Tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0): Preparation, Nucleophilic Addition Studies and Syntheses of Complex Polycyclic Systems by Dianionic Oxy-Cope Rearrangement

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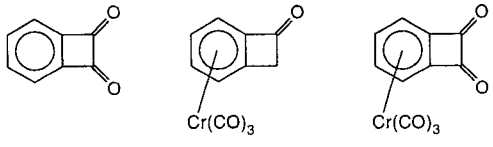
Dedicated to the memory of Stephanie Zimmermann

Abstract: The tricarbonylchromium complex **3** of 1,2-dioxobenzocyclobutene (**1**) is easily prepared by hydrolysis of diacetal **4**. Complex **3** stereoselectively undergoes both single and double nucleophilic addition reactions at the keto groups. As a consequence, addition of excess alkenyllithium to **3** gives rise to a dianionic oxy-Cope rearrangement yielding benzocyclooctenedione complexes with good diastereoselectivity. Trapping of the bis(enolate) intermediate with chlorotrimethylsilane gives bis(enolether) **23**. Subsequent addition of two different alkenyllithium derivatives yields the asymmetrically substituted rearrangement product **15**. To some extent, dependent on the method of hydrolysis, an intramolecular aldol addition follows the dianionic oxy-Cope rearrangement. This results in the formation of benzoanellated bicyclo[3.3.0]octane derivatives and, in the case of 1-cyclopentenyllithium as the alkenylmetal, in the tetraquinane system **19**. The *trans*-anellation of one of the cyclopentane rings in *trans*-**20** has been verified by an X-ray structural analysis. The highly substituted rearrangement product **21**/**22** is formed only in small yield; in solution the bis(enol) tautomeric form **22** is favored over diketone **21**.

Keywords
asymmetric syntheses · chromium complexes · diones · oxy-Cope rearrangements · polycycles

Introduction

Since the first synthesis carried out by Cava et al. in 1963,[1] the synthetic potential of 1,2-dioxobenzocyclobutene (**1**) has attracted continuous interest. In particular, much attention has been paid to the addition of carbon nucleophiles like Grignard or organolithium reagents to one of the keto groups of **1**. In a more methodological work, Liebeskind et al. added different



1 **2** **3**

alkynyl and aryl nucleophiles to **1** to obtain monoadducts which upon heating underwent a rearrangement to form the corresponding naphthoquinones.[2, 3] The alkynyllithium monoadducts were also used for a palladium-catalyzed ring expansion as a route to indanone derivatives. Moore et al made use of the transformation of **1** into naphthoquinone derivatives in the syntheses of naturally occurring naphthoquinones like nanaomycine D and deoxyfrenolycine.[4, 5]

The reactivity of **1** with organometallic reagents has also been investigated. Here, interest was focused principally on insertion reactions of metal fragments into the highly strained four-membered ring.[6–10] The metallacyclopentanes bearing acyl complex moieties thus formed were transformed to naphthoquinones by a variety of methods.

The complexation of **1** to a metal fragment was hitherto unknown. In the light of the well-developed chemistry of (η^6-arene)tricarbonylchromium(0) complexes,[11–14] coordination of **1** with chromium should be feasible. A tricarbonylchromium complex of **1** would be an attractive target for at least three reasons: a) As has been found in recent investigations of tricarbonyl(η^6-1-oxobenzocyclobutene)chromium(0) (**2**),[15, 16] the electron-withdrawing effect of the tricarbonylchromium moiety should be transferred to the keto groups through the rigid ligand with the π orbitals of the aromatic ring and those of the keto groups parallel to one another. Thus an increased electrophilicity of the keto groups is to be expected. b) Complexation of the aromatic ring in **1** eliminates one plane of symmetry in **1** and causes a differentiation of *endo* and *exo* faces of the coordinated ligand which should result in highly stereoselective nucleophilic additions. c) It is expected that electron withdrawal by the tricarbonylchromium(0) moiety will facilitate ring-opening reactions. This could lead to new reactions of the organic ligand which are not observed in the uncomplexed case.

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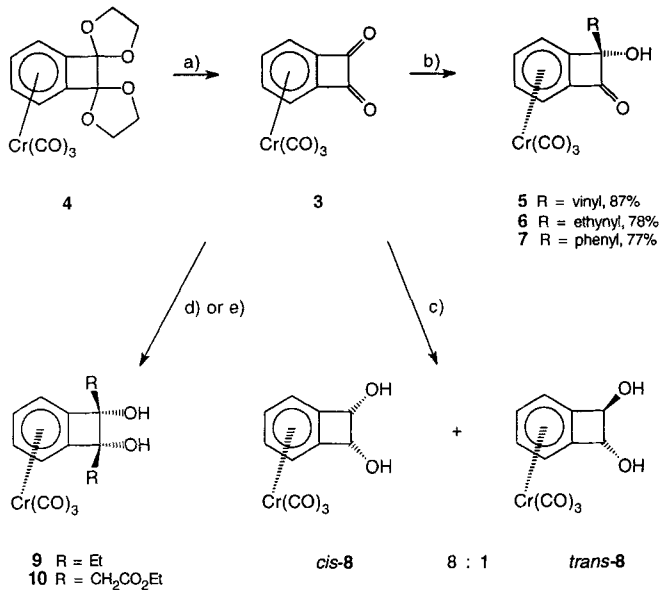
In this paper, we report in detail the evaluation of the described concept by synthesis of tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**3**) and reactions of **3** with carbon nucleophiles. Parts of this work have been published as preliminary communications.[17, 18]

Results and Discussion

Synthesis and properties of tricarbonyl(η^6-1,2-dioxobenzocylobutene)chromium(0) (3): As expected from the similar case of **2**,[15] attempts at the direct complexation of **1** to a tricarbonylchromium(0) fragment failed. This is reasonable given the variety of known insertion reactions into the four-membered ring of **1**.[6–10] Therefore, the known tricarbonylchromium(0) complex **4**[19] of the 1,2-bis(ethylenedioxy) derivative of **1** was employed as starting material for the preparation of **3**. Deprotection of the two keto groups was possible under strongly acidic conditions by suspending **4** in concentrated aqueous hydrochloric acid under exclusion of air. Following this procedure, **3** was isolated in 85–95% yield. The deep red solid was fully characterized, including an X-ray structural analysis showing that the bicyclic ligand is not completely planar, but that the anellated cyclobutenedione ring is bent towards the metal atom by about 8°.[17]

The ^{13}C NMR data of **3** deserve special attention. The comparatively small chemical shift of the carbonyl ligands ($\delta = 228.3$) indicates strong backbonding between the carbonyl ligands and the chromium atom. This shows that the electron withdrawal by the two keto groups in **3** is perfectly transferred to the metal fragment by the coplanar keto and aromatic π orbitals. Furthermore, the shift of $\Delta\delta = 48$ ppm for the signals of the quarternary aromatic carbon atoms on coordination is noted. One can interpret this as a stronger coordination of the π bond between these two atoms effecting a strain reduction in the anellated four-membered ring. This hypothesis is supported by inspection of the ^1J(C,C) coupling constants for the analogous monoketone complex **2**, available from 2D INADEQUATE measurements (**2** was chosen for this study because of its asymmetry).[20] In contrast, the X-ray data of diketone complex **3** showed equal bond distances for the aromatic π bonds (within the accuracy of measurement).[17] Because of the experimental error, it is very difficult to discuss the so-called Mills–Nixon Effect[21] on the basis of X-ray data only.[22] Coupling constants ^1J(C,C) apparently provide a more sensitive measure.

Single nucleophilic additions to 3: As an initial test of the assumed strong acceptor properties of the keto groups in **3**, addition of several Grignard reagents was envisaged. As in the uncomplexed case,[2, 3] these additions took place at −78 °C, affording the corresponding monoadducts **5**–**7** in good yields (Scheme 1). Whereas the yield for the ethynyl adduct **6** is comparable to the one in the uncomplexed series, the yield for the phenyl adduct **7** is about 20% higher. The vinyl adduct **5** is unknown in the uncomplexed case, probably because treatment of **1** with vinyllithium leads to a complex mixture of products (vide infra). To avoid side reactions, the transformations are carried out by slow addition of two equivalents (R = vinyl) or four equivalents (R = ethynyl, phenyl) of the precooled Grignard reagents to the solution of **3**. Monoadducts **5**–**7** were obtained as single diastereomers (*de* ≥ 90%, NMR). In analogy to a vinyl Grignard adduct of **2**, which has been subjected to an X-ray structure analysis,[16] compounds **5**–**7** are assumed to be *endo* alcohols.



Scheme 1. a) HCl (conc.), 25 °C, 2 h, 85–95%. b) 1. RMgBr (2–4 equiv), −78 °C; 2. H_3O^+. c) 1. $LiAlH_4$, −78 °C; 2. H_3O^+, 90%. d) 1. EtMgI (10 equiv), −78 °C; 2. H_3O^+ (twice), 60%. e) 1. LiHMDS, EtOAc (4 equiv); 2. **3**, −78 °C; 3. H_3O^+, 88%.

Double nucleophilic additions to 3: Reduction of **3** takes place at −78 °C with lithium aluminum hydride as a hydride donor to afford diol complex **8** in 90% yield (Scheme 1). This experiment highlights again the enhanced acceptor character of the keto groups in complex **3**, because in the case of uncomplexed **1**, the reduction with the same reagent in boiling diethyl ether occurs in only 30% yield.[23] Diol complex **8** is formed as a 8:1 mixture of *cis* and *trans* diastereomers, presumably resulting from a competition of steric and coulomb interactions. For the same reason as discussed for the monoadducts **5**–**7**, strong evidence exists for a *cis*–*endo* configuration of the main product. Hitherto, treatment of **1** with phenyllithium in a temperature range of −60 to +25 °C represented the only example of a double nucleophilic addition taking place without opening of the four-membered ring.[24] According to the authors, the synthesis of the diadduct was successfully completed by an extremely careful aqueous workup of the reaction mixture. On the other hand, it is known from the work of Cava that treatment of **1** with phenylmagnesium bromide leads exclusively to the formation of 1,3-diphenylisobenzofuran.[1]

Complexation of **1** by a tricarbonylchromium(0) fragment renders the double addition of a simple nucleophile like ethylmagnesium iodide more feasible. Treatment of **3** with an excess of the Grignard reagent at −78 °C leads to a mixture of the corresponding mono- and diadduct (1:1, NMR) which, after workup, was again subjected to the same conditions. By this route diethyl adduct **9** is accessible in 60% yield as a single *cis*–*endo* diastereomer. With a more powerful nucleophile such as the ester enolate of ethyl acetate, double addition takes place in a single operation at −78 °C in high yield. Again, the *cis*–*endo* diastereomer **10** is exclusively formed (*de* ≥ 90%). The twofold addition of the enolate of ethyl acetate can also be observed in the uncomplexed case (Scheme 2). Under identical conditions, a 5:4 mixture of the *cis* and *trans* diastereoisomers of **11** is accessible in 85% yield. One crystallization from diethyl ether/pentane provides diastereomerically enriched material (*cis*-**11**: white solid, *de* = 90%; *trans*-**11**: colorless oil, *de* = 80%, NMR). Comparison of the NMR spectra of the two diastereomers of **11** with those obtained from a decomplexed

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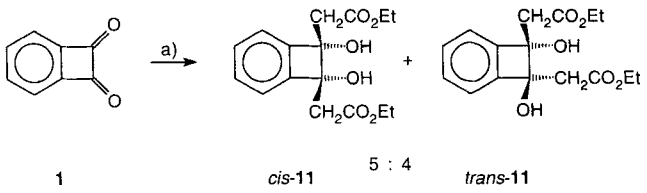


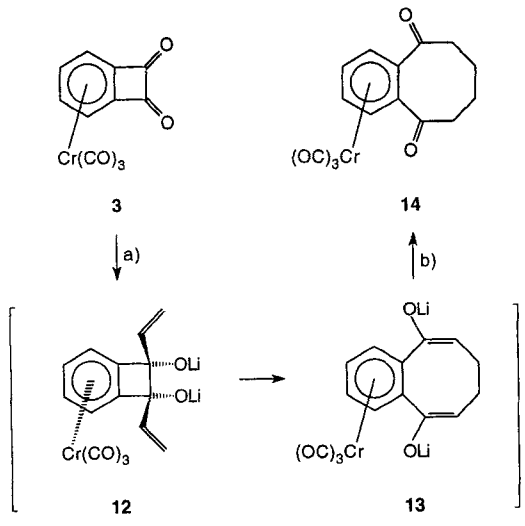
1 *cis*-11 *trans*-11

Scheme 2. a) 1. LiHMDS, EtOAc (4 equiv), −78 °C; 2. H_3O^+, 85%.

sample from *cis–endo* complex **10** allows the assignment of the relative configurations.

All attempts to synthesize the diphenyl adduct of **3** failed. Starting from the monoadduct **7**, addition of phenylmagnesium bromide was carried out in a temperature range from −78 to −5 °C. After aqueous workup, 1,3-diphenylisobenzofuran was obtained in 40% yield in analogy to the work of Cava.[1] The formation of this product is reasonable assuming a hypothetical double adduct as an intermediate. In contrast to the uncomplexed case[24] the ring opening of the hypothetical diphenyl adduct of **3** may be facilitated (vide infra).

Double anionic oxy-Cope rearrangements of dialkenyl adducts of 3: Double additions of vinylic nucleophiles to diketo complex **3** have been regarded as particularly interesting, because corresponding reactions are unknown in the uncomplexed case. Based on the double addition of simple nucleophiles like ethylmagnesium iodide to **3**, compounds containing a diallyl diol substructure should be accessible, and could serve as starting materials for oxy-Cope rearrangements.[25, 26] Therefore, **3** was treated with an excess of vinyllithium at −78 °C (Scheme 3).



3 **14** **12** **13**

Scheme 3. a) Vinyllithium (6 equiv), −78 °C. b) H_3O^+, 87%.

After hydrolysis at −78 °C and workup, we obtained the tricarbonylchromium(0) complex of 5,10-dioxobenzocyclooctene **14** in 87% yield instead of the simple diadduct expected. The constitution of **14** is elucidated by spectroscopic and elemental analysis as well as by comparison of NMR spectra derived from decomplexed material with those published for the organic ligand of **14**.[27] Obviously, a sequential transformation of **3** by a double addition of vinyllithium and subsequent double anionic oxy-Cope rearrangement has occurred.

This transformation can be regarded as a consequence of the results already described and examples from the literature: presumably, di-*exo*-vinyl di-*endo*-diolate **12** is formed in analogy to diadducts **9** and **10**. In **12**, the synperiplanar orientation of the vinyl groups is a necessary prerequisite for an anionic oxy-Cope rearrangement. This was shown by Salaün[28] who succeeded in the transformation of *cis*-divinylcyclobutanols into cyclooctenone derivatives under the conditions of an anionic oxy-Cope rearrangement. Application of the same conditions for the corresponding *trans* diastereomer leads to an open-chain compound which is formally the product of a retro-hetero ene reaction.

The low temperature for the rearrangement step from **12** to **13** is remarkable. In related cases,[29–32] a temperature of at least 0 °C is necessary to carry out this step. Several factors render the dianionic oxy-Cope rearrangement of **12** favorable: a) The rigid skeleton results in geometric proximity of the vinyl groups. This was also found to be advantageous for monoanionic oxy-Cope rearrangements in norbornene derivatives.[33] b) The electron withdrawal by the metal fragment is the most probable reason for the ease with which the distal bond of the four-membered ring is opened. Moreover, the double anionic oxy-Cope rearrangement must be regarded as the driving force for the double addition, which was comparatively sluggish with the alkyl Grignard reagent.

Whatsoever the influence of the metal fragment may be, the analogous treatment of uncomplexed **1** with vinylmagnesium bromide failed completely. Instead of 5,10-dioxobenzocyclooctene, a complex mixture was obtained consisting of several vinyl-group-containing species. The desired product of the oxy-Cope rearrangement could only be detected in traces. With vinyllithium, a product of double addition, double anionic oxy-Cope rearrangement and subsequent transannular aldol reaction could be isolated in 15% yield beside other reaction products.[32]

Despite the manyfold use of the anionic oxy-Cope rearrangements reported for the construction of complicated carbon skeletons, the attention paid to the dianionic version is rather slight. We therefore treated **3** with several alkenyllithium derivatives to explore the scope and limitations of this reaction.

Treatment of the monovinyl adduct **5** with 2-propenyllithium under the conditions described above opens the way to the asymmetrically substituted 5,10-benzocyclooctenedione derivative **15** in 60% yield (Table 1). Although it has so far not been possible to determine the relative configuration of the newly formed chiral center, it is believed that the methyl group is on the coordinated face of the ligand. This hypothesis is supported by the fact that hydrolysis of a dienolate analogous to **13** takes place from the outside of the eight-membered ring (vide infra) finally leading to an *endo*-orientation of the methyl group.

Treatment of diketo complex **3** with excess 2-propenyllithium, 1-lithio-1-phenylethene and 1-cyclopentenyllithium at −78 °C followed by hydrolysis with aqueous diluted hydrochloric acid at the same temperature affords similiar types of product mixtures. Beside benzocyclooctendiones **17** and **20**, cyclopentaanellated indanones **16** and **18** and the benzoanellated tetraquinane **19**, formally generated by a subsequent transannular aldol reaction of their eight-membered ring counterparts, are isolated as the major components (**18** is accompanied by two diastereomeric benzocyclooctenediones, which could not be separated and completely characterized). Separation of the products is possible by crystallization and column chromatography. The constitution of products **16** to **20** can be unambiguously elucidated by inspection of their spectroscopic data. The relative configurations of the diastereomeric complexes *trans*-**17** and *cis*-**17** are derived from their symmetry properties obtained from their NMR spectra. X-ray structure analyses show the relative con-

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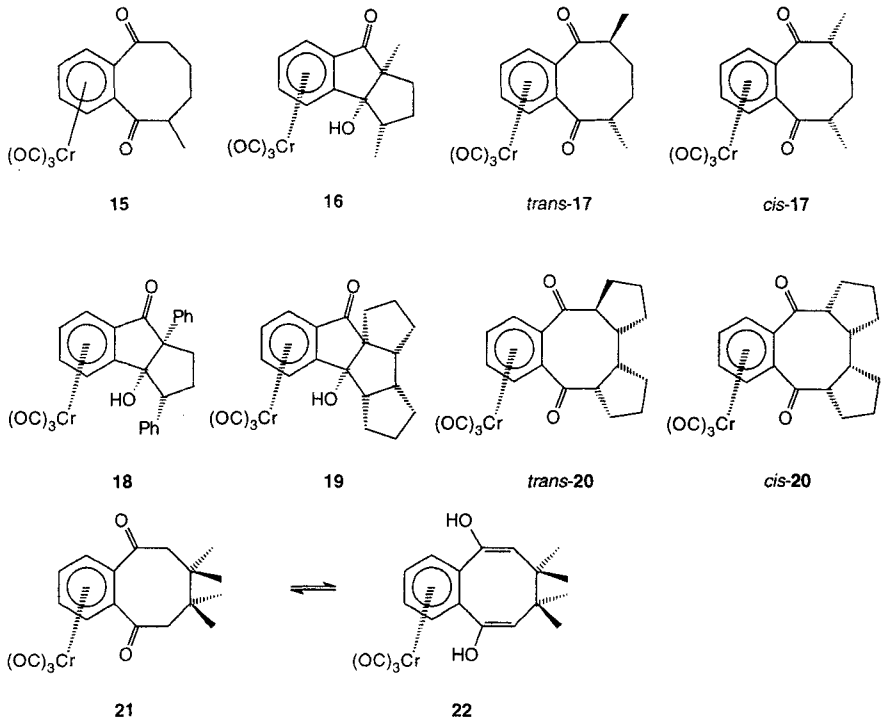
Table 1. Dianionic oxy-Cope rearrangements with substituted alkenyllithium derivatives.



S. M. [a]	Alkenyllithium	Hydrolysis	Products (yield)
5	2-propenyllithium	HCl (aq)	**15** (60%)
3	2-propenyllithium	HCl (aq)	**16** (48%), *trans*-**17** (10%), *cis*-**17** (4%)
3	2-propenyllithium	CF_3SO_3H	**16** (8%), *trans*-**17** (29%), *cis*-**17** (11%)
3	1-lithio-1-phenylethene	HCl (aq)	**18** (30%) + side products
3	1-cyclopentenyllithium	HCl (aq)	**19** (22%), *trans*-**20** (20%)
3	1-cyclopentenyllithium	CF_3SO_3H	**19** (9%), *trans*-**20** (27%), *cis*-**20** (10%)
3	2-Methyl-1-propenyllithium	HCl (aq)	**21**/**22** (9%)

[a] S. M. = starting material.

figurations of **16**[34] and **19**,[18] whereas that of **18** is assumed to be the same as that of the closely related product **16**. For the doubly cyclopentaanellated benzocyclooctenedione *trans*-**20**, the NMR spectra revealed the existence of a non-C_s symmetric compound. Because *trans*-**20** bears two asymmetric carbon atoms more than *trans*-**17** the relative configuration was not accessible in all details by this way. Therefore *trans*-**20** was subjected to an X-ray structure analysis.[35]

Figure 1 shows the structure of *trans*-**20** in the solid state. The molecule possesses a boat–boat conformation.[36] The analysis confirms a *cis,cis,trans*-anellation of the cyclopentane rings. Therefore the hydrogen atoms in the α-positions of the keto groups must be positioned on different faces of the organic ligand, thus explaining the large difference in the chemical shift for the signals of these atoms in the ^{1}H NMR spectra ($\Delta\delta$ = 0.57 ppm). Additionally, the X-ray structure analysis reveals that the eight-membered ring in *trans*-**20** is sterically crowded, thus disrupting the coplanarity of the keto groups and the aromatic ring. This steric strain is also reflected in nonequivalent C–C bonds within the η^6-benzene moiety.[37] As in similar compounds, the $Cr(CO)_3$ unit forms an eclipsed conformation with the ligand.[38]

Information concerning the stereochemical course of the reaction is available from the relative configurations of the products, particulary of those derived from the reaction of **3** with 1-cyclopentenyllithium. Most probably, the addition of two equivalents of the alkenyllithium derivative forms a *cis*-dialkenyl intermediate which undergoes a double anionic oxy-Cope rearrangement. In this step, the relative configurations of the stereogenic centers in the β position to the enolate moieties of the bisenolate **24** are determined (Scheme 4). Thus it becomes obvious that the relative *cis* configuration of these two centers has to be the same in all three products, **19**, *trans*-**20**, and *cis*-**20**. Independent of the kind of alkenyllithium derivative used, the bisenolate intermediate should be the common precursor for the eight-membered ring complexes as well as for the aldol products. This hypothesis was confirmed by trapping the bisenolate derived from the reaction of **3** and 2-propenyllithium with trimethylsilyl trifluoromethane sulfonate. Bis(trimethylsilyl) enol ether **23** was formed in 60% yield as the only product (Scheme 5). The conformation of the bis(enolate) intermediate seems to be crucial for the stereochemical outcome of the reaction sequence. The following explanations are again concerned with the reaction of **3** with 1-cyclopentenyllithium: inspection of a molecular model of bis(enolate) **24** indicates that the boat conformer **24a** should be the primary product. Protonation of one of the enolate double bonds from the outside face of the ring opens the way for a transannular aldol addition leading exclusively to tetraquinane **19**. Because hydrolysis with aqueous hydrochloric acid at −78 °C can be regarded as a slow reaction (the main quantity of the reagent being frozen) the aldol process is fast as compared with a second protonation. Therefore, the aldol products become

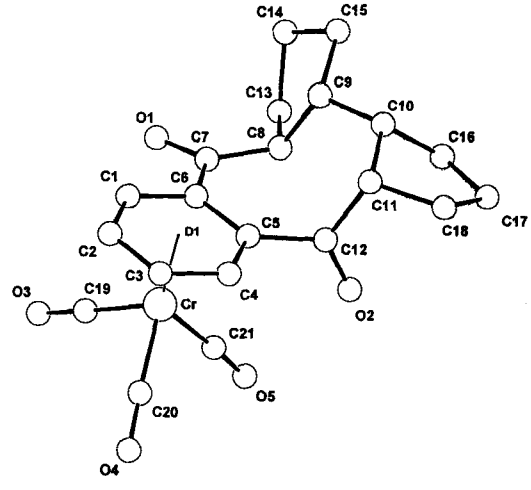
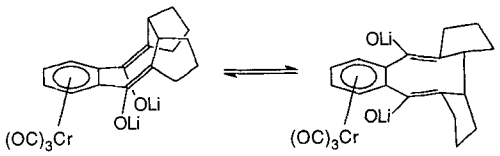
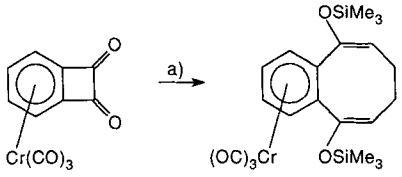


Fig. 1. Crystal structure of *trans*-**20** [35]. Selected bond lengths (Å) and angles (°) (numbering is arbitrary): Cr–C1 2.185(2), Cr–C2 2.212(2), Cr–C3 2.185(2), Cr–C4 2.196(2), Cr–C5 2.197(2), Cr–C6 2.199(2), C1–C2 1.401(3), C1–C6 1.416(3), C2–C3 1.384(4), C3–C4 1.404(3), C4–C5 1.405(3), C5–C6 1.430(3), C5–C12 1.517(3), C6–C7 1.513(3), C7–C8 1.510(3), C7–O1 1.208(3), C8–C9 1.577(3), C8–C13 1.539(3), C9–C10 1.524(3), C9–C15 1.535(3), C10–C11 1.556(3), C10–C16 1.532(3), C11–C12 1.508(3), C11–C18 1.532(3), C12–O2 1.205(2); C5-C6-C7 125.8(2), C6-C7-C8 119.8(2), C7-C8-C9 109.2(2), C8-C9-C10 116.7(2), C9-C10-C11 117.2(2), C10-C11-C12 110.8(2), C11-C12-C5 116.1(2).



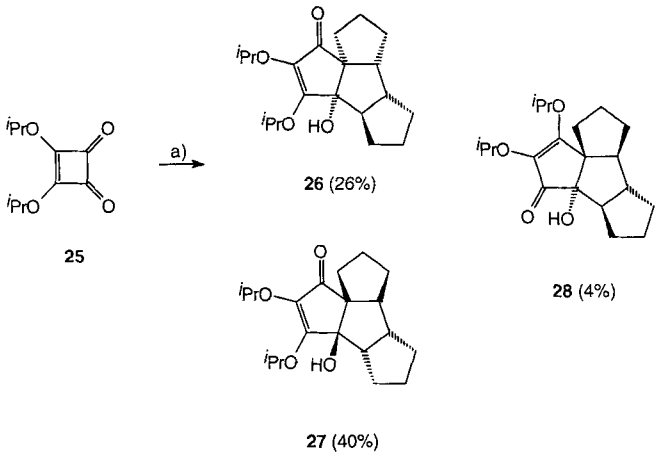
24a 24b

Scheme 4.



3 23

Scheme 5. a) 1. 2-Propenyllithium (6 equiv), −78 °C; 2. $CF_3SO_3SiMe_3$, −40 °C, 60%.



25

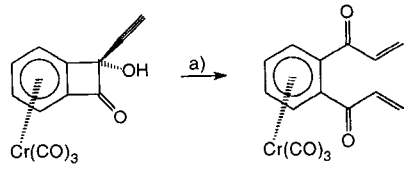
Scheme 6. a) 1. 1-Cyclopentenyllithium (exc.), −78 to 25 °C; 2. $NaHCO_3$ aq.

the major component of the product mixtures. On the other hand, one would expect that double protonation of a bisenolate conformer like **24a** would lead to the *cis*-benzocyclooctenediones *cis*-**17** and *cis*-**20**, but the observed products are predominantly the *trans* diastereomers. The formation of the *trans* diastereomers can be explained by assuming an equilibrium between **24a** and the flatter, twisted conformer **24b** in which *gauche* interactions are minimized and the direction of the proton attack is no longer effectively controlled. Alternatively, the preference for the *trans* over the *cis* diastereomers could derive from an epimerization under the acidic workup conditions caused by transannular interactions. Both explanations are in accord with the observation that a change in the conditions of hydrolysis leads to different product ratios. With strong trifluoromethanesulfonic acid instead of aqueous HCl, the *trans* configurated benzocyclooctenediones *trans*-**17** and *trans*-**20** become the major components of the product mixture, and the aldol products are isolated as side products.

A recently published report of a similiar reaction of the squaric acid ester **25** with 1-cyclopentenyllithium supports the central role of a bis(enolate) conformer corresponding to **24a**.[39, 40] The authors used molecular mechanics calculations for their bis(enolate) to show that the boat conformer possesses an energy minimum. Therefore, the relative conformation of their product **26** (Scheme 6) obtained by hydrolysis with an aqueous $NaHCO_3$ solution is similiar to that found for **19**. The observation that one of the cyclopentane rings is *trans*-anellated could perhaps be explained assuming different conformations of the *monoenolate* precursors for **19** and **26**. Attention should be focussed on the fact that only **26** is derived from an oxy-Cope rearrangement whereas the tetraquinanes **27** and **28** are products of an electrocyclic ring opening of the cyclobutene ring followed by an electrocyclization and transannular aldol reaction. This reaction path is reasonable because in **25** addition of the 1-cyclopentenyllithium takes place to form both the *cis* and the *trans* adducts. Thereby it is geometrically impossible for the *trans* adduct to undergo an oxy-Cope rearrangement.[28] In contrast, the face differentiation in chromium complex **3** guarantees a uniform sequential transformation consisting of a double nucleophilic *cis* addition, a dianionic oxy-Cope rearrangement, and, possibly, a transannular aldol addition.

A limitation of the described procedure of double addition of alkenyllithium derivatives to **3** and subsequent dianionic oxy-Cope rearrangement is elaborated by means of β-disubstituted alkenyllithium derivatives. Treatment of **3** with 2-methyl-1-propenyllithium provides **21** in only 9% yield (Table 1). Interestingly, diketone **21** is in equilibrium with the dienol **22**, most likely to reduce *gauche* interactions of the four methyl groups. In acetone and dichloromethane, the dienol **22** is the major component as indicated by ^{13}C NMR. The reaction of **3** with (1-lithiomethylene)cyclohexane and treatment of the reaction solution with trimethylsilyl trifluoromethanesulfonate did not lead to the isolation of the expected product at all. However, a product possessing the correct molecular mass (m/z = 604, MS) was isolated in 26% yield, but the constitution has not yet been elucidated.

In a preliminary experiment, the integration of triple bonds[41] into the rearrangement process was investigated. Monoalkynyl adduct **6** was treated with vinyllithium (Scheme 7). The only compound isolated from the very dark green reaction mixture was the *ortho* disubstituted complex **29** (the yield was diminished in the course of the chromatographic purification of **29**, which tended to polymerize very fast). **29** is believed to be formed by the addition of vinyllithium to the keto group of **6** followed by a retro-ene-like rearrangement.



6 29

Scheme 7. a) 1. Vinyllithium (6 equiv), −78 °C; 2. H_3O^+, 15%.

Finally, an additional point should be mentioned. Generation of divinyldiolates from **3**, **25**,[39, 40] or acenaphthenequinone[31] leaves no doubt that divinyl*di*olates are indeed formed. In contrast, other oxy-Cope rearrangements described as dianionic start from the divinyldiols,[29, 30] which are deprotonated by base. One cannot be sure at which point in the double deprotonation sequence the rearrangement really takes place.

Conclusion

In summary, the reaction sequence of double addition of alkenyllithium derivatives to tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**3**) followed by a double anionic oxy-Cope rearrangement was shown to be a powerful method for the construction of complicated polycyclic carbon skeletons. Natu-

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ral compounds containing triquinane[42] and tetraquinane[43] fragments are widely known. The synthesis of eight-membered-ring-containing compounds has been a source of continuous interest in the last few years.[44] The method described represents an excellent and fast route to this kind of compound. Further studies to explore the use of this method in organic synthesis are under way in our laboratories.

Experimental Section

All operations were performed in an argon atmosphere in flame-dried vessels. M.p. (uncorrected): Büchi SMP-20, determined in sealed glass capillaries in an argon atmosphere. IR: Nicolet 7199 FT-IR. ^{1}H NMR: Bruker WH400 (400.1 MHz), AM200 (200.1 MHz). ^{13}C NMR: Bruker WH400 (100.6 MHz), AM200 (50.3 MHz); signal multiplicities were determined either by inspection of gated spectra (^1J(C,H) coupling constants are omitted for space economy) or by application of the DEPT technique; chemical shifts refer to $\delta_{TMS} = 0$ according to the chemical shifts of residual solvent signals. MS: Varian 311A. HRMS: Finnigan MAT820. Preparative column chromatography: SiO_2, $\varnothing$ 0.04–0.063 mm (230–400 mesh ASTM), Ar saturated, flash technique [45]. Elemental analyses: Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim an der Ruhr (Germany). Commercially available reagents were employed. 1,2-dioxobenzocyclobutene (**1**) [46], tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**3**) [17,34], vinyllithium [47], and the alkenyllithium derivatives used [48] are synthesized according to literature procedures.

General procedure A for aqueous workup: After addition of an aqueous reagent solution to the reaction mixture, the organic layer was diluted with diethyl ether and the layers were separated. The aqueous phase was extracted with equal volumes of diethyl ether until the extract remained colorless. The combined organic layers were washed with water (three times) and dried over $MgSO_4$. After filtration the volatile components were evaporated in vacuo to give the crude product.

Tricarbonyl(η^6-1,2-dihydroxybenzocyclobutene)chromium(0) (8): A red solution of **3** (1.00 g, 3.73 mmol) in diethyl ether (250 mL) was added dropwise to a suspension of lithium aluminum hydride in diethyl ether (20 mL) at −78 °C. The yellow suspension obtained was stirred for 2 h at −78 °C. The excess of lithium aluminum hydride was decomposed by adding ethyl acetate (5 mL) at −25 °C. After the mixture had been stirred for a further 2 h, hydrolysis was carried out by addition of 1 M aqueous hydrochloric acid followed by aqueous workup. The crude product was dissolved in a minimum amount of diethyl ether and the solution was treated with a sixfold amount of pentane, whereupon **8** partially precipitated. Crystallization was completed at −30 °C to afford a light yellow powder (910 mg, 3.30 mmol, 90%). Compound **8** was obtained as a mixture of two diastereomers (*cis*-**8**:*trans*-**8** = 89:11). M.p. 151 °C; ^{1}H NMR (200 MHz, [D$_8$]THF): *cis-endo*-**8**: δ = 4.42 (br, 2H, OH), 4.96 (s, 2H, 1(2)-H), 5.25 + 5.48 (AA'BB' system, 2 × 2H, 3(6)-H, 4(5)-H); *trans*-**8** (some signals are covered by those of the major diastereomer): δ = 4.68 (br, 1H, OH), 4.73 (br, 1H, OH), 5.16 (m, 1H, 1-H or 2-H), 5.39 (d, 1H, 3-H or 6-H), 5.65 (dd, 1H, ^3J(H,H) = 6 Hz, 4-H or 5-H); ^{13}C NMR (50 MHz, [D$_8$]THF): *cis-endo*-**8**: δ = 73.0 (d, C-1(2)), 88.2 (d, C-4(5)), 92.4 (d, C-3(6)), 121.0 (s, C-2a(6a)), 233.6 (s, CO); *trans*-**8**: δ = 78.7 (d, C-1 or C-2), 80.9 (d, C-1 or C-2), 89.3 (d, 2C, arom. C), 91.3 (d, arom. C), 94.7 (d, arom. C), 115.7 (s, C-2a or C-6a), 117.2 (s, C-2a or C-6a), 234.0 (s, CO); IR (KBr): $\tilde{\nu}$ = 3390 (br, OH), 3080 (w), 2940 (w), 1970 (s, CO), 1880 (s, CO), 1400 (m), 1310 (w), 1205 (m), 665 (m), 575 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%): 272 (46) [M^+], 244 (12) [M^+ − CO], 216 (28) [M^+ − 2CO], 189 (20), 188 (95) [M^+ − 3CO], 170 (64), 102 (54), 91 (12), 69 (10), 53 (11) [^{53}Cr$^+$], 52 (100) [^{52}Cr$^+$]; $C_{11}H_8CrO_5$ (272.18): calcd C 48.54, H 2.96, Cr 19.10; found C 48.54, H 3.00, Cr 19.18.

General procedure B for single additions of nucleophiles to tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (3): A solution of the Grignard reagent cooled to −78 °C was added in small portions over a period of 4 h to a THF/diethyl ether solution of **3** at −78 °C. A color change from red to orange-yellow and finally brown is observed. After complete addition the solution is stirred for 16 h at −78 °C followed by hydrolysis with 2 M aqueous hydrochloric acid and workup.

Tricarbonyl(η^6-2-*endo*-hydroxy-1-oxo-2-*exo*-vinylbenzocyclobutene)chromium(0) (5): General procedure B was used with **3** (1.144 g, 4.27 mmol) in diethyl ether/THF (1:1, 200 mL), a 1.1 M solution of vinylmagnesium bromide in THF (6.65 mL, 7.32 mmol) diluted to a volume of 60 mL. Crude product **5** (1.103g, 3.73 mmol, 87%, pure by NMR, light- and air-sensitive red oil). An analytically pure sample was obtained by column chromatography (200 mg of crude **5**, 200 × 20 mm, diethyl ether:pentane = 4:1). Owing to the sensitivity of **5**, the yield was diminished by chromatography to 47%. ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.33 (dd, 1H, ^2J(*E*)-8-H,(*Z*)-8-H) = −0.8 Hz, $^3J_{cis}$(H,H) = 10.6 Hz, (*E*)-8-H), 5.40 (dd, 1H, $^3J_{trans}$(H,H) = 17.4 Hz, (*Z*)-8-H), 5.63 (dd, 1H, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 6.0 Hz, 4-H or 5-H), 5.83 (dd, 1H, $^3J(H,H)$ = 6.4 Hz, ^3J(H,H) = 6.0 Hz, 4-H or 5-H), 5.87 (d, 1H, ^3J(H,H) = 6.4 Hz, 3-H or 6-H), 6.07 (d, 1H, ^3J(H,H) = 6.0 Hz, 3-H or 6-H), 6.22 (dd, 1H, 7-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 86.4 (d, arom. C), 87.6 (d, arom. C), 93.4 (d, arom. C), 95.0 (d, arom. C), 96.0 (s, C-2), 105.8 (s, C-6a), 118.1 (t, C-8), 130.1 (s, C-2a), 136.8 (d, C-7), 188.3 (s, C-1), 231.2 (s, CO); IR (THF): $\tilde{\nu}$ = 1985 (s, CO), 1920 (s, CO), 1709 (s, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3414 (m, OH), 3208 (w), 2964 (w), 2000 (s, CO), 1931 (s, CO), 1895 (s, CO), 1744 (s, keto CO), 1636 (w), 1499 (m), 1414 (w), 1287 (m, CO), 1263 (m, CO), 1245 (m, CO), 1000 (w), 953 (m), 903 (w), 826 (m), 769 (w), 715 (w), 652 (m), 611 (s), 558 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 296 (8) [M^+], 240 (2) [M^+ − 2CO], 212 (13) [M^+ − 3CO], 194 (21), 184 (11), 69 (10), 53 (13) [^{53}Cr$^+$], 52 (100) [^{52}Cr$^+$]; $C_{13}H_8CrO_5$ (296.21): calcd C 52.71, H 2.73, Cr 17.56; found C 51.69, H 2.84, Cr 17.79.

Tricarbonyl(η^6-2-*exo*-ethynyl-2-*endo*-hydroxy-1-oxobenzocyclobutene)chromium(0) (6): General procedure B was used with **3** (836 mg, 3.12 mmol) in diethyl ether/THF (1:1, 200 mL), a 0.68 M solution of ethynylmagnesium bromide in THF (18.4 mL, 12.5 mmol), diluted to a volume of 40 mL. The solution of the crude product in dichloromethane (30 mL) was treated with hexane (5 mL) and stored for 4 d at −30 °C to furnish **6** (486 mg) as red needles. Addition of hexane (7 mL) to the mother liquor and storage at −30 °C for 4 d resulted in additional **6** (226 mg) being obtained. Yield: **6** (712 mg, 2.43 mmol, 78%). M.p. 141 °C (decomp.); ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 3.55 (s, 1H, 8-H), 5.67 (dd, 1H, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 6.4 Hz, 4-H or 5-H), 5.87 (dd, 1H, ^3J(H,H) = 6.4 Hz, $^3J(H,H)$ = 6.4 Hz, 4-H or 5-H), 5.95 (d, 1H, ^3J(H,H) = 6.4 Hz, 3-H or 6-H), 6.16 (d, 1H, $^3J(H,H)$ = 6.4 Hz, 3-H or 6-H), 6.77 (s, 1H, OH); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 80.2 (d, C-8), 80.5 (d, C-7), 86.0 (s, C-2), 86.4 (d, arom. C), 86.5 (d, arom. C), 93.4 (d, arom. C), 95.0 (d, arom. C), 105.3 (s, C-6a), 128.8 (s, C-2a), 184.0 (s, C-1), 230.7 (s, CO); IR (THF): $\tilde{\nu}$ = 1989 (s, CO), 1921 (s, CO), 1767 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3388 (w, br, OH), 3292 (w), 3103 (w), 2994 (w), 2964 (w), 1992 (s, CO), 1936 (s, CO), 1745 (s, CO), 1511 (w), 1493 (w), 1426 (w), 1400 (w), 1252 (w), 1176 (m, CO), 1165 (m, CO), 1123 (m, CO), 1082 (w), 1015 (w), 893 (w), 829 (w), 748 (w), 714 (w), 694 (w), 660 (m), 640 (w), 611 (m), 599 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 294 (6) [M^+], 238 (2) [M^+ − 2CO], 210 (8) [M^+ − 3CO], 53 (9) [^{53}Cr$^+$], 52 (100) [^{52}Cr$^+$]. $C_{13}H_6CrO_5$ (294.19): calcd C 53.07, H 2.06, Cr 17.68; found C 52.95, H 2.10, Cr 17.58.

Tricarbonyl(η^6-2-*endo*-hydroxy-1-oxo-2-*exo*-phenylbenzocyclobutene)chromium(0) (7): General procedure B was used with **3** (1.180 g, 4.40 mmol) in diethyl ether/THF (1:1, 300 mL), 1.04 M solution of phenylmagnesium bromide in THF (17.3 mL, 18.0 mmol), diluted to a volume of 60 mL. Compound **7** crystallized as a red solid from a solution of the crude product in a mixture of dichloromethane/hexane (70 mL/10 mL) at −30 °C over a period of 3 d. Twofold repetition of the crystallization procedure with the material obtained by evaporation of the solvents from the mother liquor gave additional **7**. Yield: **7** (1.196 g, 3.45 mmol, 77%) as a red powder. M.p. 170 °C; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 5.69 (dd, 1H, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 6.0 Hz, 4-H or 5-H), 5.90 (dd, 1H, ^3J(H,H) = 6.0 Hz, ^3J(H,H) = 6.4 Hz, 4-H or 5-H), 5.92 (d, 1H, ^3J(H,H) = 6.0 Hz, 3-H or 6-H), 6.25 (d, 1H, ^3J(H,H) = 6.4 Hz, 3-H or 6-H), 6.38 (s, 1H, OH), 7.36 (m, 3H, *m*-H, *p*-H), 7.50 (d, 2H, ^3J(H,H) = 6.4 Hz, *o*-H); ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 86.3 (d, arom. C), 88.1 (d, arom. C), 93.7 (d, arom. C), 95.1 (d, arom. C), 96.8 (s, C-2), 106.6 (s, C-6a), 127.1 (d, *m*-C), 129.2 (d, *o*-C), 129.3 (d, *p*-C), 130.6 (s, C-2a), 140.1 (s, *ipso*-C), 188.3 (s, C-1), 231.4 (s, CO); IR (THF): $\tilde{\nu}$ = 1984 (s, CO), 1919 (s, CO), 1748 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3443 (w, br, OH), 3074 (m), 1985 (s, CO), 1920 (s, CO), 1748 (s, keto CO), 1598 (w), 1583 (w), 1496 (m), 1448 (m), 1421 (w), 1400 (w), 1334 (w), 1230 (w), 1190 (w), 1161 (w), 1132 (w), 1055 (w), 959 (w), 899 (w), 827 (w), 773 (m), 741 (w), 702 (m), 663 (w), 646 (w), 604 (m), 522 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 346 (4) [M^+], 290 (3) [M^+ − 2CO], 262 (13) [M^+ − 3CO], 244 (13), 234 (23), 165 (17), 53 (12) [^{53}Cr$^+$], 52 (100) [^{52}Cr$^+$]. $C_{17}H_{10}CrO_5$ (346.27): calcd C 58.96, H 2.92, Cr 15.02; found C 59.02, H 3.04, Cr 14.98.

Tricarbonyl(η^6-1,2-di-*exo*-ethyl-1,2-di-*endo*-hydroxybenzocyclobutene)chromium(0) (9): The red solution of **3** (385 mg, 1.43 mmol) in diethyl ether/THF (1:1, 100 mL) was added over a period of 5 h to a cooled (−78 °C) 0.87 M solution of ethylmagnesium iodide (16.1 mL, 14.0 mmol). The orange-yellow solution obtained was stirred at −78 °C for a further 16 h and then hydrolyzed with 2 M aqueous hydrochloric acid (10 mL). Workup provided a mixture of the mono- and diaddition products (1:1, NMR). This mixture was added to a solution containing ethylmagnesium iodide (10.0 mmol) at −78 °C as in the described procedure. Aqueous workup and column chromatography (200 × 30 mm, diethyl ether:pentane = 2:1) gives **9** (284 mg, 0.87 mmol, 60%) as a yellow solid. M.p. 102 °C (decomp.); ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 1.13 (t, 6H, CH$_3$, ^3J(H,H) = 7.8 Hz), 1.86 (q, 4H, CH$_2$), 5.38 + 5.74 (AA'BB' line system, 2 × 2H, 3(6)-H, 4(5)-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 9.1 (q, CH$_3$), 27.5 (t, CH$_2$), 84.4 (s, C-1(2)), 88.7 (d, C-4(5)), 93.0 (d, C-3(6)), 123.8 (s, C-2a(6a)), 233.9 (s, CO); IR (THF): $\tilde{\nu}$ = 1963 (s, CO), 1893 (s, CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3410 (w, br, OH), 3089 (w), 2970 (w), 2939 (w), 2880 (w), 1969 (s, CO), 1880 (s, CO), 1514 (w), 1458 (w), 1399 (w), 1378 (w), 1295 (w), 1263 (w), 1188 (w), 1147 (w), 1093 (w), 1052 (w), 821 (w), 756 (w), 710 (w), 663 (m), 628 (m), 536 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 328 (25) [M^+], 300 (4) [M^+ − CO], 272 (31) [M^+ − 2CO], 245 (17) [M^+ − 3CO, ^{53}Cr], 244 (76) [M^+ − 3CO, ^{52}Cr], 226 (32), 158 (82), 143 (37), 129 (24), 128 (28), 53 (12) [^{53}Cr$^+$],

52 (100) [$^{52}Cr^+$]; $C_{15}H_{16}CrO_5$ (328.31): calcd C 54.87, H 4.92, Cr 15.84; found C 54.86, H 5.00, Cr 15.73.

Tricarbonyl(η^6-1,2-di-*exo*-ethoxycarbonylmethylene-1,2-di-*endo*-hydroxybenzocyclobutene)chromium(0) (10): To a cooled (−78 °C) solution of lithium bis(trimethylsilyl)amide (1.983 g, 12.14 mmol) in THF (50 mL) ethyl acetate (1.070 g, 12.14 mmol, 1.19 mL) was added. The resulting ester enolate solution was stirred for 15 min at −78 °C and then treated with **3** (814 mg, 3.04 mmol) in THF (40 mL) over a period of 1 h. After being stirred for a further 30 min the yellow solution was hydrolyzed at −78 °C by addition of 7 M aqueous hydrochloric acid (30 mL). Aqueous workup yielded a yellow solid, which was recrystallized from dichloromethane to afford **10** (1.190 g, 2.68 mmol, 88%) as a yellow powder. M.p. 128 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 1.27 (t, 6H, CH_3, ^3J(H,H) = 7.0 Hz), 2.99 (s, 4H, CH_2), 4.19 (q, 4H, CH_2CH_3), 5.43 + 5.89 (AA'BB' line system, 2 × 2H, 3(6)-H, 4(5)-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 14.5 (q, CH_3), 39.7 (t, CH_2), 61.2 (t, CH_2CH_3), 81.8 (s, C-1(2)), 90.1 (d, C-3(6)), 93.4 (d, C-4(5)), 122.6 (s, C-2a(6a)), 171.0 (s, CH_2CO), 233.8 (s, CO); IR (THF): $\tilde{\nu}$ = 1973 (s, CO), 1896 (s, CO), 1740 (m, ester CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3326 (m, OH), 3097 (w), 2985 (w), 2940 (w), 1990 (s, CO), 1880 (s, CO), 1733 (s, ester CO), 1715 (s, ester CO), 1514 (w), 1465 (w), 1432 (w), 1375 (m), 1347 (m), 1312 (m), 1239 (s, CO), 1204 (s, CO), 1165 (m), 1143 (m), 1121 (m), 1029 (m), 897 (w), 852 (w), 825 (w), 793 (w), 668 (m), 627 (s), 532 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 444 (14) [M^+], 388 (17) [$M^+ - 2CO$], 360 (30) [$M^+ - 3CO$], 343 (30), 342 (76) [$M^+ - (CH_2CO_2Et + CH_3)$], 256 (20), 195(17), 53 (12) [$^{53}Cr^+$], 52 (100) [$^{52}Cr^+$]; $C_{19}H_{20}CrO_9$ (444.39): calcd C 51.35, H 4.54, Cr 11.70; found C 51.22, H 4.57, Cr 11.68.

1,2-Di(ethoxycarbonylmethylene)-1,2-dihydroxybenzocyclobutene (11): A mixture of lithium bis(trimethylsilyl)amide (653 mg, 4.00 mmol) and ethyl acetate (352 mg, 4.00 mmol) in THF (20 mL) was stirred for 15 min at −78 °C. A solution of 1,2-dioxobenzocyclobutene (**I**, 132 mg, 1.00 mmol) in THF (25 mL) was added dropwise at −78 °C, and the resulting solution was stirred for a further 30 min. Hydrolysis with 7 M aqueous hydrochloric acid (20 mL) and workup afforded pure **11** (262 mg, 0.85 mmol, 85%) as a mixture of diastereomers (*cis*-**11**:*trans*-**11** = 5:4, NMR). Crystallization from diethyl ether/pentane (1:1, 10 mL) gave *cis*-**11** (134 mg, white solid, m.p. 77 °C, *de* = 90% (NMR)) and *trans*-**11** (128 mg, colorless oil, *de* = 80% (NMR)); *cis*-**11**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (t, 6H, ^3J(H,H) = 7.2 Hz, CH_3), 2.90 (s, 4H, CH_2), 4.25 (q, 4H, CH_2CH_3), 7.36 (m, 4H, 3(6)-H, 4(5)-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (q, CH_3), 39.4 (t, CH_2), 60.8 (t, CH_2CH_3), 81.4 (s, C-1(2)), 123.1 (d, C-4(5)), 130.0 (d, C-3(6)), 147.0 (s, C-2a(6a)), 171.2 (s, CO); *trans*-**11**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.25 (t, 6H, CH_3, ^3J(H,H) = 7.2 Hz), 2.99 (s, 4H, CH_2), 4.17 (q, 4H, CH_2CH_3), 7.30 (m, 4H, 3(6)-H, 4(5)-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (q, CH_3), 40.2 (t, CH_2), 60.9 (t, CH_2CH_3), 83.1 (s, C-1(2)), 122.4 (d, C-4(5)), 129.9 (d, C-3(6)), 145.1 (s, C-2a(6a)), 173.4 (s, CO); IR (KBr): $\tilde{\nu}$ = 3368 cm^{-1} (s, OH), 3072 (w), 2981 (m), 2934 (w), 2905 (w), 1734 (s, ester CO), 1459 (w), 1370 (m), 1329 (m), 1219 (s, CO), 1175 (m), 1088 (m, CO), 1039 (w), 1021 (w), 938 (w), 895 (w), 772 (w), 752 (w), 653 (w), 557 (w); MS (70 eV, CI (NH_3)): *m/z* (%) = 326 (100) [$M^+ + NH_4$], 291 (40), 280 (23), 238 (30); $C_{16}H_{20}O_6$ (308.34): calcd C 62.32, H 6.54; found C 62.07, H 6.55.

Reaction of tricarbonyl(η^6-2-*endo*-hydroxy-1-oxo-2-*exo*-phenylbenzocyclobutene)chromium(0) (7) with phenylmagnesium bromide: A solution of **7** (347 mg, 1.00 mmol) in diethyl ether/THF (1:1, 100 mL) was added to a cooled (−78 °C) 0.52 M solution of phenylmagnesium bromide (11.6 mL, 6.00 mmol) over a period of 6 h. The resulting brown solution was warmed to −5 °C over a period of 16 h, then cooled to −78 °C and hydrolyzed with aqueous 2 M hydrochloric acid (20 mL). After workup, the brown oil was crystallized from acetone to afford 1,3-diphenylisobenzofurane (108 mg, 0.40 mmol, 40%, identified by comparison of the NMR spectra with those obtained from commercially available material).

General procedure C for the double nucleophilic addition of alkenyllithium derivatives to 3 and subsequent double anionic oxy-Cope rearrangement: A solution of **3** in diethyl ether/THF (1:1) was added to a cooled (−78 °C) solution of the alkenyllithium derivative (6 equiv) over a period of 6 h. The resulting intensely dark red solution was stirred for a further 16 h at −78 °C before hydrolysis was carried out by one of two different procedures: a) A 2 M aqueous solution of hydrochloric acid (10 mL) was added at −78 °C. b) One equivalent (with regard to the amount of the alkenyllithium derivative) of trifluoromethanesulfonic acid was added at −78 °C. Aqueous workup was carried out in both cases according to general procedure A above.

Tricarbonyl(η^6-6,7,8,9-tetrahydrobenzocyclooctene-5,10-dion)chromium(0) (14): General procedure C was used with **3** (421 mg, 1.57 mmol) in diethyl ether/THF (1:1, 120 mL), a 0.48 M vinyllithium solution in THF (20 mL, 9.6 mmol), hydrolysis according to method (a). The crude oily product was crystallized from a concentrated solution in acetone at −30/−78 °C. After recrystallization from diethyl ether, **14** was obtained as orange-red needles (442 mg, 1.37 mmol, 87%). M.p. 145–146 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 1.95 (m, 4H, 7(8)-H), 2.73 (m, 4H, 6(9)-H), 5.87 (m, 4H, 1(4)-H, 2(3)-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 25.3 (t, C-7(8)), 41.3 (t, C-6(9)), 93.3 (d, C-1(4)), 93.8 (d, C-2(3)), 105.4 (s, C-4a(10a)), 202.3 (s, C-5(10)), 231.7 (s, CO); IR (THF): $\tilde{\nu}$ = 1984 (s, CO), 1919 (s, CO), 1682 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3087 (w), 2976 (w), 2948 (w), 2902 (w), 2872 (w), 1977 (s, CO), 1921 (s, CO), 1894 (s, CO), 1679 (s, keto CO), 1456 (w), 1318 (w), 1260 (m), 1214 (w), 1189 (w), 1145 (m), 1092 (w), 998 (w), 933 (w), 666 (m), 648 (m), 615 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 324 (12) [M^+], 268 (8) [$M^+ - 2CO$], 241 (25) [$M^+ - 3CO$, ^{53}Cr], 240 (100) [$M^+ - 3CO$, ^{52}Cr], 53 (9) [$^{53}Cr^+$], 52 (71) [$^{52}Cr^+$]. $C_{13}H_{12}CrO_5$ (324.27): calcd C 55.56, H 3.74, Cr 16.04; found C 55.66, H 3.79, Cr 16.12.

Tricarbonyl(η^6-6,7,8,9-tetrahydro-6-methylbenzocyclooctene-5,10-dione)chromium(0) (15): General procedure C was used with **5** (220 mg, 0.82 mmol) in diethyl ether/THF (1:1, 70 mL), a 0.58 M solution of 2-propenyllithium in THF (9.9 mL, 5.74 mmol) diluted to a volume of 20 mL, hydrolysis according to procedure (a). Chromatography of the crude product (250 × 30 mm, diethyl ether:pentane = 2:1) provided **15** (165 mg, 0.49 mmol, 60%) as a red oil (*de* ≥ 90% (NMR)). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 1.21 (d, 3H, CH_3, ^3J(H,H) = 6.6 Hz), 1.85 (m, 2H, 7-H/8-H), 2.10 (m, 2H, 7-H/8-H), 2.60 (m, 2H, 9-H), 3.02 (m, 1H, 6-H), 5.60 (d, 1H, ^3J(H,H) = 6.1 Hz, 1-H or 4-H), 5.74 (dd, 1H, ^3J(H,H) = 6.1 Hz, ^3J(H,H) = 6.4 Hz, 2-H or 3-H), 6.01 (dd, 1H, ^3J(H,H) = 6.1 Hz, ^3J = 6.4 Hz, 2-H or 3-H), 6.08 (d, 1H, ^3J(H,H) = 6.4 Hz, 1-H or 4-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 15.1 (q, CH_3), 23.2 (t, C-7 or C-8), 31.6 (t, C-7 or C-8), 39.0 (t, C-9), 46.2 (d, C-6), 91.5 (d, C-1 or C-4), 92.9 (d, C-1 or C-4), 94.5 (d, C-2 or C-3), 94.6 (d, C-2 or C-3), 97.1 (s, C-4a or C-10a), 115.4 (s, C-4a or C-10a), 199.8 (s, C-5 or C-10), 207.7 (s, C-5 or C-10), 231.8 (s, CO); IR (THF): $\tilde{\nu}$ = 1980 (s, CO), 1911 (s, CO), 1680 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3082 (w), 2930 (w), 1983 (s, CO), 1906 (s, CO), 1677 (s, keto CO), 1592 (w), 1456 (w), 1377 (w), 1276 (w), 998 (w), 649 (m), 616 (m) cm^{-1}; MS (70 eV, EI): m/z (%) = 338 (14) [M^+], 282 (11) [$M^+ - 2CO$], 255 (20) [$M^+ - 3CO$, ^{53}Cr], 254 (69) [$M^+ - 3CO$, ^{52}Cr], 252 (22), 172 (13), 53 (12) [$^{53}Cr^+$], 52 (100) [$^{52}Cr^+$]. $C_{16}H_{14}CrO_5$ (338.30): calcd C 56.80, H 4.18, Cr 15.37; found C 56.69, H 4.23, Cr 15.24.

Reactions of 3 with 2-propenyllithium:

1. General procedure C was used with **3** (423 mg, 1.58 mmol) in diethyl ether/THF (5:1, 80 mL), a 0.34 M solution of 2-propenyllithium in diethyl ether (32.5 mL, 11.04 mmol), hydrolysis according to procedure (a). Consecutive treatment of the crude product (red oil) with dichloromethane (2 mL) and diethyl ether (2 mL) provided **16** (238 mg). Solvent was removed in vacuo from the combined washing solutions, and the residue was chromotographed (280 × 20 mm, ethyl acetate:pentane = 1:3) to give *cis*-**17** (21 mg, R_f = 0.47), **16** (31 mg, R_f = 0.36), and *trans*-**17** (59 mg, R_f = 0.29). Yield: **16** (269 mg, 0.76 mmol, 48%) as an orange solid, *trans*-**17** (59 mg, 0.17 mmol, 10%) as an orange oil, and *cis*-**17** (21 mg, 0.06 mmol, 4%) as a red oil.

2. General procedure C was used with **3** (287 mg, 1.07 mmol) in diethyl ether/THF (1:1, 50 mL), a 0.45 M solution of 2-propenyllithium in diethyl ether (15 mL, 6.75 mmol), hydrolysis according to procedure (b) with trifluoromethanesulfonic acid (1.013 g, 6.75 mmol). Chromatography of the crude product (200 × 30 mm, ethyl acetate:pentane = 1:5) affords *cis*-**17** (40 mg, 0.11 mmol, 11%, R_f = 0.25), **16** (30 mg, 0.09 mmol, 8%, R_f = 0.18), and *trans*-**17** (110 mg, 0.31 mmol, 29%, R_f = 0.13).

Tricarbonyl(η^6-1,2,3,3a-tetrahydro-3a-*endo*-hydroxy-3,8a-di-*endo*-methylcyclopenta-[*a*]-inden-8(8*a*)-one)chromium(0) (16): M.p. 188 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.15 (d, 3H, ^3J(H,H) = 6.8 Hz, $CHCH_3$), 1.39 (s, 3H, CCH_3), 1.65 (m, 2H, 1-H), 1.77 (m, 1H, 2-H or 3-H), 1.93 (m, 2H, 2-H or 3-H), 2.17 (s, 1H, OH), 5.44 (m, 1H, arom. H), 5.69 (m, 3H, arom. H); ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 13.2 (q, CH_3), 23.4 (q, CH_3), 33.3 (t, C-1), 36.4 (t, C-2), 49.0 (d, C-3), 61.8 (s, C-8a), 85.5 (s, C-3a), 86.7 (d, C-4 or C-7), 87.5 (d, C-4 or C-7), 93.5 (d, C-5 or C-6), 95.3 (s, C-7a) 96.4 (d, C-5 or C-6), 129.8 (s, C-3b), 208.4 (s, C-8), 232.2 (s, CO); IR (THF): $\tilde{\nu}$ = 1979 (s, CO), 1910 (s, CO), 1718 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3450 (w, br, OH), 3085 (w), 2973 (w), 2958 (w), 2926 (w), 2869 (w), 1984 (s, CO), 1912 (s, CO), 1895 (s, CO), 1687 (m, keto CO), 1522 (w), 1424 (w), 1378 (w), 1293 (w), 1227 (w), 1202 (w), 1148 (w), 1033 (w), 999 (w), 975 (w), 834 (w), 656 (m), 618 (m), 531 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 352 (16) [M^+], 296 (15) [$M^+ - 2CO$], 269 (30) [$M^+ - 3CO$, ^{53}Cr], 268 (100) [$M^+ - 3CO$, ^{52}Cr], 238 (34), 52 (44) [$^{52}Cr^+$]. $C_{17}H_{16}CrO_5$ (352.33): calcd C 57.95, H 4.59, Cr 14.76; found C 57.81, H 4.63, Cr 14.87.

Tricarbonyl(η^6-6,7,8,9-tetrahydro-*trans*-6,9-dimethylbenzocyclooctene-5,10-dione)chromium(0) (*trans*-17): ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.15 (d, 3H, CH_3, ^3J(H,H) = 6.4 Hz), 1.26 (d, 3H, CH_3, ^3J(H,H) = 6.4 Hz), 1.58 (m, 1H, 7-H or 8-H), 1.90 (m, 2H, 7-H, 8-H), 2.21 (m, 1H, 7-H or 8-H), 2.76 (m, 2-H, 6-H, 9-H), 5.29 (d, 1H, 1-H or 4-H, ^3J(H,H) = 6.2 Hz), 5.40 (dd, 1H, 2-H or 3-H, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 6.2 Hz), 5.68 (dd, 1H, 2-H or 3-H, ^3J(H,H) = 6.2 Hz, ^3J(H,H) = 6.4 Hz), 6.07 (d, 1-H or 4-H, ^3J(H,H) = 6.4 Hz); ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 14.1 (q, CH_3), 17.0 (q, CH_3), 29.8 (t, C-7 or C-8), 31.4 (t, C-7 or C-8), 31.4 (d, C-6 or C-9), 46.4 (d, C-6 or C-9), 90.4 (d, C-2 or C-3), 91.1 (d, C-1 or C-4), 92.9 (d, C-1 or C-4), 93.5 (d, C-2 or C-3), 95.3 (s, C-4a or C-10a), 114.5 (s, C-4a or C-10a), 202.0 (s, C-5 or C-10), 207.1 (s, C-5 or C-10), 230.8 (s, CO); IR (THF): $\tilde{\nu}$ = 1984 (s, CO), 1919 (s, CO), 1684 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3087 (w), 2973 (w), 2937 (w), 2874 (w), 1981 (s, CO), 1909 (s, CO), 1682 (s, keto CO), 1507 (w), 1459 (m), 1377 (w), 1337 (w), 1194 (m), 1103 (w), 1031 (w), 994 (w), 961 (w), 937 (w), 906 (w), 836 (w), 756 (w), 651 (m), 615 (m), 524

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(w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 352 (12) [M^+], 296 (11) [$M^+ - 2CO$], 269 (22) [$M^+ - 3CO$, ^{53}Cr], 268 (88) [$M^+ - 3CO$, ^{52}Cr], 266 (55), 53 (11) [$^{53}Cr^+$], 52 (100) [$^{52}Cr^+$]. $C_{17}H_{16}CrO_5$ (352.33): calcd C 57.95, H 4.59, Cr 14.76; found C 57.82, H 5.06, Cr 14.18.

Tricarbonyl(η⁶-6,7,8,9-tetrahydro-6,9-di-*endo*-methylbenzocyclooctene-5,10-dione)chromium(0) (*cis*-17): ^1H NMR (200 MHz, [D$_6$]acetone): δ = 1.28 (d, 6H, CH_3, $^3J(H,H)$ = 7.0 Hz), 1.71 (m, 4H, 7(8)-H), 2.90 (m, 2H, 6(9)-H), 5.77 + 5.93 (AA'BB' system, 2 × 2H, 1(4)-H, 2(3)-H).

Tricarbonyl[η⁶-7,8-dihydro-6,9-dimethyl-5,10-bis(trimethylsilyloxy)benzocyclooctene]chromium(0) (23): General procedure C was used with **3** (290 mg, 1.08 mmol) in diethyl ether/THF (1:1, 70 mL), a 0.65 M solution of 2-propenyllithium in diethyl ether (9.96 mL, 6.48 mmol), diluted with THF (10 mL), but instead of hydrolysis trimethylsilyl trifluoromethanesulfonate (8.05 g, 36.2 mmol) was added at −78 °C. The resulting solution was stirred for 3 h at −40 °C, then cooled to −78 °C and treated with triethylamine (20 mL). Workup included extraction of the organic layer with a saturated aqueous solution of $NaHCO_3$ and water, drying over $MgSO_4$ and solvent removal in vacuo. The residual brown oil was chromatographed (230 × 30 mm, ethyl acetate:pentane = 1:12) to provide **23** as an orange solid, which was recrystallized from diethyl ether to give **23** (322 mg, 0.65 mmol, 60%) as yellow needles. M.p. 132 °C; ^1H NMR (200 MHz, CD_2Cl_2): δ = 0.10 (s, 18H, $Si(CH_3)_3$), 1.17 (s, 6H, CH_3), 2.13 + 3.21 (AA'BB' line system, 2 × 2H, *endo*-7(8)-H, *exo*-7(8)-H), 5.38 + 5.81 (AA'BB' line system, 2 × 2H, 1(4)-H, 2(3)-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 0.8 (q, $Si(CH_3)_3$), 19.8 (q, CH_3), 33.5 (t, C-7(8)), 93.0 (d, C-1(4)), 96.1 (d, C-2(3)), 111.4 (s, C-4a(10a)), 123.5 (s, C-6(9)), 138.7 (s, C-5(10)), 234.0 (s, CO); IR (THF): $\tilde{\nu}$ = 1964 (s, CO), 1889 (s, CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 2958 (m), 2930 (m), 2860 (m), 2831 (m), 1968 (s, CO), 1877 (s, CO), 1660 (w), 1450 (m), 1375 (w), 1278 (m), 1256 (s), 1214 (m), 1197 (s), 1163 (m), 1142 (m), 1107 (s), 1047 (w), 1014 (w), 957 (w), 874 (s), 843 (s), 756 (m), 724 (w), 673 (m), 659 (m), 628 (s), 515 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 496 (22) [M^+], 413 (42) [$M^+ - 3CO$, ^{53}Cr], 412 (100) [$M^+ - 3CO$, ^{52}Cr], 322 (61) [$M^+ - (3CO + C_3H_{10}OSi)$], 232 (53) [$M^+ - (3CO + 2C_3H_{10}OSi)$], 199 (25), 182 (26), 167 (25), 126 (33), 73 (64) [$C_3H_{10}OSi^+$], 52 (56) [$^{52}Cr^+$]. $C_{23}H_{32}CrO_5Si_2$ (496.75): calcd C 55.61, H 6.51, Si 11.31, Cr 10.47; found C 55.65, H 6.57, Si 11.24, Cr 10.35.

Tricarbonyl(η⁶-1,2,3,4a-tetrahydro-3a-*endo*-hydroxy-3,8a-di-*endo*-phenylcyclopenta[*a*]inden-8(8a)-one)chromium(0) (18): General procedure C was used with **3** (350 mg, 1.31 mmol) in diethyl ether/THF (1:1, 80 mL), 1-lithio-1-phenylethene (9.14 mmol) in 20 mL of diethyl ether, hydrolysis according to procedure (*a*). Chromatography of the crude product (30 × 220 mm, diethyl ether:pentane = 1:1) afforded **18** (186 mg, 0.39 mmol, 30%) as an orange powder. M.p. 212 °C; ^1H NMR (200 MHz, [D$_8$]THF): δ = 2.14 (m, 1H, 1-H or 2-H), 2.41 (m, 2H, 1-H, 2-H), 2.78 (m, 1H, 1-H or 2-H), 2.99 (s, 1H, OH), 3.09 (dd, 1H, 3-H, $^3J(H,H)$ = 3.3 Hz, $^3J(H,H)$ = 12.5 Hz), 4.97 (d, 1H, 4-H or 7-H, $^3J(H,H)$ = 6.1 Hz), 5.42 (dd, 1H, 5-H or 6-H, $^3J(H,H)$ = 6.1 Hz, $^3J(H,H)$ = 6.4 Hz), 5.85 (dd, 1H, 5-H or 6-H, $^3J(H,H)$ = 6.1 Hz, $^3J(H,H)$ = 6.4 Hz), 6.09 (d, 1H, 4-H or 7-H, $^3J(H,H)$ = 6.4 Hz), 7.30 (m, 10H, phenyl *H*); ^{13}C NMR (50 MHz, [D$_8$]THF): δ = 35.0 (t, C-1 or C-2), 39.4 (t, C-1 or C-2), 61.3 (d, C-3), 70.9 (s, C-8a), 83.9 (d, arom. *C*), 86.5 (s, C-3a or C-7a), 89.7 (d, arom. C), 90.7 (d, arom. C), 95.4 (s, C-3a or C-7a), 97.3 (d, arom. C), 127.7 (d, *p*-C), 127.9 (d, *p*-C), 128.4 (d, *o*-C or *m*-C), 128.6 (d, *o*-C or *m*-C), 129.7 (d, *o*-C or *m*-C), 130.1 (s, C-3b), 130.9 (d, *o*-C or *m*-C), 138.0 (s, *ipso*-C), 142.6 (s, *ipso*-C), 204.0 (s, C-8), 231.3 (s, CO); IR (THF): $\tilde{\nu}$ = 1980 (s, CO), 1908 (s, CO), 1714 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3450 (w, br, OH), 3064 (w), 3029 (w), 2968 (w), 2930 (w), 1978 (s, CO), 1902 (s, CO), 1708 (s, keto CO), 1602 (w), 1517 (w), 1496 (w), 1449 (w), 1377 (w), 1321 (w), 1262 (w), 1205 (w), 1101 (w), 1029 (w), 910 (w), 773 (w), 756 (w), 700 (m), 654 (m), 612 (m), 527 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 476 (9) [M^+], 420 (1) [$M^+ - 2CO$], 393 (44) [$M^+ - 3CO$, ^{53}Cr], 392 (100) [$M^+ - 3CO$, ^{52}Cr], 52 (78) [$^{52}Cr^+$]. HRMS for $C_{27}H_{20}CrO_5$: calcd 476.07379; found 476.07269.

Reaction of 3 with cyclopentenyllithium:

1. General procedure C was used with **3** (498 mg, 1.86 mmol) in diethyl ether/THF (1:1, 105 mL), a 0.51 M solution of cyclopentenyllithium in diethyl ether (24 mL, 12.3 mmol), hydrolysis according to procedure (a). The crude product is chromatographed (200 × 30 mm, ethyl acetate:pentane = 1:4) to afford **19** (165 mg, 0.41 mmol, 22%, R_f = 0.44) and *trans*-**20** (153 mg, 0.38 mmol, 20%, R_f = 0.34), both as red oils, which can be crystallized from dichloromethane/hexane.

2. General procedure C was used with **3** (417 mg, 1.56 mmol) in diethyl ether/THF (1:1, 100 mL), a 0.57 M solution of cyclopentenyllithium in diethyl ether (16.4 mL, 9.3 mmol), hydrolysis according to procedure (b) with trifluoromethanesulfonic acid (1.426 g, 9.5 mmol, 0.84 mL). The crude product was chromatographed (230 × 30 mm, ethyl acetate:pentane = 1:4) to give **19** (57 mg, 0.14 mmol, 9%), *cis*-**20** (62 mg, 0.15 mmol, 10%, R_f = 0.41) as a red oil, and *trans*-**20** (169 mg, 0.42 mmol, 27%).

Tricarbonyl{η⁶-1,2,3,3a,3b,4,5,6,6a,6b-decahydro-6b-*endo*-hydroxy-*endo*-cyclopenta-[5,6]-*endo*-pentaleno-[4,5-*a*]-inden-11(11*a*)-one}chromium(0) (19): M.p. 166 °C; ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.62 (m, 4H, aliph. H), 1.86 (m, 6H, aliph. H), 2.01 (m, 1H, aliph. H), 2.09 (m, 1H, aliph. H), 2.20 (s, 1H, OH), 2.55 (m, 2H, aliph. H), 2.80 (m, 1H, aliph. H), 5.44 (dd, 1H, 8-H or 9-H, $^3J(H,H)$ = 5.8 Hz, ^3J = (H,H) 5.8 Hz), 5.63 (d, 1H, 7-H or 10-H, $^3J(H,H)$ = 5.8 Hz), 5.65 (dd, 1H, 8-H or 9-H, $^3J(H,H)$ = 5.8 Hz, $^3J(H,H)$ = 6.4 Hz), 5.72 (d, 1H, 7-H or 10-H, $^3J(H,H)$ = 6.4 Hz); ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 26.2 (t, aliph. C), 27.4 (t, aliph. C), 28.5 (t, aliph. C), 30.0 (t, aliph. C), 31.5 (t, aliph. C), 36.1 (t, aliph. C), 49.4 (d, C-3a or C-3b), 52.3 (d, C-3a or C-3b), 61.1 (d, C-6a), 76.4 (s, C-11a), 85.5 (s, C-6b), 86.6 (d, C-7 or C-10), 87.8 (d, C-7 or C-10), 87.8 (d, C-8 or C-9), 95.8 (s, 10a), 93.2 (d, C-8 or C-9), 131.7 (s, C-6c), 208.4 (s, C-11), 232.2 (s, CO); IR (THF): $\tilde{\nu}$ = 1979 (s, CO), 1911 (s, CO), 1712 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3486 (w, OH), 3086 (w), 2951 (w), 2924 (w), 2872 (w), 1979 (s, CO), 1919 (s, CO), 1899 (s, CO), 1690 (m, keto CO), 1521 (w), 1449 (w), 1427 (w), 1328 (w), 1283 (w), 1228 (w), 1192 (w), 1090 (w), 1049 (w), 827 (w), 652 (m), 617 (m), 535 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 404 (11) [M^+], 448 (9) [$M^+ - 2CO$], 321 (26) [$M^+ - 3CO$, ^{53}Cr], 320 (100) [$M^+ - 3CO$, ^{52}Cr], 52 (73) [$^{52}Cr^+$]. $C_{21}H_{20}CrO_5$ (404.41): calcd C 62.36, H 4.99, Cr 12.86; found C 62.28, H 5.04, Cr 12.94.

Tricarbonyl(η⁶-1,2,3,3a,3b,4,5,6,6a,12a-decahydro-3a,3b,6a-*endo*-12a-*exo*-dicyclopenta[*d,f*]benzocyclooctene-7,12-dione)chromium(0) (*trans*-20): M.p. 195 °C; ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.51 (m, 4H, aliph. H), 1.65 (m, 1H, aliph. H), 1.78 (m, 3H, aliph. H), 1.89 (m, 1H, aliph. H), 2.07 (m, 2H, aliph. H), 2.30 (m, 1H, aliph. H), 2.53 (m, 1H, aliph. H), 2.58 (m, 1H, aliph. H), 2.87 (m, 1H, 6a-H or 12a-H), 3.44 (m, 1H, 6a-H or 12a-H), 5.03 (d, 8-H or 11-H, $^3J(H,H)$ = 6.0 Hz), 5.38 (dd, 1H, 9-H or 10-H, $^3J(H,H)$ = 6.0 Hz, $^3J(H,H)$ = 6.4 Hz), 5.61 (dd, 1H, 9-H or 10-H, $^3J(H,H)$ = 6.0 Hz, $^3J(H,H)$ = 6.4 Hz), 6.17 (d, 1H, 8-H or 11-H, $^3J(H,H)$ = 6.4 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 22.9 (t, aliph. C), 24.3 (t, aliph. C), 27.0 (t, aliph. C), 29.5 (t, aliph. C), 29.6 (t, aliph. C), 34.1 (t, aliph. C), 45.2 (d, C-3a or C-3b), 47.4 (d, C-3a or C-3b), 57.1 (d, C-6a or C-12a), 89.4 (d, C-8 or C-11), 90.5 (d, C-9 or C-10), 91.8 (d, C-8 or C-11), 92.0 (s, C-7a or C-11a), 92.6 (d, C-9 or C-10), 120.8 (s, C-7a or C-11a), 198.3 (s, C-7 or C-12), 208.2 (s, C-7 or C-12), 230.8 (s, CO); IR (THF): $\tilde{\nu}$ = 1984 (s, CO), 1919 (s, CO), 1683 (m, keto CO) cm^{-1}; (KBr): $\tilde{\nu}$ = 3085 (w), 2955 (m), 2871 (m), 1973 (s, CO), 1902 (s, CO), 1682 (s, keto CO), 1506 (w), 1439 (w), 1365 (w), 1341 (w), 1284 (w), 1248 (w), 1181 (m), 1049 (w), 987 (w), 834 (w), 651 (s), 619 (s), 523 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 404 (10) [M^+], 348 (11) [$M^+ - 2CO$], 321 (28) [$M^+ - 3CO$, ^{53}Cr], 320 (100) [$M^+ - 3CO$, ^{52}Cr], 52 (48) [$^{52}Cr^+$]. $C_{21}H_{20}CrO_5$ (404.41): calcd C 62.36, H 4.99, Cr 12.86; found C 62.32, H 5.02, Cr 12.69.

Tricarbonyl(η⁶-1,2,3,3a,3b,4,5,6,6a,12a-decahydro-3a,3b,6a,12a-*endo*-dicyclopenta[*d,f*]benzocyclooctene-7,12-dione)chromium(0) (*cis*-20): ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.76 (m, 6H, aliph. H), 1.92 (m, 6H, aliph. H), 2.27 (m, 2H, aliph. H), 2.76 (m, 2H, aliph. H), 5.55 + 5.75 (AA'BB' line system, 2 × 2H, 8(11)-H + 9(10)-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 22.7 (t, aliph. C), 27.5 (t, aliph. C), 28.8 (t, aliph. C), 46.4 (d, C-3a(3b)), 54.8 (d, C-6a(12a)), 92.1 (d, C-8(11)), 93.2 (d, C-9(10)), 103.0 (s, C-7a(11a)), 202.3 (s, C-7(12)), 230.7 (s, CO); MS (70 eV): *m/z* (%) = 404 (11) [M^+], 348 (11) [$M^+ - 2CO$], 321 (28) [$M^+ - 3CO$, ^{53}Cr], 320 (100) [$M^+ - 3CO$, ^{52}Cr], 318 (23), 52 (48) [$^{52}Cr^+$].

Crystal structure determinations for *trans*-20: [35] Enraf-Nonius CAD-4 diffractometer, $Mo_{K\alpha}$ radiation, λ = 0.71069 Å, graphite monochromator, *T* = 20 °C. During data collection 25 standard reflections were periodically measured as a general check of crystal and instrument stability. No significant changes were observed. The structure was solved by heavy-atom methods (SHELX-86) and completed by difference Fourier syntheses (GFMLX). Formula $C_{21}H_{20}O_5Cr$, M_r = 404.4 g mol^{-1}, crystal color red, crystal size 0.35 × 0.35 × 0.28 mm, *a* = 8.153(1), *b* = 16.328(2), *c* = 13.827(1) Å, β = 91.88(1)°, *V* = 1839.7 Å^3, d_{calcd} = 1.46 g cm^{-3}, μ = 6.34 cm^{-1}, *F*(000) = 840 e, *Z* = 4, crystal system monoclinic, space group $P2_1/c$ [no. 14], scan mode ω − 2θ, $2\theta_{max}$ = 54.9, $[(\sin\theta)/\lambda]$ = 0.65 Å^{-1}, 4525 measured reflections (±*h*, +*k*, +*l*), 4193 independent reflections, 3453 observed reflections [$I > 2\sigma(I)$] for 304 refined parameters, H-atom positions calculated and kept fixed in the final stage of refinement, *R* = 0.038, R_w = 0.048, residual electron density 0.38 e Å^{-3}.

Tricarbonyl(η⁶-6,7,8,9-tetrahydro-7,7,8,8-tetramethylbenzocyclooctene-5,10-dione)chromium(0) (21): General procedure C was used with **3** (487 mg, 1.82 mmol) in diethyl ether/THF (1:1, 90 mL), a 0.38 M solution of 2-methyl-1-propenyllithium in diethyl ether/THF (1:1, 28 mL, 10.6 mmol), hydrolysis according to procedure (a). The crude product was chromatographed (230 × 30 mm, ethyl acetate:pentane = 1:3) providing **21** (62 mg, 0.16 mmol, 9%, purity >95% (NMR)) as a red oil. ^1H NMR (200 MHz, CD_2Cl_2) of the dienol: δ = 1.97 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 5.46 + 5.60 (AA'BB' line system, 2 × 2H, 1(4)-H, 2(3)-H)), 6.32 (s, 2H, 6(9)-H); ^{13}C NMR (50 MHz, [D$_6$]acetone) of the dienol: δ = 20.9 (q, CH_3), 28.5 (q, CH_3), 50.1 (s, C-7(8)), 93.0 (d, C-1(4) or C-2(3)), 93.1 (d, C-1(4) or C-2(3)), 109.8 (s, C-4a(10a)), 122.8 (d, C-6(9)), 158.2 (s, C-5(10)), 232.3 (s, CO); IR (KBr): $\tilde{\nu}$ = 2964 (w), 2929 (w), 1978 (s, CO), 1898 (s, CO), 1668 (m, keto CO), 1611 (m), 1446 (m), 1377 (m), 1174 (w), 863 (w), 759 (w), 661 (m), 625 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 380 (1) [M^+], 322 (8) [$M^+ - (CO + 2CH_3)$], 294 (18) [$M^+ - (2CO + 2CH_3)$], 266 (11) [$M^+ - (3CO + 2CH_3)$], 226 (24), 212 (30), 210 (27), 53 (12) [$^{53}Cr^+$], 52 (100) [$^{52}Cr^+$].

Reaction of 6 with vinyllithium: A solution of **6** (188 mg, 0.64 mmol) in diethyl ether/THF (1:1, 50 mL) was added to a 0.44 M solution of vinyllithium in THF (10.0 mL, 4.4 mmol) at −78 °C over a period of 4 h. The resulting green-black

solution was stirred at −78 °C for 16 h, then hydrolyzed with hydrochloric acid (10 mL) and worked up. The ^{13}C NMR spectra of the obtained material shows only the signals of tricarbonyl[η^6-1,2-bis(1-oxopropenyl)benzene]chromium(0) (**29**). The material was further purified by chromatography (200 × 20 mm, ethyl acetate:pentane = 1:2) to afford **29** (32 mg, 0.10 mmol, 15%) as a red oil. ^1H NMR (200 MHz, [D$_6$]acetone): δ = 5.86 + 6.02 (AA'BB' line system, 2 × 2H, 3(6)-H + 4(5)-H), 5.91 (dd, 2H, (*E*)-9(12)-H, ^2J(H,H) = −1.2 Hz, $^3J_{cis}$(H,H) = 10.3 Hz), 6.22 (dd, 2H, (*Z*)-9(12)-H, $^3J_{trans}$(H,H) = 17.3 Hz), 6.84 (dd, 2H, 8(11)-H); ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 92.9 (d, C-3(6) or C-4(5)), 93.7 (d, C-3(6) or C-4(5)), 106.5 (s, C-1(2)), 130.1 (d, C-8(11)), 134.2 (t, C-9(12)), 189.8 (s, C-7(10)), 231.3 (s, CO); IR (KBr): $\tilde{\nu}$ = 3083 (w), 2962 (w), 2928 (w), 1977 (s, CO), 1898 (s, CO), 1691 (s, keto CO), 1603 (w), 1515 (w), 1426 (w), 1147 (w), 1095 (w), 1051 (w), 1023 (w), 934 (w), 653 (m), 617 (m), 524 (w) cm^{-1}; MS: Decomposition.

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[1] M. P. Cava, D. R. Napier, R. J. Pohl, *J. Am. Chem. Soc.* **1963**, *85*, 2076–2080.
[2] L. S. Liebeskind, S. Iyer, C. F. Jewell Jr., *J. Org. Chem.* **1986**, *51*, 3065–3067.
[3] L. S. Liebeskind, *Tetrahedron* **1989**, *45*, 3053–3060.
[4] O. H. W. Decker, H. W. Moore, *J. Org. Chem.* **1987**, *52*, 1174–1175.
[5] L. D. Foland, O. H. W. Decker, H. W. Moore, *J. Am. Chem. Soc.* **1989**, *111*, 989–995.
[6] S. H. Cho, K. R. Wirtz, L. S. Liebeskind, *Organometallics* **1990**, *9*, 3067–3072.
[7] S. L. Baysdon, L. S. Liebeskind, *Organometallics* **1982**, *1*, 771–775.
[8] L. S. Liebeskind, C. F. Jewell Jr., *J. Organomet. Chem.* **1985**, *285*, 305–319.
[9] L. S. Liebeskind, S. L. Baysdon, M. S. South, S. Iyer, J. P. Leeds, *Tetrahedron* **1985**, *41*, 5839–5853.
[10] J. A. Evans, G. F. Everitt, R. D. W. Kemmitt, D. R. Russell, *J. Chem. Soc. Chem. Commun.* **1973**, 158–159.
[11] M. F. Semmelhack, G. R. Clark, J. L. Garcia, J. J. Harrison, Y. Thebtaranonth, W. Wulff, A. Yamashita, *Tetrahedron* **1981**, *37*, 3957–3965.
[12] A. Solladié-Cavallo in *Advances in Metal–Organic Chemistry, Vol. 1* (Ed.: L. S. Liebeskind), Jai, London, **1989**, pp. 99–133.
[13] S. G. Davies, S. J. Coote, C. L. Goodfellow in *Advances in Metal–Organic Chemistry, Vol. 2* (Ed.: L. S. Liebeskind), Jai, London, **1991**, pp. 1–57.
[14] M. Uemura in *Advances in Metal–Organic Chemistry, Vol. 2* (Ed.: L. S. Liebeskind), Jai, London, **1991**, pp. 195–245.
[15] H. G. Wey, H. Butenschön, *Angew. Chem.* **1991**, *103*, 871–873; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 880–881; M. Brands, H. G. Wey, R. Krämer, C. Krüger, H. Butenschön, *Liebigs Ann.* **1993**, 253–265.
[16] M. Brands, H. G. Wey, R. Goddard, H. Butenschön, *Inorg. Chim. Acta* **1994**, *220*, 175–186.
[17] M. Brands, R. Goddard, H. G. Wey, H. Butenschön, *Angew. Chem.* **1993**, *105*, 285–287; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 267–269.
[18] M. Brands, J. Bruckmann, C. Krüger, H. Butenschön, *J. Chem. Soc. Chem. Commun.* **1994**, 999–1000.
[19] H. G. Wey, P. Betz, I. Topalovič, H. Butenschön, *J. Organomet. Chem.* **1991**, *411*, 369–374.
[20] H. Butenschön, B. Gabor, R. Mynott, H. G. Wey, *Z. Naturforsch. B* **1995**, *50b*, 483–487.
[21] W. H. Mills, I. G. Nixon, *J. Chem. Soc.* **1930**, 2510–2524.
[22] J. S. Siegel, *Angew. Chem.* **1994**, *106*, 1808–1810; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1721–1723.
[23] M. P. Cava, R. P. Stein, *J. Org. Chem.* **1966**, *31*, 1866–1869.
[24] E. Palomino, A. P. Schaap, M. J. Heeg, *Tetrahedron Lett.* **1989**, *30*, 6797–6800.
[25] L. A. Paquette, *Angew. Chem.* **1990**, *102*, 642–660; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 609–626.
[26] R. K. Hill in *Comprehensive Organic Synthesis, Vol. 5* (Ed.: B. M. Trost), Pergamon, Oxford, **1991**, pp. 785–826.
[27] D. McIntyre, G. R. Proctor, L. Rees, *J. Chem. Soc. C* **1966**, 985–989.
[28] J. P. Barnier, J. Ollivier, J. Salaün, *Tetrahedron Lett.* **1989**, *30*, 2525–2528.
[29] P. Geetha, C. A. M. A. Huq, K. Rajagopalan, S. Swaminathan, *Tetrahedron Lett.* **1982**, *23*, 569–570.
[30] S. Saito, T. Yamamoto, M. Matsuoka, T. Moriwake, *Synlett* **1992**, 239–240.
[31] R. W. Alder, D. Colclough, F. Grams, A. G. Orpen, *Tetrahedron* **1990**, *46*, 7933–7940.
[32] C. Clausen, H. Butenschön, **1994**, unpublished results.
[33] M. E. Jung, J. E. Hudspeth, *J. Am. Chem. Soc.* **1978**, *100*, 4309–4311.
[34] M. Brands, Dissertation, Ruhr-Universität Bochum, **1993**.
[35] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59126.
[36] F. A. L. Anet, *Top. Curr. Chem.* **1974**, *45*, 169–220.
[37] Y. Wang, K. Angermund, R. Goddard, C. Krüger, *J. Am. Chem. Soc.* **1987**, *109*, 587–589.
[38] M. J. McGlinchey, *Adv. Organomet. Chem.* **1992**, *34*, 285–325.
[39] J. T. Negri, T. Morwick, J. Doyon, P. D. Wilson, E. R. Hickey, L. A. Paquette, *J. Am. Chem. Soc.* **1993**, *115*, 12189–12190.
[40] L. A. Paquette, T. Morwick, *J. Am. Chem. Soc.* **1995**, *117*, 1451–1452.
[41] T. Morwick, J. Doyon, L. A. Paquette, *Tetrahedron Lett.* **1995**, *36*, 2369–2372.
[42] L. A. Paquette, *Top. Curr. Chem.* **1984**, *119*, 1–158.
[43] T. Anke, J. Heim, F. Knoch, U. Mocek, B. Steffan, W. Steglich, *Angew. Chem.* **1985**, *97*, 714–716; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 709–711.
[44] N. A. Petasis, M. A. Patane, *Tetrahedron* **1992**, *48*, 5757–5821.
[45] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.
[46] M. S. South, L. S. Liebeskind, *J. Org. Chem.* **1982**, *47*, 3815–3821.
[47] D. Seyferth, M. A. Weiner, *J. Am. Chem. Soc.* **1961**, *83*, 3583–3586.
[48] L. Brandsma, H. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer, Berlin **1987**.