green solution thus obtained was then diluted with pentane (200 mL) and treated with aqueous ammonia solution (10%, 3 × 75 mL). The organic layer was separated, dried with Na_2SO_4, and the solvent was removed in vacuo. Crude **3** (Figure 4) could be purified chromatographically as described above. Yield: 0.98 g (61%); m.p. 92 °C. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.37 (d, *J* = 6 Hz, 1 H, 7-H), 7.29 (d, *J* = 6 Hz, 1 H, 4-H), 7.22 (dd, *J* = 6 Hz, 6 Hz, 1 H, 6-H), 7.13 (dd, *J* = 6 Hz, 6 Hz, 1 H, 5-H), 7.07 (d, *J* = 9 Hz, 1 H, 3′-H), 6.78 (s, 1 H, 3-H), 6.69 (dd, *J* = 9 Hz, 5 Hz, 1 H, 4′-H), 6.18 (dd, *J* = 6 Hz, 5 Hz, 1 H, 5′-H), 5.74 (t, *J* = 8 Hz, 1 H, 1′-H), 5.60 (td, *J* = 8 Hz, 6 Hz, 1 H, 6′-H), 3.56 (s, 2 H, 1-H), 2.35 (t, *J* = 8 Hz, 2 H, 7′-H). − ^{13}C NMR ($CDCl_3$, 100.4 MHz): δ = 146.6 (C-7a), 145.5 (C-3a), 142.7 (C-2), 134.4 (C-2′), 131.5 (C-4′), 130.1 (C-3′), 127.0 (C-3), 126.9 (C-5′), 126.4 (C-6), 124.5 (C-5), 123.7 (C-6′), 123.4 (C-7), 120.7 (C-4), 119.7 (C-1′), 39.1 (C-1), 27.7 (C-7′). − MS (EI); *m*/*z* (%): 206 (100) [M^+], 191 (43) [$M - CH_3]^+$, 115 (26) [$M - C_7H_7]^+$, 91 (76) [$M - C_9H_7]^+$, 65 (5) [$M - C_9H_7 - C_2H_2]^+$. − $C_{16}H_{14}$ (206.3): calcd. C 93.16, H 6.84; found C 92.01, H 6.81



3

Figure 4. Numbering scheme for **3**

1*H*-Inden-2-yl Trifluoromethanesulfonate (4): A solution of diisopropylamine (2.1 mL, 15.0 mmol) in THF (15 mL) was treated with *n*-butyllithium (5.3 mL of a 2.5 M solution in hexane, 13.3 mmol) at −78 °C and the resulting mixture was allowed to warm to room temperature. The LDA solution thus obtained was then cooled to −78 °C once more, whereupon a solution of 2-indanone (1.39 g, 10.52 mmol) in THF (11 mL) was added. After 15 min at −78 °C, stirring was continued for 2 h at ambient temperature. The enolate solution was then treated with a solution of *N*,*N*-bis(trifluoromethanesulfonyl)aniline (4.20 g, 11.76 mmol) in THF (25 mL) at −78 °C and the resulting mixture was stirred at room temperature for 10 h. It was then diluted with aqueous NH_4Cl solution (20 mL) and extracted with diethyl ether (3 × 40 mL). After removal of the solvent from the combined extracts, the oily residue was purified by column chromatography on silica (4% H_2O) using petroleum ether/dichloromethane (5:1) as eluent to afford the sulfonate **4** as a yellow oil, which was dried in vacuo. Yield: 2.05 g (74%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.42−7.24 (m, 4 H, C_6H_4), 6.70 (s, 1 H, 1-H), 3.68 (s, 2 H, 3-H).

Manganese Complex 5: At −50 °C, a solution of **3** (0.98 g, 4.75 mmol) in THF (40 mL) was treated with *n*-butyllithium (2.0 mL of a 2.5 M solution in hexane, 5.0 mmol). After stirring for 60 min, a solution of $Mn(pyridine)_2(CO)_3Br$ (2.10 g, 5.57 mmol) in THF (60 mL) was added dropwise and the resulting mixture was refluxed for 3 h. Removal of the solvent in vacuo and purification of the residue by column chromatography on alumina (4% H_2O)

eluting with petroleum ether/dichloromethane (5:1) afforded **5** as a yellow crystalline solid. Yield: 1.04 g (64%); m.p. 41 °C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44 (d, 2 H, C_6 ring: CH), 7.09−7.07 (m, 3 H, C_6 ring: CH + C_7 ring: CH), 6.74 (s, 2 H, C_5 ring: CH), 6.23−6.19 (m, 2 H, C_7 ring: CH), 5.73 (t, 1 H, C_7 ring: CH), 5.54 (dt, 1 H, C_7 ring: CH), 2.40 (t, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$, 100.4 MHz): δ = 224.9 (Mn−CO), 132.7 (C_7 ring: CH), 130.5 (C_7 ring: C-2), 129.3, 127.0 (C_7 ring: CH), 126.4, 125.2 (C_6 ring: CH), 122.9, 119.1 (C_7 ring: CH), 108.9 (C_5 ring: C-1), 103.1 ($C_{5/6}$ ring: C), 69.9 (C_5 ring: CH), 27.5 (CH_2). − MS (EI); *m*/*z* (%): 344 (11) [M^+], 316 (4) [M − CO]$^+$, 288 (5) [M − 2CO]$^+$, 260 (64) [M − 3CO]$^+$, 205 (100) [M − 3CO − Mn]$^+$, 191 (28) [M − 3CO − Mn − CH_2]$^+$, 178 (7) [M − 3CO − Mn − H − C_2H_2]$^+$. − IR (KBr): ν (CO) = 2010, 1935, 1914 cm^{-1}. − $C_{19}H_{13}MnO_3$ (344.3): calcd. C 66.29, H 3.81; found C 65.89, H 4.19.

Manganese Benzosesquifulvalene Complex 6: At −78 °C, a solution of **5** (130 mg, 0.38 mmol) in dichloromethane (5 mL) was treated with a solution of $(Ph_3C)BF_4$ (90 mg, 0.27 mmol) in dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature and stirring was continued for 1 h. On addition of diethyl ether (80 mL), **6** precipitated as a red-brown crystalline solid and was collected by filtration. Yield: (70 mg, 60%). − ^{1}H NMR (CD_3CN, 250 MHz): δ = 9.16 (m, 2 H, C_7 ring: CH), 8.87 (m, 4 H, C_7 ring: CH), 7.78 (m, 2 H, C_6 ring: CH), 7.30 (m, 2 H, C_6 ring: CH), 6.44 (s, 2 H, C_5 ring: CH). − ^{13}C NMR (CH_3CN, 100.4 MHz): δ = 224.9 (Mn−CO), 166.7 (C_7 ring: C-1), 154.1 (C_7 ring: CH), 153.5 (C_7 ring: CH), 150.8 (C_7 ring: CH), 129.8 (C_6 ring: CH), 126.0 (C_6 ring: CH), 106.6 ($C_{5/6}$ ring: C), 98.7 (C_5 ring: C-1), 77.3 (C_5 ring: CH). − MS (FAB POS); *m*/*z* (%): 343 (100) [M^+], 287 (8) [M − 2CO]$^+$, 259 (65) [M − 3CO]$^+$, 204 (67) [M − 3CO − Mn]$^+$, 178 (10) [M − 3CO − Mn − C_2H_2]$^+$. − IR (KBr): ν (CO) = 2017, 1953, 1928 cm^{-1}. − UV/Vis (CH_2Cl_2): λ (lg ε) = 297 (4.17), 501 (4.45) nm. − UV/Vis (CH_3CN): λ (lg ε) = 296 (4.05), 354 (4.09), 471 (4.25) nm. − $C_{19}H_{12}BF_4MnO_3$ (430.0): calcd. C 53.07, H 2.81; found C 53.42, H 3.68.

Mixture of Manganese−Chromium Complexes 7a, 7b: A mixture of $(MeCN)_3Cr(CO)_3$ (0.83 g, 3.20 mmol) and **5** (0.85 g, 2.47 mmol) was dissolved in THF (50 mL) and the resulting solution was refluxed for 60 min The solvent was then removed in vacuo and the residue was extracted with dichloromethane. Purification by column chromatography on alumina (4% H_2O) eluting with petroleum ether/dichloromethane (4:1) afforded the mixture **7a/7b** as a red-brown solid. Yield: 0.74 g (62%). − MS (EI); *m*/*z* (%): 480 (21) [M^+], 424 (8) [M − 2CO]$^+$, 396 (46) [M − 3CO]$^+$, 368 (10) [M − 4CO]$^+$, 340 (69) [M − 5CO]$^+$, 312 (100) [M − 6CO]$^+$, 257 (87) [M − 6CO − Mn]$^+$, 205 (24) [M − 6CO − Mn − Cr]$^+$. − IR (KBr): ν (CO) = 2060, 2018, 1938 cm^{-1}. − $C_{22}H_{13}CrMnO_6$ (480.3): calcd. C 55.02, H 2.73; found C 55.60, H 3.08

Manganese−Chromium Benzosesquifulvalene Complex 8: At −78 °C, a solution of **7** (0.74 g, 1.54 mmol) in dichloromethane (10 mL) was treated with a solution of $(Ph_3C)BF_4$ (0.41 g, 1.24 mmol) in dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature, whereupon stirring was continued for a further 90 min. On addition of diethyl ether (90 mL), **8** was precipitated as orange-brown crystals and was collected by filtration. Yield: 0.55 g (79%). − ^{1}H NMR (CD_3CN, 250 MHz): δ = 7.64 (m, 2 H, C_6 ring: CH), 7.28 (m, 2 H, C_6 ring: CH), 6.74−6.50 (m, 6 H, C_7 ring: CH), 6.16 (s, 2 H, C_5 ring: CH). − ^{13}C NMR (CD_3CN, 100.4 MHz): δ = 225.40 (Cr−CO), 221.46 (Mn−CO), 129.21 (C_6 ring: CH), 125.99 (C_6 ring: CH), 119.45 (C_7 ring: C-1), 105.77 (C_7 ring: CH), 105.31 ($C_{5/6}$ ring: C), 104.85 (C_7 ring: CH), 102.07 (C_5 ring: C-1), 101.91 (C_7 ring: CH), 74.17 (C_5 ring: CH). − MS (FAB POS); *m*/*z* (%): 479 (66) [M^+], 423 (34) [M − 2CO]$^+$, 395 (85) [M − 3CO]$^+$, 259 (42), [M − 6CO − Cr]$^+$, 204 (63), [M − 6CO − Cr − Mn]$^+$. − IR (KBr): ν (CO) = 2012, 1923, 1873 cm^{-1}. − UV/Vis (CH_2Cl_2): λ (lg ε) = 321 (2.77), 486 (2.44) nm. − UV/Vis (CH_3CN): λ (lg ε) = 299 (3.38), 468 (2.86) nm. − $C_{22}H_{12}BCrF_4MnO_6$ (566.1): calcd. C 46.68, H 2.14; found C 45.32, H 2.65

X-ray Crystal Structure Analysis of 8:[39] $C_{22}H_{12}BCrF_4MnO_6$, M_r = 566.1, dark brown crystal, dimensions 0.65 × 0.25 × 0.20 mm, *a* = 16.486(3) Å, *b* = 7.992(1) Å, *c* = 17.548(5) Å, β = 102.60(2)°, *V* = 2256.4(8) Å^3, $\rho_{calcd.}$ = 1.666 g cm^{-3}, *F*(000) = 1128 e, μ = 9.173 mm^{-1}, no absorption correction applied, *Z* = 4, monoclinic, space group $P2_1/a$ (No. 14), λ = 1.54176 Å, *T* = 293 K, ω scans, 2850 reflections collected in the θ range between 2.58 and 59.94° (−18 ≤ *h* ≤ 17, 0 ≤ *k* ≤ 8, 0 ≤ *l* ≤ 19), 2834 observed reflections [$I \geq 2\sigma(I)$], 320 refined parameters, R = 0.0962, wR^2 = 0.2516, max. residual electron density 0.926 (−0.463) e Å^{-3}. Data were collected with an Enraf−Nonius Turbo-CAD4 diffractometer equipped with a rotating anode generator. Structure solution with SHELXS-86, structure refinement with SHELXL-93, graphics with ORTEP.

7-(Trimethylsilylethynyl)-1,3,5-cycloheptatriene (9): A solution of trimethylsilylacetylene (3.04 g, 30.0 mmol) in THF (10 mL) was treated with *n*-butyllithium (12.4 mL, 2.5 M solution in hexane, 31.0 mmol) at −40 °C. After stirring for 30 min at ambient temperature, the acetylide solution was added to a suspension of $(C_7H_7)BF_4$ (5.0 g, 28.1 mmol) in THF (100 mL) at −40 °C. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm to room temperature, whereupon saturated NH_4Cl solution (100 mL) was added. The resulting mixture was extracted with diethyl ether (3 × 50 mL) and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent and distillation of the residue at 0.07 mbar and 50−52 °C afforded **9** as a clear, yellowish oil. Yield: 4.36 g (82%). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.63 (m, 2 H, 3,4-H), 6.18 (m, 2 H, 2,5-H), 5.33 (dd, 2 H, 1,6-H), 2.50 (tt, 1 H, 7-H), 0.20 (s, 9 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 130.9 (C-3,4), 124.6 (C-2,5), 123.0 (C-1,6), 108.0 (*C*≡C−$SiMe_3$), 84.5 (C≡*C*−$SiMe_3$), 32.6 (C-7), 0.1 ($SiCH_3$).

3-Ethynyl-1,3,5-cycloheptatriene (10): A solution of **9** (4.0 g, 21.2 mmol) in DMF (40 mL) was heated to 150 °C for 3 h. After evaporation of the solvent, the dark-brown concentrated reaction mixture was taken up in methanol and treated with a catalytic amount of KF (50 mg). The resulting mixture was stirred for 3 days at room temperature, then cooled to 0 °C, whereupon the product was separated by adding saturated NH_4Cl solution (60 mL). Extraction with diethyl ether (3 × 10 mL), drying of the combined extracts over $MgSO_4$, and careful removal of the solvent in vacuo afforded crude **10**, which could be obtained as a colorless liquid by distillation at 15 mbar. Yield: 1.52 g (62%). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.95 (d, *J* = 6 Hz, 1 H, 4-H), 6.19 (d, *J* = 9 Hz, 1 H, 2-H), 6.17 (dd, *J* = 9 Hz, 6 Hz, 1 H, 5-H), 5.51 (dt, *J* = 9 Hz, 7 Hz, 1 H, 6-H), 5.39 (dt, *J* = 9 Hz, 7 Hz, 1 H, 1-H), 3.02 (s, 1 H, C≡CH), 2.28 (dd, *J* = 7 Hz, 7 Hz, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$, 100.4 MHz): δ = 137.1 (C-4), 128.2 (C-2), 126.3 (C-5), 124.4 (C-3), 124.0 (C-6), 121.8 (C-1), 85.4 (*C*≡CH), 77.1 (C≡*C*H), 27.6 (C-7). − MS (EI); *m*/*z* (%): 116 (41) [M^+], 115 (100) [M − H]$^+$.

3-(Trimethylstannylethynyl)-1,3,5-cycloheptatriene (11): Me_3SnNMe_2 (1.8 g, 8.6 mmol) was added to **10** (1.0 g, 8.6 mmol) and the reaction mixture was stirred without a solvent for 5 min at ambient temperature. After evaporation of the Me_2NH formed, **11** was isolated in quantitative yield as a yellow-orange oil, which was suffi-

ciently pure for use in further reactions. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.91 (d, 1 H, CH), 6.16 (d + dd, 2 H, CH), 5.44 (m, 2 H, CH), 2.28 (t, 2 H, CH_2), 0.31 ($SnCH_3$). – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 136.3, 128.5, 126.4 (CH), 125.7 (Sn−C≡C−*C*), 123.6, 121.8 (CH), 110.6, 93.3 (C≡C), 27.6 (CH_2), −7.7 ($SnCH_3$).

Manganese Complex 12: $(C_5H_4I)Mn(CO)_3$ (2.44 g, 7.39 mmol) and **11** (1.80 g, 6.45 mmol) were dissolved in DMF (50 mL) and $Pd(CH_3CN)_2Cl_2$ (60 mg) was added. The solution turned brown and stirring was continued for 12 h at room temperature. After the addition of diethyl ether (50 mL) followed by a solution of KF (750 mg) in water (25 mL), the mixture was stirred for 1 h while argon was bubbled through it. The organic phase was then separated and washed with water (3 × 100 mL). The combined aqueous phases were extracted with diethyl ether (2 × 50 mL) and the ethereal extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, the crude product was purified by chromatography on silica (4% H_2O) eluting with petroleum ether/CH_2Cl_2 (10:1). Evaporation of the solvent from the appropriate fraction afforded **12** as a yellow oil, which solidified on storage in a refrigerator at 4 °C. Yield: 2.05 g (87%). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.91 (d, 1 H, C_7 ring: CH), 6.18 (m, 2 H, C_7 ring: CH), 5.46 (m, 2 H, C_7 ring: CH), 5.00 (br. s, 2 H, C_5 ring: CH), 4.69 (br. s, 2 H, C_5 ring: CH), 2.31 (t, 2 H, CH_2). – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 224.3 (Mn−CO), 136.7, 127.8, 126.3 (C_7 ring: CH), 124.5 (C_7 ring: C-3), 124.1, 122.0 (C_7 ring: CH), 90.5 (C_5 ring: C-1), 86.0 (C_5 ring: CH), 83.1 (C≡C), 82.0 (C_5 ring: CH), 81.4 (C≡C), 27.6 (CH_2). – MS (EI); *m*/*z* (%): 318 (84) [M^+], 262 (71) [M − 2CO]$^+$, 234 (100) [M − 3CO]$^+$, 179 (62) [M − 3CO − Mn]$^+$. – IR(KBr): $\tilde{\nu}$ = 2222 (C≡C), 2021, 1932 (CO) cm^{-1}. – $C_{17}H_{11}MnO_3$ (318.2): calcd. C 64.17, H 3.48; found C 64.10, H 3.77.

Manganese−Chromium Complex 14: To a solution of **12** (1.0 g, 3.1 mmol) in THF (20 mL) was added $(CH_3CH_2CN)_3Cr(CO)_3$ (1.1 g, 3.8 mmol) as a solid. The mixture was stirred at ambient temperature for 3 days. After removal of the solvent in vacuo, the crude product was purified by chromatography on silica (4% H_2O) eluting with petroleum ether/CH_2Cl_2 (3:1). Evaporation of the solvent afforded **14** as an orange-red crystalline solid. Yield: 770 mg (55%). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.29 (d, 1 H, C_7 ring: CH), 5.09 (s, 2 H, C_5 ring: CH), 5.00 (d, 1 H, C_7 ring: CH), 4.83 (t, 1 H, C_7 ring: CH), 4.74 (s, 2 H, C_5 ring: CH), 3.39 (m, 2 H, C_7 ring: CH), 2.95 (m, 1 H, 7-*endo*-H), 1.83 (dm, 1 H, 7-*exo*-H). – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 231.2 (Cr−CO), 224.1 (Mn−CO), 103.9, 100.7, 99.2 (C_7 ring: CH), 94.9 (C_7 ring: C-3), 89.5 (C_5 ring: C-1), 86.8, 86.6, 82.3, 82.2 (C_5 ring: diastereotopic CH), 81.1, 78.4 (C≡C), 57.5, 56.7 (C_7 ring: CH), 23.9 (CH_2). – MS (EI): *m*/*z* (%) = 454 (3) [M^+], 398 (3) [M − 2CO]$^+$, 370 (8) [M − 3CO]$^+$, 314 (6) [M − 5CO]$^+$, 286 (19) [M − 6CO]$^+$, 234 (27) [M − 6CO − Cr]$^+$, 179 (35) [M − 6CO − Mn − Cr]$^+$, 52 (100) Cr^+. – IR (KBr): ν (CO) = 2023, 1955, 1925, 1890 cm^{-1}. – $C_{20}H_{11}CrMnO_6$ (454.2): calcd. C 52.88, H 2.44; found C 52.06, H 2.65.

Manganese−Chromium Complex 15: A solution of **14** (0.50 g, 1.10 mmol) in dichloromethane (15 mL) was added dropwise to a stirred solution of $(Ph_3C)BF_4$ (0.33 g, 1.00 mmol) in dichloromethane (5 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirring was continued for 2 h. The reaction mixture was then poured into rapidly stirred diethyl ether (100 mL), which led to the precipitation of **15** as a dark-yellow, crystalline solid. Crystallization from dichloromethane afforded **15**·CH_2Cl_2 as red crystals. Yield: 535 mg (90%). – ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 6.76 (m, 2 H, C_7 ring: CH), 6.64 (m, 2 H, C_7 ring: CH), 6.49 (d, 2 H, C_7 ring: CH), 5.31 (m, 2 H, C_5 ring: CH), 4.88 (m, 2 H, C_5 ring: CH). – ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ = 224.2 (Cr−CO), 219.7 (Mn−CO), 107.1 (C_7 ring: C-1), 105.2 (C_7 ring: CH), 104.8 (C_7 ring: CH), 104.2 (C_7 ring: CH), 91.8 (C_5 ring: C-1), 89.6 (C_5 ring: CH), 85.4 (C≡C), 83.8 (C_5 ring: CH), 75.6 (C≡C). – MS (ESI): *m*/*z* (%) = 453 (100) [M^+], 369 (88) [M − 3CO]$^+$, 313 (100) [M − 5CO]$^+$, 285 (24) [M − 6CO]$^+$. – IR (KBr): $\tilde{\nu}$ = 2227 (C≡C), 2061, 2022, 1935 (CO) cm^{-1}. – UV/Vis (CH_2Cl_2): λ (lg ε) = 266 (4.24), 309 (4.18), 449 (3.74) nm. – UV/Vis (CH_3CN): λ (lg ε) = 300 (4.24), 334 (4.12), 429 (3.75) nm. – $C_{20}H_{10}BCrF_4MnO_6{\cdot}CH_2Cl_2$ (625.0): calcd. C 40.36, H 1.94; found C 39.83, H 1.82.

X-ray Crystal Structure Analysis of 15·CH_2Cl_2:[39] $C_{20}H_{10}BCrF_4MnO_6{\cdot}CH_2Cl_2$, M_r = 625.0, dark-red crystal, dimensions 0.30 × 0.15 × 0.05 mm, *a* = 20.387(1) Å, *b* = 7.354(1) Å, *c* = 32.882(1) Å, β = 96.12(1)°, *V* = 4901.8(7) Å^3, $\rho_{calcd.}$ = 1.694 g cm^{-3}, *F*(000) = 2480 e, μ = 12.42 cm^{-1}, absorption correction (0.707 ≤ *T* ≤ 0.941), *Z* = 8, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 30148 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.65 Å^{-1}, 11195 independent (R_{int} = 0.041) and 8158 observed reflections [$I \geq 2\sigma(I)$], 649 refined parameters, *R* = 0.052, wR^2 = 0.127, max. residual electron density 1.17 (−1.08) e Å^{-3}, hydrogens calculated and refined as riding atoms, two chemically identical molecules with different conformations in the asymmetric unit. Data were collected with a Nonius KappaCCD diffractometer equipped with a rotating anode generator. Programs used: data acquisition COLLECT, data reduction DENZO-SMN, absorption correction SORTAV, structure solution SHELXS-86, structure refinement SHELXL-97, graphics DIAMOND.

Hyper Raleigh Scattering: For the experimental set-up, see ref.[34c] As the incident light source a Nd:YAG laser with a wavelength of 1064 nm was used. All measurements were made in dry CH_2Cl_2 or CH_3NO_2 with concentrations in the range 10^{-6} to 10^{-4} M and *p*-nitroaniline (*p*-NA) as a reference [$\beta_{p\text{-NA}}(CH_2Cl_2) = 21.6 \times 10^{-30}$ esu; $\beta_{p\text{-NA}}(CH_3NO_2) = 34.6 \times 10^{-30}$ esu]. The solutions were kept in darkness to prevent decomposition by daylight and were checked by recording UV/Vis spectra. An estimate of β absorption corrections was calculated as suggested in ref.[40] All compounds were checked for nonfluorescence by using interference filters of varying peak transmittance.[41]

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