Lithiated Heterocycles as Substrates for Dianionic Oxy-Cope Rearrangements − Chelation Accounts for Regioselective Enolate Hydrolysis

Beate Voigt,[a] Rudolf Wartchow,[b] and Holger Butenschön*[a]

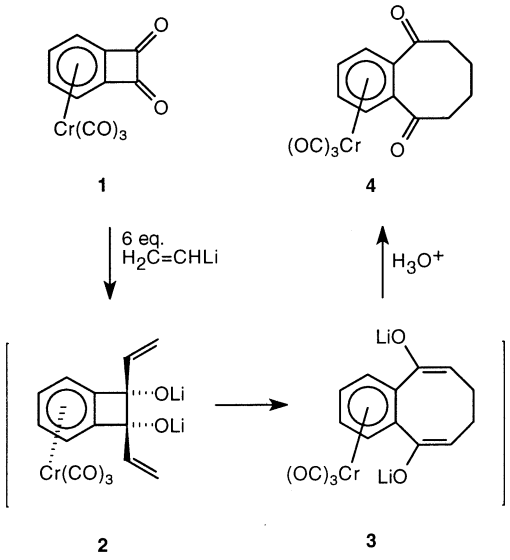
Keywords: Chromium / Dianionic oxy-Cope rearrangement / Heterocycles / Lithiation / Rearrangements

Lithiated heterocycles and phenyllithium were tested as alkenyllithium components in the dianionic oxy-Cope rearrangement taking place upon their addition to (η^6-benzocyclobutenedione)tricarbonylchromium (**1**). It was found that, with 5-lithio-2,3-dihydrofuran, the rearrangement and subsequent intramolecular aldol addition takes place diastereoselectively. Treatment of **1** with phenyllithium, 2-lithio-*N*-methylpyrrole, 2-lithiofuran, or 2-lithiothiophene, however, resulted only in the formation of single adducts and proximally or distally ring-opened diadducts, presumably because of the activation energy required to negate the aromatic character of two added anions. When, therefore, the monovinyl adduct *rac*-**19** was used as starting material, addition both of 2-lithiofuran and of 2-lithiothiophene resulted in the desired dianionic oxy-Cope rearrangements, followed by intramolecular aldol addition. Remarkably, the intramolecular aldol addition takes place with complete regioselectivity, meaning that the bis(enolate) hydrolysis is regioselective. This is explained by a chelate stabilization of one enolate moiety in preference to the other one, hydrolysis of which is thus highly favored.

Introduction

The selective synthesis of highly complex organic compounds in a low number of reaction steps is an attractive way to demonstrate the potential of a synthetic method or a reaction sequence. This is particularly the case when the reaction conditions are unusually mild, thus allowing the use even of sensitive substrates. In the field of pericyclic reactions, deprotonation of participating hydroxy functional groups in certain cases allows the alkoxy anion driven reaction to take place at temperatures much lower than in the corresponding electroneutral version. This is usually the case when the alkoxide moiety ends up as a part of a resonance-stabilized enolate function.[1] A prominent example of this type of oxy anion acceleration is the anionic oxy-Cope rearrangement discovered by Evans and Golob in 1975,[2] which has frequently been applied since then.[3,4]

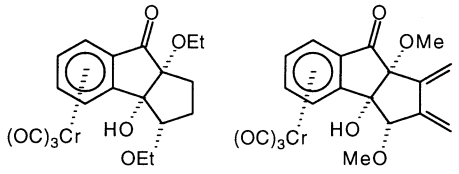
In the last decade, there have appeared publications by the Paquette group and by ourselves describing dianionic rearrangements upon double addition of vinylmetal reagents to squaric acid esters[5,6] and to (η^6-benzocyclobutenedione)tricarbonylchromium(0) (**1**),[7−11] taking place at temperatures as low as −78 °C. While double additions to squaric acid esters usually proceed in an *anti* fashion (however, *syn* double addition is observed with suitable chelate assistance[12]), followed by a sequence of pericyclic reactions and a final intramolecular aldol addition resulting in oligoquinanes, the double addition of alkenylmetal reagents to **1** occurs in a *syn* fashion, causing a dianionic oxy-Cope rearrangement to occur, resulting in benzocyclooctenedione complexes. For example, the reaction between **1** and vinyllithium proceeds through *syn* diadduct **2** and bis(enolate) **3** to give complex **4**.[8,10] With a number of alkenyllithium reagents, intramolecular aldol adducts such as **5**−**7** were obtained in good yields and with complete diastereoselectivity.[7]



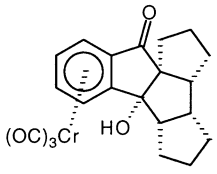
Here we report results from our experiments involving nonaromatic and aromatic heterocyclic alkenyllithium compounds, which can be incorporated with high degrees of diastereoselectivity into highly complex polycycles. The latter reactions are remarkable because they require the abolition of the aromaticity of the heterocycles. A few so-called aromatic oxy-Cope rearrangements and aromatic anionic

[a] Institut für Organische Chemie, Universität Hannover, Schneiderberg 1B, 30167 Hannover, Germany
Fax: (internat.) + 49-(0)511/762-4616
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de
[b] Institut für Anorganische Chemie, Universität Hannover Callinstraße 9, 30167 Hannover, Germany

  1434−193X/01/0713−2519 $ 17.50+.50/0



rac-**5** *rac*-**6**

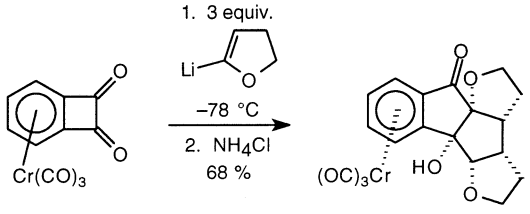


rac-**7**

oxy-Cope rearrangements have been reported,[13–16] and so experiments using phenyllithium are also included. The only report of an aromatic dianionic oxy-Cope rearrangement is the early example reported by Alder et al., who treated acenapthenequinone with 1-lithionaphthalene and observed reaction at ambient temperature.[17]

Results and Discussion

The reaction between **1** and 3 equiv. of 5-lithio-2,3-dihydrofuran at −78 °C gave, after hydrolysis with ammonium chloride, the tetracyclic heterocycle *rac*-**8** in 68% yield as the only product. Compound *rac*-**8** was characterized spectroscopically, with the relative configuration assigned on the basis of comparison of the NMR spectra of *rac*-**8** with those of closely related compounds, such as the corresponding carbocycle **7**.[10]

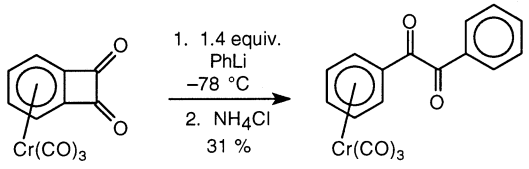


1 *rac*-**8**

The experiment underlines the striking stereochemical differences between the dianionic oxy-Cope rearrangement induced by addition of vinylmetal to **1** and the more complicated rearrangement processes induced by addition of alkenylmetal to diisopropyl squarate. This latter process, when carried out with 5-lithio-2,3-dihydrofuran, gives 4 isomeric racemic products in 52%, 15%, 6%, and 4% yields.[18] In contrast to squaric acid esters, the dione ligand in **1** is attacked exclusively from the *exo* face, as a result of the steric shielding of the *endo* face by the tricarbonychromium group. In addition, Michael type addition processes are impossible in **1**.

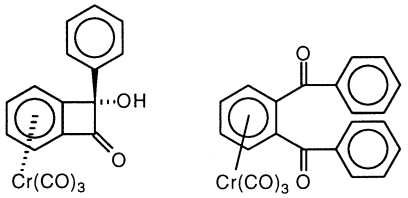
Having established the possibility of dianionic oxy-Cope rearrangements with a heterocyclic vinylmetal, we were interested in investigating the feasibility of metallated aromatic heterocycles in this type of reaction. This was regarded as less likely, because with two added aromatic systems their aromaticity would have to be abolished in the course of the rearrangement. In this context, the reaction between **1** and phenyllithium was briefly investigated before the testing of heterocyclic lithiated aromatics. There is one literature report that uncomplexed benzocyclobutenedione reacts with phenyllithium at low temperatures to give the diadduct without any rearrangement.[19] The reaction between benzocyclobutenedione and a phenyl Grignard reagent results in the formation of 1,3-diphenylisobenzofuran.[20,21]

Treatment of the tricarbonylchromium complex **1** with phenyllithium gave a variety of products, depending on the reaction conditions.[22] Upon addition of a solution of **1** in diethyl ether/THF (1:1) to a solution of phenyllithium in diethyl ether at −78 °C, selective formation of (benzil)-tricarbonylchromium(0) (**9**), which could not be completely purified by recrystallization, was observed in 31% yield as a result of a proximal ring opening. Proximal ring-opening reactions of **1** are frequently observed upon treatment of **1** with heteroatomic nucleophiles, giving 2-oxo-2-phenylacetic acid derivatives.[23] The reaction producing **9** is less common, as it involves a carbon nucleophile and thus gives rise to a 1,2-diketone.[11]



1 **9**

When the phenyllithium solution was added very quickly, monoadduct *rac*-**10** was obtained in addition to **9** (17%), in 23% yield. Rapid addition of an excess of phenyllithium resulted in 20% of *rac*-**10**[10] and 20% of diketone complex **11** under otherwise unchanged reaction conditions. The mechanism of the formation of **11** is unclear; in addition to a distal ring opening it must involve an oxidation process. Presumably the full conjugation is a driving force in the formation of **11**.

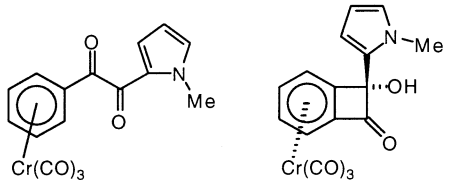


rac-**10** **11**

As *N*-methylpyrrole, furan, and thiophene are considered less aromatic in character,[24] we next tried to effect dianionic oxy-Cope rearrangements using these heterocycles.

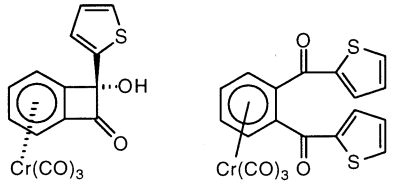
However, all reactions between **1** and 2-lithio-*N*-methylpyrrole, 2-lithiothiophene, or 2-lithiofuran resulted in the formation of ring-opened products similar to those obtained with phenyllithium.

Addition of 3 equiv. of 2-lithio-*N*-methylpyrrole[25] to a solution of **1** in diethyl ether/THF (1:1) at −78 °C gave a 22% yield of 1,2-dione **12**, which closely corresponds to **9**. When, instead, a solution of **1** was added to the anion, only 12% of **12** was obtained, together with 52% of monoadduct *rac*-**13**.



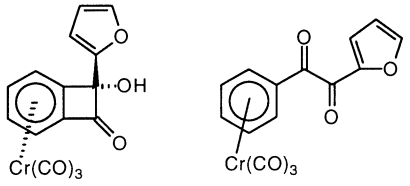
12 *rac*-**13**

Even when **1** was treated with a sixfold excess of 2-lithiothiophene,[26] monoadduct *rac*-**14** was obtained as the main product (66%), together with some of the distal ring-opened product **15** (23%). Again, in addition to the distal ring opening, some kind of oxidation process must be involved to account for the minor product.

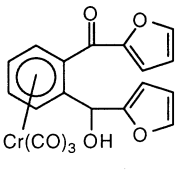


rac-**14** **15**

Addition of 4 equiv. of 2-lithiofuran to **1** in THF at −78 °C resulted in the formation of a mixture of monoadduct *rac*-**16** (26%) and diketone **17** (10%). When a fivefold excess of the anion was added to **1** instead, 27% of *rac*-**16** and 44% of diastereomerically pure hydroxy ketone *rac*-**18** were obtained, while no oxidation of *rac*-**18** to a dione corresponding to **15** was observed.

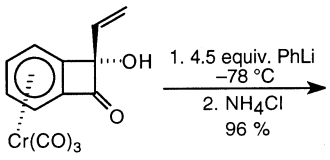


rac-**16** **17**

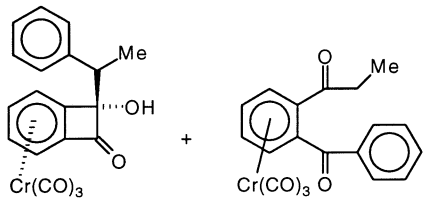


rac-**18**

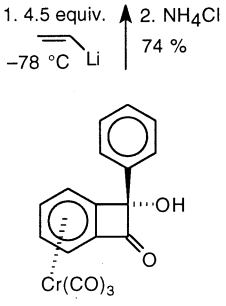
The results obtained so far indicate that incorporation of two lithiated aromatics in the dianionic oxy-Cope rearrangement is hardly possible, as the energy of activation necessary to overcome the aromaticity of two components is apparently too high. In order to effect the desired rearrangement, we next examined the use of only one aromatic component. For this purpose we used vinyl monoadduct *rac*-**19** as the starting material.[8,10] Treatment of *rac*-**19** with 4 equiv. of phenyllithium at −78 °C unexpectedly resulted in the formation of adducts *rac*-**20** and *rac*-**21**, each of which was obtained in 48% yield.



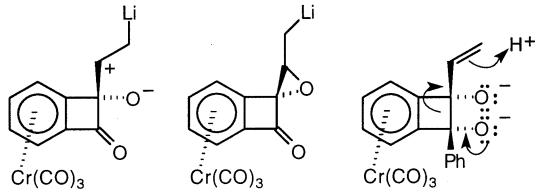
rac-**19**



rac-**20** 1:1 *rac*-**21**



rac-**25**

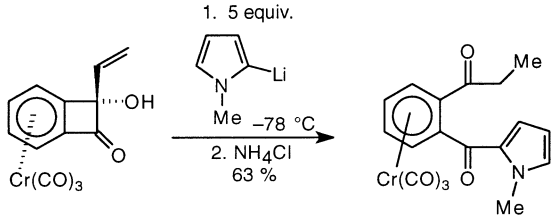


rac-**22** *rac*-**23** *rac*-**24**

Compound *rac*-**20** is the product of an electrophilic addition of phenyllithium to the vinylic double bond in the alkoxide derived from *rac*-**19**. We think that the secondary carbenium ion formed by addition of Li^+ at the terminal carbon atom is stabilized by the neighboring alkoxide moiety. The intermediate may be viewed as the zwitterionic *rac*-

22 or the strained *rac*-**23**. Compound *rac*-**21** appears to be the product of an addition of PhLi at the oxo group, followed by a fragmentation of *rac*-**24** and hydrolysis of the formed enolate. No dianionic oxy-Cope rearrangement was observed; apparently the reaction channels producing *rac*-**20** and *rac*-**21** are much more active. This was also the case when the order of the additions was reversed; when phenyl monoadduct *rac*-**25**[10] was treated with 4.5 equiv. of vinyllithium, a 74% yield of *rac*-**21** was isolated.

A corresponding reaction was observed when *rac*-**19** was treated with 5 equiv. of the heterocyclic 2-lithio-*N*-methylpyrrole at −78 °C. Distally ring-opened dione *rac*-**26** was obtained in 63% yield as the only isolated product.

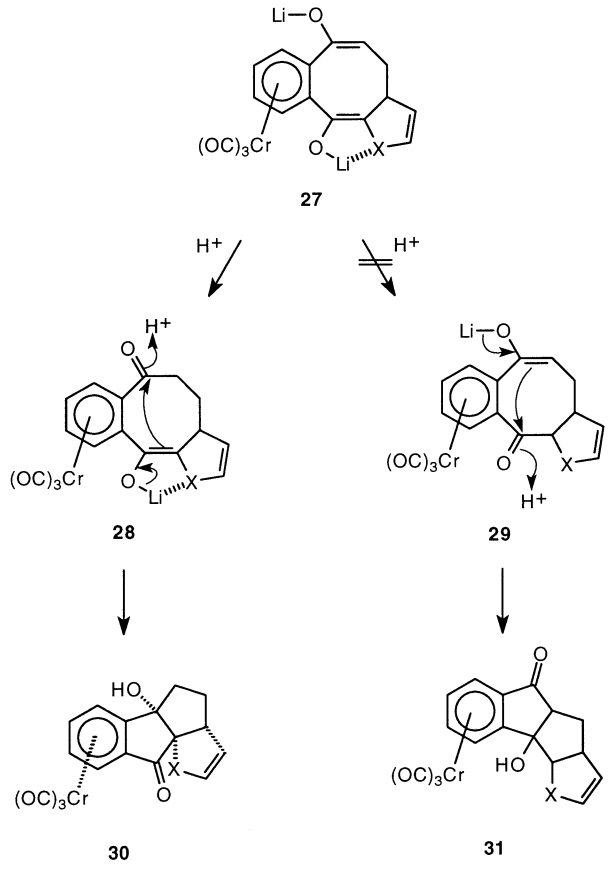


rac-**19** *rac*-**26**

2-Lithiothiophene and 2-lithiofuran were tested next. There is one report of a thermal Cope rearrangement involving a thiophene system[27] in addition to the already mentioned work of Moore, who used 2-lithiothiophene and 2-lithiofuran in anionic oxy-Cope rearrangements.[15] Either compound, 2-lithiothiophene or 2-lithiofuran, was usable successfully, with the dianionic oxy-Cope rearrangement taking place with abolition of the aromaticity of the heterocycles.

The dianionic oxy-Cope rearrangement gives the bis(enolate) **27** as the primary rearrangement product. Depending on which of the unequal enolate moieties is hydrolyzed first, either compound **28** or compound **29** should form, resulting in aldol adducts **30** and **31**, respectively. Should both hydrolyses take place, a mixture of isomers of type **30** and **31** would be expected. Much to our delight, the aldol addition following the rearrangement took place with complete regioselectivity; upon treatment of *rac*-**19** with 3 equiv. of 2-lithiofuran or 2-lithiothiophene at −78 °C (followed by hydrolysis with ammonium chloride), aldol adducts *rac*-**32** and *rac*-**33** − both corresponding to **30** − were obtained in 66% and 50% yields, respectively, as the only isolated reaction products. No product corresponding to the alternative aldol adduct **31** was found. In conclusion, hydrolysis of the enolate moiety adjacent to the anellated heterocycle in the bis(enolate) **27** appears to be much less likely than that of the opposite enolate unit. An explanation for this effect might be chelation of the lithium ion between the enolate function and a lone electron pair of the heteroatom in the anullated ring.

Intramolecular aldol reactions, including transannular cyclizations, have recently been reviewed by Heathcock.[28] In unsymmetrical versions, steric factors are in most cases invoked to explain the observed regioselectivity. Usually the



reactions are performed starting from the respective dialdehydes, diketones, or oxo aldehydes, under conditions of acid or base catalysis. In contrast, the reaction reported here starts from a bis(enolate) resulting from the dianionic oxy-Cope rearrangement, which is selectively protonated under chelate control.

Compounds *rac*-**32** and *rac*-**33** were characterized spectroscopically. However, clear-cut assignment of the relative configurations was found not to be possible on the basis of

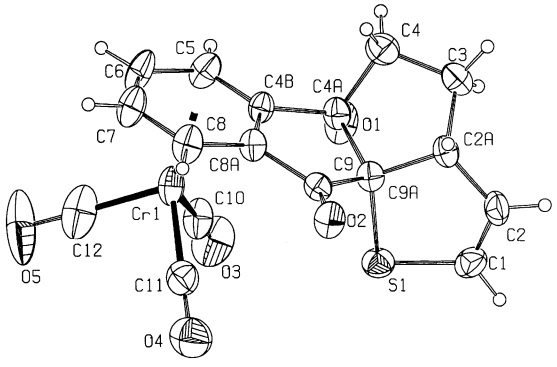
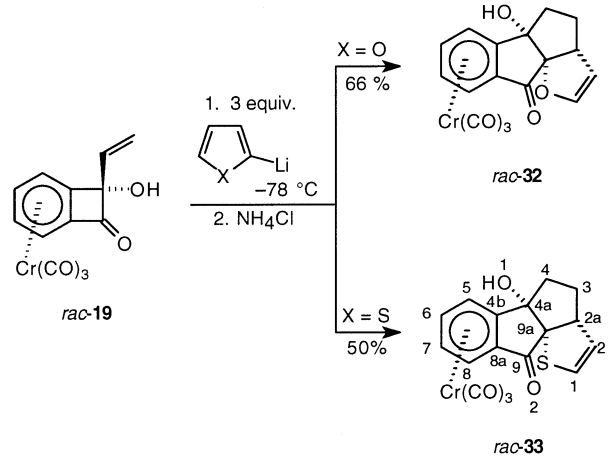


Figure 1. Structure of *rac*-**33** in the crystal and atom numbering scheme; selected bond lengths [A]: S1−C1 1.747(8), S1−C9a 1.814(7), C1−C2 1.304(10), C2−C2a 1.482(9), C2a−C3 1.536(9), C2a−C9a 1.522(8), C3−C4 1.523(9), C4−C4a 1.496(10), C4a−O1 1.418(6), C4a−C9a 1.564(8), C4a−C4b 1.505(7), C4b−C8a 1.424(7), C4b−C5 1.395(8), C5−C6 1.375(9), C6−C7 1.441(8), C7−C8 1.376(8), C8−C8a 1.422(7), C8a−C9 1.458(8), C9−C9a 1.552(7), C9−O2 1.209(6), Cr−C4b 2.221(6), Cr−C5 2.242(8), Cr−C6 2.197(8), Cr−C7 2.199(7), Cr−C8 2.207(6), Cr−C8a 2.171(5)



the NMR spectra. The stereochemistry of the intramolecular aldol addition had so far always[7−11] followed the rule that the oxo group generated in the first hydrolysis step is attacked by the second enolate from the face opposite to the tricarbonylchromium group. An X-ray crystal structure analysis of *rac*-**33** finally confirmed that this rule had also been obeyed in this case (Figure 1), the analysis clearly confirming the relative configuration. The tricarbonylchromium fragment features an *anti* conformation, which presumably is the reason for the relatively large bond length of the opposite bond C4b−C8a [1.424(7) Å].

The reactions producing *rac*-**32** and *rac*-**33** are the first examples of aromatic dianionic oxy-Cope rearrangements. The enol ether functionality thus incorporated might be useful for such further reactions as hydrolysis, ozonolysis, or cycloaddition. This perspective is fascinating because it allows highly complicated polycycles to be constructed diastereoselectively in only a few reaction steps and in an atom-economic fashion. Further investigations along these lines are in progress in our laboratories.

Experimental Section

General: See ref.[11]

General Procedure 1 (GP1) and General Procedure 2 (GP2): See ref.[11]

Tricarbonyl{η⁶-1,2,3,3a,3b,4,5,6,6a,6b-decahydro-6b-*endo*-hydroxy-11*H*-1,6-dioxa-*endo*-cyclopenta[5,6]-*endo*-pentaleno[4,5-*a*]inden-11-one}chromium(0) (*rac*-8): GP2. A solution of *tert*-butyllithium in pentane (1.6 M, 1.64 mL, 2.62 mmol) was added dropwise at −78 °C to 2,3-dihydrofuran (195 mg, 2.78 mmol) in THF (10 mL).[29,30] After completion of addition, the mixture was stirred at 0 °C for 30 min and then cooled to −78 °C. Compound **1** (250 mg, 0.93 mmol) in diethyl ether/THF (1:1, 20 mL) was added. Workup was with 20 mL of sat. aq. NH_4Cl. The resulting red oil was purified by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/THF, 10:1), to give 258 mg (0.63 mmol, 68%) of *rac*-**8** (R_f = 0.13), orange solid, m.p. 170 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3448 cm^{-1} (m, br, OH), 3084 (m, arom. CH), 2952 (m, $-CH_2-$), 2884 (m), 1980 (s, CO), 1908 (s, CO), 1716 (s, CO, ketone), 1520 (m), 1424 (w), 1276 (w), 1172 (m), 1144 (w), 1092 (m, C−O), 1072 (m, C−O), 1016 (m), 888 (m), 652 (m), 616 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.94−2.28 (m, 4 H, aliph. H), 2.70 (m, 1 H, aliph. H), 2.98 (m, 1 H, aliph. H), 3.61 (s, 1 H, OH), 3.91 (m, 1 H, aliph. H), 4.11−4.39 (m, 4 H, aliph. H), 5.28 (dd, 1 H, 2-H or 3-H, ^3J = 6.4 Hz, ^3J = 6.0 Hz), 5.64 (m, 2 H, 2-H or 3-H, 1-H or 4-H), 5.78 (d, 1 H, 1-H or 4-H, ^3J = 6.0 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$, APT): δ = 28.4 (+, C-8 or C-9), 30.4 (+, C-8 or C-9), 42.6 (−, C-8a or C-8b), 49.1 (−, C-8a or C-8b), 70.3 (+, C-7 or C-10), 73.4 (+, C-7 or C-10), 80.1 (+, C-11b), 85.3 (−, C-1 or C-2 or C-3 or C-4), 90.0 (−, C-1 or C-2 or C-3 or C-4), 91.2 (−, C-11a), 93.5 (−, C-1 or C-2 or C-3 or C-4), 93.7 (+, C-4a or C-5a), 96.0 (+, C-4a or C-5a), 125.0 (+, C-11c) 201.6 (+, C-5), 299.4 (+, CO). − MS (70 eV, 150 °C): *m/z* (%) = 408 (5) [M^+], 353 (10), 352 (33) [M^+ − 2 CO], 324 (28) [M^+ − 3 CO], 323 (100) [M^+ − 3 CO, −H], 294 (13), 277 (15), 276 (51), 246 (25), 232 (20), 220 (14), 202 (12), 165 (14), 115 (10), 109 (18), 80 (31), 53 (19), 52 (98) [^{52}Cr]. − HRMS ($C_{19}H_{16}CrO_7$): calcd. 408.030113; found 408.0301. − $C_{19}H_{16}CrO_7$ (408.3): calcd. C 55.89; H 3.95; found C 55.39, H 3.96.

Tricarbonyl(η⁶-1,2-diphenylethane-1,2-dione)chromium(0) (9): GP1. A cold (−78 °C) solution of phenyllithium in diethyl ether (1.4 M, 0.9 mL, 1.32 mmol) was slowly added to **1** (250 mg, 0.93 mmol) in diethyl ether/THF (1:1). Workup with 2 N HCl (10 mL) and column chromatography of the obtained red oil (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether, 2:1) afforded 100 mg (0.28 mmol, 31%) of **9** (R_f = 0.30), dark red solid (cryst. from $CHCl_3$), m.p. 80 °C. − IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1} (w, arom. CH), 1996 (s, CO), 1920 (s, CO), 1900 (s, CO), 1676 (m, CO-ketone), 1644 (s, CO-ketone), 1592 (m), 1512 (m), 1496 (w), 1448 (m), 1412 (m), 1384 (w), 1324 (m), 1288 (w), 1208 (s), 1176 (m), 1160 (m), 1064 (m), 1004 (m), 860 (m), 796 (m), 720 (m), 696 (m), 648 (s), 600 (s), 528 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24 [dd, 5(7)-H, ^3J = 6.4 Hz, ^3J = 6.8 Hz), 5.80 (dd, 1 H, 6-H, ^3J = 6.0 Hz, ^3J = 6.4 Hz), 6.21 [d, 2 H, 4(8)-H, ^3J = 6.0 Hz], 7.55 (dd, 2 H, *m*-H), 7.69 (dd, 1 H, *p*-H), 8.30 (d, 2 H, *o*-H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 88.2 [−, C-4(8)], 89.7 (+, C-3), 95.6 [−, C-5(7)], 96.2 (−, C-6), 128.9 (−, *m*-C), 130.0 (−, *o*-C), 132.2 (−, *p*-C), 135.2 (+, *ipso*-C), 188.9 (+, C-1 or C-2), 191.7 (+, C-1 or C-2), 229.5 (+, CO). − MS (70 eV, 140 °C): *m/z* (%) = 346 (1) [M^+], 290 (2) [M^+ − 2CO], 262 (9) [M^+ − 3CO], 234 (16), 182 (10), 165 (20), 152 (5), 108 (8), 105 (28), 91 (17), 80 (12), 77 (29), 53 (11) [^{53}Cr], 52 (100) [^{52}Cr]. − HRMS ($C_{17}H_{10}CrO_5$): calcd. 345.993333; found 345.9948. − $C_{17}H_{10}CrO_5$ (346.3): calcd. C 58.97, H 2.91, found C 58.85, H 2.97.

Tricarbonyl(η⁶-1,2-dibenzoylbenzene)chromium(0) (11): GP2. A solution of phenyllithium in diethyl ether (0.7 M, 5.3 mL, 3.71 mmol) was added at −78 °C to **1** (250 mg, 9.32 mmol) in diethyl ether/THF (1:1, 30 mL). After completion of addition, the mixture was stirred for 30 min and worked up with sat. aq. NH_4Cl (29 mL). The resulting red oil was purified twice by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1) to afford 64 mg (0.18 mmol, 20%) of *rac*-**10** (R_f = 0.40); 80 mg (0.18 mmol, 20%) of **11**, red solid, m.p. 141 °C, (R_f = 0.20).

11: IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w, arom. CH), 3064 (w, arom. CH), 1976 (s, CO), 1924 (s, CO), 1900 (s, CO), 1656 (m, CO ketone), 1596 (m), 1448 (m), 1312 (m), 1272 (s), 916 (m), 736 (m), 700 (m), 652 (m), 636 (m), 612 (m), 524 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.47 + 5.63 [AA′BB′ line system, 2 × 2 H, 2(5)-H + 3(4)-H], 7.40 (m, 4 H, *m*-H), 7.49 (m, 2 H, *p*-H), 7.77 (m, 4 H, *o*-H). − ^{13}C NMR (100 MHz, $CDCl_3$, APT): δ = 89.7 [−, C-2(5) or C-3(4)], 92.6 [C-2(5) or C-3(4)], 105.6 [+, C-1(6)], 128.8 (−, *m*-C), 128.8 (−, *o*-C), 133.0 (−, *p*-C), 136.4 (−, *ipso*-C), 192.3 [+, C-7(8)], 229.5 (+, CO). − MS (70 eV, 170 °C): *m/z* (%) = 422 (1) [M^+], 366 (36) [M^+ − 2CO], 339 (39), 338 (46) [M^+ − 3 CO], 321 (12), 311 (28), 310 (42), 270 (38), 209 (51), 152 (42), 77 (62), 53 (41),

52 (100) [^{52}Cr]. − HRMS ($C_{23}H_{14}CrO_5$): calcd. 422.024633; found 422.0235. − $C_{23}H_{14}CrO_5$ (422.4): calcd. C 65.40, H 3.34; found C 65.07, H 3.57.

Tricarbonyl[η^6-1-(1-methyl-2-pyrrolyl)-2-phenyl-1,2-ethanedione]-chromium(0) (12) and *rac*-Tricarbonyl[η^6-2-*endo*-hydroxy-2-*exo*-(1-methylpyrrol-2-yl)-1-oxobenzocyclobutene]chromium(0) (*rac*-13). − a) GP1. A solution of *tert*-butyllithium in pentane (1.6 M, 2.6 mL, 4.16 mmol) was added dropwise at −78 °C to a cold solution of *N*-methylpyrrole (600 mg, 7.40 mmol) in THF (10 mL).[25] After warming to 25 °C, the mixture was again cooled to −78 °C and compound **1** (250 mg, 0.93 mmol) in diethyl ether/THF (1:1, 20 mL) was added. Workup with sat. aq. NH_4Cl (20 mL) and purification of the red oil obtained twice by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether, 1:1) afforded 71 mg (0.20 mmol, 22%) of **12** (R_f = 0.22), red solid, m.p. 113 °C. − **b)** GP2. A solution of *tert*-butyllithium in pentane (1.6 M, 1.7 mL, 2.72 mmol) was added dropwise to *N*-methylpyrrole (300 mg, 3.70 mmol) in diethyl ether (20 mL).[25] After stirring at 25 °C for 90 min the mixture was again cooled to −78 °C and treated with **1** (250 mg, 0.93 mmol) in diethyl ether/THF (1:1, 20 mL). Workup with sat. aq. NH_4Cl (20 mL) and column chromatography of the red oil obtained (*l* 400 mm, ∅ 30 mm, diethyl ether /petroleum ether, 1:1) afforded two fractions. − I: 169 mg (4.84 mmol, 52%) of *rac*-**13**, orange solid, m.p. 130 °C. − IR (KBr): $\tilde{\nu}$ = 3496 cm^{-1} (s, br, OH), 3070 (m, arom. CH), 1984 (s, CO), 1912 (s, CO), 1748 (s, CO-ketone), 1672 (m), 1372 (m), 1172 (m), 1152 (m), 1124 (m), 1044 (w), 900 (w), 740 (s), 652 (s), 608 (s), 520 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.24 (s, 1 H, OH), 3.89 (s, 3 H, C*H*$_3$), 5.53 (dd, 1 H, 4-H or 5-H, ^3J = 6.0 Hz, ^3J = 5.5 Hz), 5.57 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 5.94 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 6.01 (d, 2 H, ^3J = 2.0 Hz), 6.68 (dd, 1 H, ^3J = 2.0 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 35.6 (−, *C*H$_3$), 85.0 (−, C-3 or C-4 or C-5 or C-6), 85.8 (−, C-3 or C-4 or C-5 or C-6), 91.9 (−, C-3 or C-4 or C-5 or C-6), 92.1 (−, C-3 or C-4 or C-5 or C-6), 92.5 (+, C-2), 103.9 (+, C-6a), 107.3 (−, pyrrolyl-C), 111.0 (−, pyrrolyl-C), 126.1 (−, pyrrolyl-C), 127.7 (+, C-2a), 127.7 (+, *ipso*-C), 185.0 (+, C-1), 229.3 (+, CO). − $C_{16}H_{11}CrNO_5$ (349.3): calcd. C 55.01, H 3.18; found C 55.08, H 3.43. − II: 39 mg (0.11 mmol, 12%) of **12**. − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1} (w, arom. CH), 2950 (w, −CH_2−), 1980 (s, CO), 1965 (s, CO), 1890 (s, CO), 1668 (s, CO-ketone), 1620 (s, CO-ketone), 1422 (m), 1403 (s), 1263 (m), 1223 (m), 802 (m), 748 (m), 673 (m), 659 (m), 622 (m). − ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 4.05 (s, 3 H, C*H*$_3$), 5.63 [dd, 2 H, 5(7)-H, ^3J = 6.4 Hz, ^3J = 6.8 Hz], 6.16 (dd, 1 H, 6-H), 6.26 (dd, 1 H, pyrrolyl-H, ^3J = 4.2 Hz, ^3J = 4.4 Hz), 6.39 [d, 2 H, 4(8)-H], 7.00 (dd, 1 H, pyrrolyl-H, ^3J = 1.6 Hz, ^3J = 4.2 Hz), 7.32 (m, 1 H, pyrrolyl-H). − ^{13}C NMR (50 MHz, [D$_6$]acetone, APT): δ = 37.5 (−, *C*H$_3$), 91.0 [−, C-4(8)], 92.7 (+, C-3), 97.6 [−, C-5(7)], 110.5 (−, pyrrolyl-C), 125.5 (+, *ipso*-C), 127.9 (−, pyrrolyl-C), 135.7 (−, pyrrolyl-C), 181.4 (+, C-1), 190.4 (+, C-2), 231.7 (+, CO). − MS (70 eV, 150 °C): *m*/*z* (%) = 349 (49) [M$^+$], 293 (5) [M$^+$ − CO], 292 (14) [M$^+$ − 2 CO], 265 (21) [M$^+$ − 3 CO], 247 (25), 238 (12), 237 (41), 222 (16), 196 (30), 168 (18), 53 (13), 52 (100) [^{52}Cr]. − HRMS ($C_{16}H_{11}CrNO_5$): calcd. 349.004232; found 349.0089. − $C_{16}H_{11}CrNO_5$ (349.26): calcd. C 55.01, H 3.18; found C 54.17, H 3.35.

Tricarbonyl[η^6-2-*endo*-hydroxy-1-oxo-2-*exo*-(2-thienyl)-benzocyclobutene]chromium(0) (*rac*-14) and [η^6-1,2-Bis(2-thiophenoyl)benzene]tricarbonylchromium(0) (15): GP2. A solution of butyllithium in hexane (1.6 M, 6.25 mL, 10.0 mmol) was added dropwise at 25 °C to thiophene (924 mg, 11.0 mmol) in diethyl ether (50 mL). The mixture was stirred at 25 °C for 30 min and then cooled to −78 °C. Further treatment was with **1** (500 mg, 1.86 mmol) in diethyl ether/THF (1:1, 50 mL), workup with sat. aq. NH_4Cl (20 mL). The red oil obtained was separated by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1) yielding two fractions. − I (R_f = 0.55): 432 mg (1.22 mmol, 66%) of *rac*-**14**, orange solid, m.p. 191 °C. − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (s, br, OH), 3079 (s, arom. CH), 2920 (w, −CH_2−), 1984 (s, CO), 1914 (s, CO), 1747 (s, CO-ketone), 1500 (m), 1424 (m), 1400 (s), 1337 (s), 1259 (m), 1244 (m), 1217 (m, C−O), 1090 (m), 1053 (m), 880 (s), 574 (s). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.74 (dd, 1 H, 4-H or 5-H, ^3J = 6.0 Hz, ^3J = 5.8 Hz), 5.95 (m, 2 H, 4-H or 5-H,. 3-H or 6-H), 6.22 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 6.82 (s, 1 H, OH), 7.01 (m, 2 H, arom. H), 7.52 (dd, 1 H, arom. H, ^3J = 4.0 Hz). − ^{13}C NMR (100 MHz, [D$_6$]acetone, DEPT): δ = 82.3 (−, C-3 or C-4 or C-5 or C-6), 83.3 (−, C-3 or C-4 or C-5 or C-6), 89.5 (−, C-3 or C-4 or C-5 or C-6), 89.9 (+, C-2), 91.0 (−, C-3 or C-4 or C-5 or C-6), 101.9 (+, C-6a), 122.1 (−, arom. C), 123.4 (−, arom. C), 123.6 (−, arom. C), 125.8 (+, C-2a), 140.0 (+, *ipso*-C), 182.5 (+, C-1), 227.0 (+, CO). − MS (70 eV, 140 °C): *m*/*z* (%) = 352 (8) [M$^+$], 295 (8) [M$^+$ − 2 CO], 268 (44) [M$^+$ − 3 CO], 240 (36), 199 (15), 171 (20), 77 (7), 53 (17), 52 (100) [^{52}Cr]. − HRMS ($C_{15}H_8CrO_5S$): calcd. 351.949756; found 351.9485. − $C_{15}H_8CrO_5S$ (352.3): calcd. C 51.11, H 2.29; found C 51.26, H 2.44. − II (R_f = 0.28): 186 mg (0.42 mmol, 23%) of **15**, red solid, m.p. 172 °C. − IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (w, arom. CH), 1980, (s, CO), 1909 (s, CO), 1631 (s, CO-ketone), 1514 (s), 1411 (s), 1355 (s), 1052 (m), 732 (m), 655 (s), 617 (s). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.91 + 6.20 [AA′BB′ line system, 2 × 2 H, 3(4)-H + 2(5)-H], 7.21 (dd, 2 H, arom. H, ^3J = 4.9 Hz,^3J = 3.9 Hz), 7.90 (d, 2 H, arom. H, ^3J = 3.9 Hz), 7.99 (d, 2 H, ^3J = 4.9 Hz). − ^{13}C NMR (50 MHz, [D$_6$]acetone, APT): δ = 91.4 [−, C-2(5) or C-3(4)], 93.3 [−, C-2(5) or C-3(4)], 107.0 [+, C-1(6)], 128.1 (−, arom. C), 134.4 (−, arom. C), 135.5 (−, arom. C), 142.3 (+, *ipso*-C), 183.5 [+, C-7(8)], 230.6 (CO). − MS (70 eV, 160 °C): *m*/*z* (%) = 434 (1) [M$^+$], 378 (21) [M$^+$ − 2 CO], 350 (71) [M$^+$ − 3 CO], 322 (82), 297 (11), 282 (9), 221 (10), 175 (10), 115 (10), 111 (25), 53 (12), 52 (100) [^{52}Cr]. − HRMS ($C_{19}H_{10}CrO_5S_2$): calcd. 433.937479; found 433.9362. − $C_{19}H_{10}CrO_5S_2$ (434.4): calcd. C 52.54, H 2.32; found C 52.48, H 2.51.

***rac*-Tricarbonyl[η^6-2-*exo*-(2-furyl)-2-*endo*-hydroxy-1-oxobenzocyclobutene]chromium(0) (*rac*-16), Tricarbonyl[η^6-1-(2-furyl)-2-phenylethane-1,2-dione]chromium (17), and *rac*-Tricarbonyl[η^6-1-(2-furoyl)-2-(furylhydroxymethyl)benzene]chromium(0) (*rac*-18). − a)** GP1. A solution of butyllithium in hexane (1.6 M, 2.4 mL, 3.84 mmol) was added dropwise at 10 °C to a solution of furan (310 mg, 4.55 mmol) in THF (5 mL). After 30 min at 10 °C, the mixture was cooled to −78 °C and treated with **1** (250 mg, 0.93 mmol) in diethyl ether/THF (1:1, 20 mL). Workup was with sat. aq. NH_4Cl (20 mL). The red oil obtained was purified three times by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether, 1:1) yielding two fractions. − I: 81 mg (0.24 mmol, 26%) of *rac*-**16**, orange solid, m.p. 153 °C. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w, arom. CH), 2004 (s, CO), 1984 (s, CO), 1916 (s, CO), 1752 (s, CO-ketone), 1500 (m), 1424 (m), 1396 (m), 1340 (m), 1180 (m), 1152 (m), 1060 (m), 1020 (m), 912 (m), 832 (m), 752 (m), 712 (m), 656 (m), 604 (s). − ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 5.69 (dd, 1 H, 4-H or 5-H), ^3J = 6.4 Hz, ^3J = 6.2 Hz), 5.89 (dd, 1 H, 4-H or 5-H, ^3J = 6.2 Hz, ^3J = 6.4 Hz), 5.96 (d, 1 H, 3-H or 6-H, ^3J = 6.4 Hz), 6.17 (d, 1 H, 3-H or 6-H, ^3J = 6.2 Hz), 6.45 (d, 1 H, furanyl-H, ^3J = 3.1 Hz), 6.48 (dd, 1 H, furanyl-H, ^3J = 3.1 Hz, ^3J = 2.0 Hz), 6.72 (s, 1 H, OH), 7.56 (d, 1 H, furanyl-H, ^3J = 2.0 Hz). − ^{13}C NMR (100 MHz, [D$_6$]acetone, DEPT): δ = 85.2 (−, C-3 or C-4 or C-5 or C-6), 86.5 (−, C-3 or C-4 or C-5 or C-6), 92.5 (−, C-3 or

C-4 or C-5 or C-6), 92.5 (+, C-2), 94.0 (−, C-3 or C-4 or C-5 or C-6), 105.3 (+, C-6a), 107.9 (−, furanyl-C), 110.3 (−, furanyl-C), 127.7 (+, C-2a), 143.5 (−, furanyl-C), 151.6 (+, ipso-C), 185.0 (+, C-1), 230.1 (+, CO). − MS (70 eV, 100 °C): *m/z* (%) = 336 (7) [M^+], 308 (8) [$M^+ - CO$], 307 (29), 281 (32) [$M^+ - 2\,CO$, ^{52}Cr], 280 (100) [$M^+ - 2\,CO$], 253 (100), 252 (100) [$M^+ - 3\,CO$], 222 (60), 177 (22), 129 (63), 53 (100), 52 (100) [^{52}Cr]. − HRMS ($C_{15}H_8CrO_6$): calcd. 335.972598; found 335.9758. − $C_{15}H_8CrO_6$ (336.2): calcd. C 53.58, H 2.40; found C 54.13, H 2.58. − II: 30 mg (0.09 mmol, 10%) of **17**, red solid, m.p. 141 °C. − IR (KBr): $\tilde{\nu}$ = 1992 (s, CO) cm^{-1}, 1920 (s, CO), 1650 (s, CO-ketone), 1644 (s, CO-ketone), 1460 (m), 1244 (m), 1016 (m), 625 (m), 604 (m). − ^1H NMR (400 MHz, $CDCl_3$): δ = 5.28 [dd, 2 H, 5(7)-H, ^3J = 6.6 Hz, ^3J = 5.5 Hz], 5.79 (dd, 1 H, 6-H, ^3J = 5.5 Hz, ^3J = 6.6 Hz), 6.30 [d, 2 H, 4(8)-H, ^3J = 5.5 Hz], 6.66 (dd, 1 H, furanyl-H, ^3J = 3.6 Hz, ^3J = 1.6 Hz), 7.49 (d, 1 H, furanyl-H, ^3J = 3.6 Hz), 7.80 (d, 1 H, furanyl-H, ^3J = 1.6 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 89.4 [−, C-4(8)], 89.8 (+, C-3), 96.2 [−, C-5(7)], 96.9 (−, C-6), 113.9 (−, furanyl- C), 125.1 (−, furanyl-C), 150.1 (+, *ipso*-C), 150.5 (−, furanyl-C), 178.6 (+, C-1), 187.3 (+, C-2), 230.3 (+, CO). − MS (70 eV, 100 °C): *m/z* (%) = 336 (2) [M^+], 308 (3) [$M^+ - CO$], 280 (42) [$M^+ - 2\,CO$], 253 (42), 252 (100) [$M^+ - 3\,CO$], 224 (33), 172 (13), 149 (25), 129 (21), 105 (79), 77 (65), 53 (60), 52 (100) [^{52}Cr]. − HRMS ($C_{15}H_8CrO_6$): calcd. 335.972598; found 335.9735. − $C_{15}H_8CrO_6$ (336.22): calcd. C 53.58, H 2.40; found C 53.61, H 2.54. − **b)** GP2. A solution of butyllithium in hexane (1.6 M, 2.8 mL, 4.48 mmol) was added to a cold (−30 °C) solution of furan (360 mg, 5.29 mmol) in diethyl ether (15 mL). The mixture was allowed to warm to 25 °C over 30 min with stirring and was then cooled to −78 °C. Diethyl ether (30 mL) was added. Further treatment was with compound **1** (150 mg, 5.60 mmol), diethyl ether/THF (1:1, 50 mL), sat. aq. NH_4Cl (20 mL). The red oil obtained was purified twice by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1) yielding two fractions. − I (R_f = 0.30): 55 mg (0.15 mmol, 27%) of *rac*-**16**. − II (R_f = 0.20): 100 mg (0.24 mmol, 44%) of *rac*-**18**, red solid, m.p. 142 °C (dec.), 1 diastereomer. − IR (KBr): $\tilde{\nu}$ = 3484 cm^{-1} (m, br, OH), 3144 (w, arom. CH), 3096 (w, arom. CH), 1972 (s, CO), 1892 (s, CO), 1648 (s, CO-ketone), 1564 (m), 1460 (m), 1388 (w), 1292 (w), 1228 (w), 1180 (m), 1144 (m), 1024 (m), 952 (m), 872 (m), 808 (m), 768 (m), 736 (m), 660 (m), 624 (m), 592 (w), 532 (w). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.78 (d, *J* = 4.5 Hz, 1 H, benzyl. C*H*), 5.31 (dd, 1 H, 3-H or 4-H, ^3J = 6.3 Hz, ^3J = 7.3 Hz), 5.64 (dd, 1 H, 3-H or 4-H), 5.80 (dd, 1 H, furanyl-H, ^3J = 6.3 Hz, ^3J = 4.4 Hz), 6.12−6.27 (m, 2 H, furanyl-H), 6.55 (dd, 1 H, furanyl-H, ^3J = 3.6 Hz, ^3J = 1.5 Hz), 7.21 (d, 1 H, furanyl-H, ^3J = 3.6 Hz), 7.26 (m, 1 H, furanyl-H), 7.63 (dd, 1 H, furanyl-H). − ^{13}C NMR (50 MHz, [D_6]acetone, APT): δ = 64.0 (−, C-6), 88.7 (−, C-2 or C-3 or C-4 or C-5), 89.9 (−, C-2 or C-3 or C-4 or C-5), 95.4 (−, C-2 or C-3 or C-4 or C-5), 95.9(−, C-2 or C-3 or C-4 or C-5), 105.0 (+, C-1a), 108.7 (−, furanyl-C), 110.9 (−, furanyl-C), 113.6 (−, furanyl-C), 116.3 (+, furanyl-C), 122.1 (−, furanyl-C), 143.4 (−, furanyl-C,), 149.5 (−, furanyl-C), 152.7 (+, furanyl-C), 156.5 (+, furanyl-C), 180.2 (+, C-1), 232.6 (+, CO). − MS (70 eV, 150 °C): *m/z* (%) = 404 (4) [M^+], 348 (16 [$M^+ - 2\,CO$], 320 (9) [$M^+ - 3\,CO$], 319 (32), 301 (9), 290 (9), 289 (26), 251 (17), 250 (12), 235 (23), 224 (28), 219 (25), 207 (15), 179 (33), 178 (17), 165 (17), 152 (15), 95 (10), 77 (9), 53 (14), 52 (100) [^{52}Cr]. − HRMS ($C_{19}H_{12}CrO_7$): calcd. 403.998813; found 403.9965. − $C_{19}H_{12}CrO_7$ (404.3): calcd. C 56.44, H 2.99; found C 56.52, H 3.32.

***rac*-Tricarbonyl[η⁶-2-*endo*-hydroxy-1-oxo-2-*exo*-(1-phenylethyl)-benzocyclobutene]chromium(0) (*rac*-20) and *rac*-Tricarbonyl[η⁶-1-benzoyl-2-propanoylbenzene)chromium(0) (*rac*-21). − a)** GP2. A solution of phenyllithium in diethyl ether (0.79 M, 3.2 mL, 2.52 mmol) was diluted by addition of diethyl ether (25 mL) and cooled to −78 °C. Further treatment was with compound *rac*-**19** (150 mg, 0.50 mmol), diethyl ether (25 mL), sat. aq. NH_4Cl (10 mL). The obtained oil was purified twice by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1) yielding two fractions. − I [R_f = 0.23, purity ca. 90% (NMR)]: 90 mg (0.24 mmol, 48%) of *rac*-**20**, orange solid, m.p. 130 °C. − IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (m, br, OH), 3064 (w, arom. CH), 3040 (w), 2980 (w, CH_3), 2936 (w, CH), 2876 (w), 1988 (s, CO), 1924 (s, CO), 1724 (s, CO-ketone), 1600 (w), 1516 (m), 1492 (w), 1448 (m), 1424 (w), 1348 (w), 1260 (m), 1132 (m), 1076 (m), 1056 (m), 948 (w), 648 (m), 616 (m), 528 (w). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.87 (d, 3 H, C*H*$_3$), 3.24 (q, 1 H, C*H*), 3.45 (s, 1 H, OH), 5.40 (dd, 1 H, 4-H or 5-H, ^3J = 6.0 Hz, ^3J = 6.2 Hz), 5.16 (m, 2 H, 4-H or 5-H or 3-H or 6-H), 6.00 (d, 1 H, 3-H or 6-H, ^3J = 6.2 Hz), 7.33 (m, 5 H, arom-H). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 9.1 (−, *C*H$_3$), 55.1 (−, *C*H), 79.4 (+, C-2), 84.6 (−, C-3, or C-4 or C-5 or C-6), 85.6 (−, C-3, or C-4 or C-5 or C-6), 89.8 (−, C-3, or C-4 or C-5 or C-6), 93.9 (−, C-3, or C-4 or C-5 or C-6), 94.9 (+, C-6a), 124.7 (−, *m*-C), 126.7 (+, C-2a), 127.2 (−, *p*-C), 128.1 (−, *o*-C), 140.9 (+, *ipso*-C), 201.3 (+, C-1), 229.5 (+, CO). − MS (70 eV, 120 °C): *m/z* (%) = 374 (8) [M^+], 318 (5) [$M^+ - 2\,CO$], 290 (9) [$M^+ - 3\,CO$], 272 (65), 257 (18), 244 (12), 221 (15), 205 (39), 192 (10), 178 (12), 165 (11), 149 (11), 115 (16), 77 (23), 53 (11), 52 (100) [^{52}Cr]. − HRMS ($C_{19}H_{14}CrO_5$): calcd. 374.042633; found 374.0472. − $C_{19}H_{14}CrO_5$ (374.3): calcd. C 60.96, H 3.76; found C 62.78, H 4.18. − II (R_f = 0.15): 92 mg (0.24 mmol, 48%) of *rac*-**21**, red solid, m.p. 123 °C. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, arom. CH), 2960 (w, $-CH_2-$), 2920 (w, $-CH_2-$), 2870 (w), 1980 (s, CO), 1912 (s, CO), 1676 (s, CO-ketone), 1448 (m), 1428 (m), 1312 (w), 1272 (m), 1236 (m), 1216 (m), 948 (m), 924 (w), 720 (w), 692 (w), 656 (m), 638 (m), 616 (m), 584 (w), 524 (m). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.00 (t, 3 H, C*H*$_3$, ^3J = 7.6 Hz), 2.75 (q, 2 H, C*H*$_2$, ^3J = 7.6 Hz), 5.39 (m, 2 H), 5.58 (dd, 1 H, 4-H or 5-H, ^3J = 6.0 Hz, ^3J = 6.4 Hz), 5.87 (d, 1 H, 3-H or 6-H, ^3J = 6.0 Hz), 7.40 (dd, 2 H, *m*-H), 7.56 (dd, 1 H, *p*-H), 7.78 (d, 2 H, *o*-H). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 8.0 (−, *C*H$_3$), 31.7 (+, *C*H$_2$), 89.4 (−, C-3 or C-4 or C-5 or C-6), 90.8 (−, C-3 or C-4 or C-5 or C-6), 91.0 (−, C-3 or C-4 or C-5 or C-6), 91.1 (−, C-3 or C-4 or C-5 or C-6), 97.7 (+, C-1 or C-2), 113.2 (+, C-1 or C-2), 128.5 (−, *m*-C), 128.8 (−, *o*-C), 133.2 (−, *p*-C), 136.5 (+, *ipso*-C), 191.4 (+, C-7), 198.8 (+, C-8), 229.6 (+, CO). − MS (70 eV, 120 °C): *m/z* (%) = 374 (1) [M^+], 318 (3) [$M^+ - 2\,CO$], 317 (12), 290 (28) [$M^+ - 3\,CO$], 262 (37), 260 (10), 235 (10), 234 (41), 231 (15), 205 (10), 77 (15), 52 (100) [^{52}Cr]. − HRMS ($C_{19}H_{14}CrO_5$): calcd. 374.024633; found 374.0246. − $C_{19}H_{14}CrO_5$ (374.3): calcd. C 60.69, H 3.76; found C 60.90, H 3.76. − **b)** A solution of vinyllithium[31] in diethyl ether (0.85 M, 1.4 mL, 1.19 mmol) was diluted with diethyl ether to a volume of 10 mL, and cooled to −78 °C. A solution of *rac*-**25**[10] (100 mg, 0.28 mmol) in diethyl ether/THF (1:1, 30 mL) was added dropwise. After completion of addition, the mixture was stirred for 5 min, and then sat. aq. NH_4Cl (10 mL) was added. Workup as in GP2. The obtained red oil was purified by column chromatography (*l* 300 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1). 79 mg (0.21 mmol, 74%) of *rac*-**21**.

Tricarbonyl{η⁶-1-[2-(*N*-methyl-2-pyrrolyl)]-2-propanoylbenzene}-chromium(0) (*rac*-26): GP2. A solution of *tert*-butyllithium in pentane (1.6 M, 1.3 mL, 2.08 mmol) was added at −78 °C to *N*-methylpyrrole (270 mg, 3.33 mmol) in THF (5 mL).[25] The mixture was allowed to warm to 25 °C over 90 min with stirring, and was then again cooled to −78 °C and diluted with THF to a volume of 25 mL. Further treatment was with compound *rac*-**19** (125 mg,

0.42 mmol), diethyl ether (25 mL), sat. aq. NH_4Cl (10 mL). The obtained red oil was purified by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1), to afford 100 mg (0.26 mmol, 63%) of *rac*-**26** (R_f = 0.52), orange solid, m.p. 121 °C. − IR (KBr): $\tilde{\nu}$ = 3112 cm^{-1} (m, arom. CH), 2976 (w, $-CH_2-$), 2940 (w, $-CH_2-$), 1980 (s, CO), 1908 (s, CO), 1680 (s, CO-ketone), 1660 (s, CO-ketone), 1524 (w), 1508 (m), 1460 (m), 1428 (m), 1404 (s), 1380 (s), 1344 (m), 1320 (m), 1236 (m), 1216 (s), 1092 (w), 1060 (m), 1024 (w), 948 (m), 912 (m), 872 (m), 832 (m), 808 (w), 736 (m), 656 (s), 616 (s), 524 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, 3 H, C*H*$_3$, ^3J = 7.2 Hz), 2.65 (q, 2 H, C*H*$_2$, ^3J = 7.2 Hz), 4.01 (s, 3 H, C*H*$_3$), 5.33 (dd, 1 H, 3-H or 6-H, ^3J = 6.0 Hz, ^3J = 5.7 Hz), 5.50 (dd, 1 H, 3-H or 6-H, ^3J = 5.7 Hz, ^3J = 6.0 Hz), 5.52 (d, 1 H, 4-H or 5-H, ^3J = 5.8 Hz), 5.76 (d, 1 H, 4-H or 5-H), 6.08 (m, 1 H, arom. H), 6.55 (m, 1 H, arom. H), 6.90 (m, 1 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 8.2 (−, *C*H$_3$), 33.1 (+, *C*H$_2$), 37.4 (−, *C*H$_3$), 89.4 (−, C-3 or C-4 or C-5 or C-6), 90.8 (−, C-3 or C-4 or C-5 or C-6), 91.1 (−, C-3 or C-4 or C-5 or C-6), 91.4 (−, C-3 or C-4 or C-5 or C-6), 100.5 (+, C-1), 108.6 (−, arom. C), 112.9 (+, C-2), 121.8 (−, arom. C), 130.2 (+, ipso-C), 132.2 (−, arom. C), 180.8 (+, C-8), 199.7 (+, C-7), 230.2 (+, CO). − MS (70 eV, 130 °C): *m*/*z* (%) = 377 (2) [M^+], 294 (9), 293 (31) [M^+ − 2 CO], 265 (12), 238 (25), 237 (100), 236 (15), 222 (13), 130 (9), 115 (6), 77 (8), 53 (11), 52 (99) [^{52}Cr]. − HRMS ($C_{18}H_{15}NCrO_5$): calcd. 377.035533; found 377.0340. − $C_{18}H_{15}NCrO_5$ (377.3): calcd. C 57.29, H 4.00; found C 57.32, H 4.01.

Tricarbonyl{η^6-3,3a,4,5,5a,10-hexahydro-5a-*endo*-hydroxy-2*H*-benzo[4,5]pentaleno[6a,1-*b*]furan-10-one}chromium(0) (*rac*-32): GP2. A solution of butyllithium in hexane (1.6 M, 1.5 mL, 2.40 mmol) was added dropwise at −30 °C to furan (180 mg, 2.64 mmol) in diethyl ether (15 mL). The mixture was allowed to warm to 25 °C over 30 min with stirring and was then cooled to −78 °C. The mixture was then diluted with diethyl ether to a volume of 30 mL. Further treatment was with compound *rac*-**19** (50 mg, 0.16 mmol), diethyl ether (20 mL), sat. aq. NH_4Cl (10 mL). The obtained red oil was purified by column chromatography (*l* 200 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1), to afford 40 mg (0.16 mmol, 66%) of *rac*-**32** (R_f = 0.22), orange solid, m.p. 80 °C. − IR (KBr): $\tilde{\nu}$ = 3468 cm^{-1} (s, br, OH), 3096 (m, arom. CH), 2960 (m, $-CH_2-$), 2936 (w, $-CH_2-$), 2872 (w), 1972 (s, CO), 1912 (s, CO), 1720 (s, CO-ketone), 1652 (w), 1616 (w), 1520 (w), 1460 (w), 1424 (w), 1308 (w), 1264 (w), 1244 (w, C−O), 1188 (w), 1132 (w), 1008 (w), 872 (w), 744 (w), 648 (m), 616 (m), 524 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.70−2.13 (m, 3 H, aliph. H), 2.20−2.40 (m, 1 H, C*H*), 3.14 (s, 1 H, OH), 3.47−3.60 (m, 1 H, C*H*), 5.08 (t, 1 H, 2-H), 5.32 (dd, 1 H, 7-H or 8-H, ^3J = 6.2 Hz, ^3J = 6.0 Hz), 5.60 (d, 1 H, 6-H or 9-H, ^3J = 6.0 Hz), 5.70 (dd, 1 H, 7-H or 8-H, ^3J = 6.0 Hz, ^3J = 6.2 Hz), 5.80 (d, 1 H, 6-H or 9-H), 6.45 (dd, 1 H, 1-H). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 32.9 (+, C-4 or C-5), 40.9 (+, C-4 or C-5), 50.2 (−, C-3a), 83.4 (+, C-5a), 84.8 (−, C-6 or C-7 or C-8 or C-9), 86.6 (−, C-6 or C-7 or C-8 or C-9), 90.4 (−, C-6 or C-7 or C-8 or C-9), 93.6 (−, C-6 or C-7 or C-8 or C-9), 96.6 (+, C-9a), 105.5 (−, C-2 or C-3), 126.0 (+, C-5b), 145.1 (−, C-2 or C-3), 152.3 (+, C-10a), 197.3 (+, C-10), 229.6 (+, CO). − MS (70 eV, 140 °C): *m*/*z* (%) = 364 (7) [M^+], 308 (10) [M^+ − 2 CO], 281 (15), 280 (52) [M^+ − 3 CO], 262 (13), 250 (48), 235 (14), 234 (51), 233 (17), 195 (48), 165 (17), 152 (12), 115 (21), 91 (11), 77 (12), 53 (13), 52 (100) [^{52}Cr]. − HRMS ($C_{17}H_{12}CrO_6$): calcd. 364.003898; found 364.0038. − $C_{17}H_{12}CrO_6$ (364.3): calcd. C 56.05, H 3.32; found C 56.31, H 3.89.

Tricarbonyl{η^6-3,3a,4,5,5a,10-hexahydro-5a-*endo*-hydroxy-2*H*-benzo[4,5]pentaleno[6a,1-*b*]thiophen-10-one}chromium(0) (*rac*-33): GP2. A solution of butyllithium in hexane (1.6 M, 1.6 mL, 2.56 mmol) was added at 25 °C to thiophene (283 mg, 3.36 mmol) in diethyl ether (5 mL). After stirring for 30 min, the mixture was cooled to −78 °C. The mixture was diluted with diethyl ether to a volume of 20 mL. Further treatment was with compound *rac*-**19** (250 mg, 8.40 mmol), diethyl ether (20 mL), sat. aq. NH_4Cl (10 mL). The obtained red oil was purified twice by column chromatography (*l* 400 mm, ∅ 30 mm, diethyl ether/petroleum ether 1:1) to afford 160 mg (0.42 mmol, 50%) of *rac*-**33** (R_f = 0.28), orange-red solid, m.p. 172 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3468 cm^{-1} (s, br, OH), 3080 (m, arom. CH), 2964 (w, $-CH_2-$), 2940 (w, $-CH_2-$), 2872 (w), 1972 (s, CO), 1920 (s, CO), 1900 (s, CO), 1720 (s, CO-ketone), 1596 (w), 1524 (m), 1436 (m), 1400 (w), 1312 (m), 1264 (m), 1216 (m, C−O), 1188 (m), 1096 (w), 1028 (w), 952 (w), 828 (m), 804 (m), 740 (m), 712 (m), 676 (m), 648 (s), 616 (s), 520 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.56−1.71 (m, 1 H, aliph. H), 1.86−2.11 (m, 1 H, C*H*), 2.16−2.43 (m, 2 H, aliph. H), 3.70 (d, 1 H, OH), 3.73−3.86 (m, 1 H, C*H*), 5.32−5.43 (m, 1 H), 5.52 (dd, 1 H, 7-H or 8-H, ^3J = 5.6 Hz, ^3J = 5.8 Hz), 5.62−5.73 (m, 3 H), 5.95 (dd, 1 H, 7-H or 8-H). − ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 34.2 (+, C-4 or C-5), 42.1 (+, C-4 or C-5), 57.9 (−, C-3a), 79.3 (+, C-5a or C-10a), 84.4 (+, C-5a or C-10a), 85.4 (−, C-6 or C-7 or C-8 or C-9), 86.4 (−, C-6 or C-7 or C-8 or C-9), 91.4 (−, C-6 or C-7 or C-8 or C-9), 92.0 (+, C-9a), 93.5 (−, C-6 or C-7 or C-8 or C-9), 122.8 (−, C-2 or C-3), 125.4 (+, C-5b), 125.7 (+, C-2 or C-3), 199.9 (+, C-10), 229.6 (+, CO). − MS (70 eV, 110 °C): *m*/*z* (%) = 380 (7) [M^+], 324 (23) [M^+ − 2 CO], 296 (11) [M^+ − 3 CO], 279 (12), 278 (46), 251 (18), 250 (60) [M^+ − 3 CO, − CO, − O, − 2 H], 195 (12), 165 (19), 141 (7), 115 (17), 97 (8), 77 (6), 91 (11), 77 (12), 53 (11), 52 (100) [^{52}Cr]. − HRMS ($C_{17}H_{12}CrO_5S$): calcd. 379.981055; found 379.9810. − $C_{17}H_{12}CrO_5S$ (380.3): calcd. C 53.69, H 3.18; found C 53.57, H 3.25.

X-ray Crystal Structure Analysis of *rac*-33:[32] $C_{17}H_{12}CrO_5S$, crystal size 0.27 × 0.38 × 0.19 mm, *a* = 1466.0(2), *b* = 727.5(1), *c* = 1603.8(2) pm, β = 111.27(10)°, *V* = 1594.0(4)·10^{-6} pm, $d_{calcd.}$ = 1.585 gcm^{-3}, *Z* = 4, crystal system monoclinic, space group $P2_1/a$ (No. 14), Stoe IPDS (Imaging Plate) diffractometer; measuring method: 150 exposures, Δφ 1.5°, 11345 measured reflections (16, 8, 18), 2490 independent and 1456 observed reflections [$I > 2\sigma(I)$], R = 0.071, R_w = 0.155 [$w = 1/\sigma^2(F)$], residual electron density 0.82 e$Å^{-3}$ close to the Cr atom.

Acknowledgments

This work was kindly supported by the Volkswagen-Stiftung and by the Fonds der Chemischen Industrie, and the joint research initiative "Biologisch aktive Naturstoffe − Synthetische Diversität". We thank Chemetall GmbH for a donation of butyllithium.

[1] J. J. Bronson, R. L. Danheiser, in: *Comprehensive Organic Synthesis* (Ed.: B. M. Trost); Pergamon Press, Oxford, **1991**, vol. 5, pp. 999−1035.
[2] D. A. Evans, A. M. Golob, *J. Am. Chem. Soc.* **1975**, *97*, 4765−4766.
[3] L. A. Paquette, *Angew. Chem.* **1990**, *102*, 642−660; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 609−626.
[4] R. K. Hill, in: *Comprehensive Organic Synthesis* (Ed.: B. M. Trost), Pergamon Press, Oxford, **1991**, vol. 5, pp. 785−826.
[5] L. A. Paquette, *Tetrahedron* **1997**, *53*, 13971−14020.
[6] L. A. Paquette, *Eur. J. Org. Chem.* **1998**, 1709−1728.
[7] H. Butenschön, *Synlett* **1999**, 680−691.
[8] M. Brands, R. Goddard, H. G. Wey, H. Butenschön, *Angew.*

Chem. **1993**, *105*, 285−287; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 267−269.
[9] M. Brands, J. Bruckmann, C. Krüger, H. Butenschön, *J. Chem. Soc., Chem. Commun.* **1994**, 999−1000.
[10] M. Brands, H. G. Wey, J. Bruckmann, C. Krüger, H. Butenschön, *Chem. Eur. J.* **1996**, *2*, 182−190.
[11] B. Voigt, M. Brands, R. Goddard, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **1998**, 2719−2727.
[12] L. A. Paquette, L. H. Kuo, J. Doyon, *J. Am. Chem. Soc.* **1997**, *119*, 3038−3047.
[13] M. E. Jung, J. E. Hudspeth, *J. Am. Chem. Soc.* **1978**, *100*, 4309−4311.
[14] E. N. Marvell, S. W. Almond, *Tetrahedron Lett.* **1979**, *20*, 2779−2780.
[15] V. J. Santora, H. W. Moore, *J. Org. Chem.* **1996**, *61*, 7976−7977.
[16] M. E. Jung, J. P. Hudspeth, *J. Am. Chem. Soc.* **1980**, *102*, 2463−2464.
[17] R. W. Alder, D. Colclough, F. Grams, A. G. Orpen, *Tetrahedron* **1990**, *46*, 7933−7940.
[18] L. A. Paquette, T. M. Morwick, J. T. Negri, R. D. Rogers, *Tetrahedron* **1996**, *52*, 3075−3094.
[19] E. Palomino, A. P. Schaap, M. J. Heeg, *Tetrahedron Lett.* **1989**, *30*, 6797−6800.
[20] M. P. Cava, D. R. Napier, R. J. Pohl, *J. Am. Chem. Soc.* **1963**, *85*, 2076−2080.
[21] M. Brands, Dissertation, Ruhr-Universität Bochum, **1993**.
[22] B. Voigt, Dissertation, Universität Hannover, **1997**.
[23] M. Brands, H. G. Wey, R. Goddard, H. Butenschön, *Inorg. Chim. Acta* **1994**, *220*, 175−186.
[24] J. March, *Advanced Organic Chemistry*; 4th ed., John Wiley & Sons, New York, **1992**.
[25] D. A. Shirley, B. H. Gross, P. A. Roussel, *J. Org. Chem.* **1955**, *20*, 225−229.
[26] M. G. Reinecke, J. G. Newsom, L.-J. Chen, *J. Am. Chem. Soc.* **1981**, *103*, 2760−2769.
[27] D. W. H. MacDowell, J. M. Purpura, *J. Org. Chem.* **1986**, *51*, 183−188.
[28] C. H. Heathcock, in: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, vol. 2, pp. 133−179.
[29] L. A. Paquette, J. F. P. Andrews, C. Vanucci, D. E. Lawhorn, J. T. Negri, R. D. Rogers, *J. Org. Chem.* **1992**, *57*, 3956−3965.
[30] P. J. Kocienski, M. Pritchard, S. N. Wadman, R. J. Withby, C. L. Yeates, *J. Chem. Soc., Perkin Trans. 1* **1992**, 3419−3429.
[31] D. Seyferth, M. A. Weiner, *J. Am. Chem. Soc.* **1961**, *83*, 3583−3586.
[32] The crystallographic data (without structure factors) of the structure described in this publication were deposited as supplementary publication no. CCDC-153141 (*rac*-**33**) at the Cambridge Crystallography Data Centre. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Received November 29, 2000
[O00612]