Reactions of benzocyclobutene chromium complexes with carbon, nitrogen and oxygen nucleophiles: nucleophilic addition and unexpected proximal ring opening reactions

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Abstract

Tricarbonyl(η^6-1-oxobenzocyclobutene)chromium(0) (**1**) can be transformed to tricarbonyl(η^6-1-*endo*-hydroxybenzocyclobutene)chromium(0) derivatives with substituents R (R = CH_3, $CH{=}CH_2$, $(CH_2)_4CH{=}CH_2$, $(CH_2)_4OSi(Me)_2tBu$) at C1 on the *exo* face of the complex. The relative configuration is proven by an X-ray crystal structure analysis of the trimethylsilyl ether **8** ($C_{16}H_{18}CrO_4Si$: $a = 8.693(1)$, $b = 9.490(1)$, $c = 11.063(1)$ Å, $\alpha = 97.51(1)$, $\beta = 110.32(1)$, $\gamma = 95.38(1)°$, triclinic, space group $P\bar{1}$ (No.2), $R = 0.037$, $R_w = 0.052$ for 4609 observed reflections. Attempts directed at an intramolecular cycloaddition of the *ortho*-quinodimethane complex derived from **17** by anion promoted ring opening unexpectedly resulted in the formation of **12** as the product of an opening of the proximal bond of the anellated ring located between the hydroxy group and the coordinated aromatic ring in **16**. The fact that the intermolecular cycloaddition reaction for **16** is possible in the presence of a dienophile is taken as evidence for an equilibrium between the alcoholate **17** and the two ring opened products **16** and **18**. The proximal ring opening of **6** is not observed when the free organic ligand **21** is used as the educt. Ketone complexes **1** and **25** undergo proximal ring opening reaction when treated with alcoholate or primary amines.

Key words: Crystal structures; Chromium complexes; Benzocyclobutenone complexes; Benzocyclobutenedione complexes; Ring opening

Introduction

Since the discovery of (η^6-arene)tricarbonylchromium(0) complexes by Fischer and Öfele [1] in 1957, numerous of these complexes have been used as reagents in organic chemistry [2–5]. The reason for this is the alteration of the properties of the aromatic ligand when coordinated to the metal fragment [6]. The electron withdrawing effect of the tricarbonyl chromium group lowers the electron density of the arene and increases the electrophilicity of benzylic keto or aldehyde groups incorporated in side chains or anellated rings of the organic ligand [6, 7]. In addition the steric bulk of the metal fragment blocks the coordinated face of the arene, rendering reactions by attack from the uncoordinated face more favourable. For this reason, (η^6-arene)tricarbonylchromium(0) complexes have been widely used in asymmetric synthesis [2, 4].

Whereas studies concerning the electronic and steric effects of the tricarbonyl chromium group in nucleophilic additions to 1-tetralone and 1-indanone were carried out twenty years ago in the laboratories of Jackson [8–14], Jaouen [15–18] and des Abbayes [19–21], reactions of complexes benzocyclobutenes have only been investigated in the last few years [22–29]. The synthesis of various (η^6-benzocyclobutene)tricarbonylchromium(0) complexes is possible via the usual complexation techniques using hexacarbonylchromium(0) [30, 31], triammine tricarbonylchromium(0) [32, 33] and tricarbonyl(η^6-naphthalene)chromium(0) [23]. In contrast to the corresponding synthesis of 1-indanone and 1-tetralone complexes, tricarbonyl(η^6-1-oxobenzocyclobutene)chromium(0) (**1**) [34] and tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**25**) [35] are not available by direct complexation of their ligands with $Cr(CO)_6$ or $(NH_3)_3Cr(CO)_3$ because side reactions dominate [36–38]. **1** and **25** have thus been synthesised by complexation of their ethane diol acetals [26, 28] and subsequent hydrolysis under strong acidic conditions

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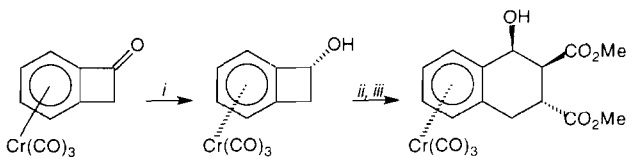


1 *rac*-**2** *rac*-**3**

Scheme 1. Reagents and conditions: *i*: $LiAlH_4$, −78 °C, 99%, d.e. ≥ 99%; *ii*: n-BuLi, −78 °C; *iii*: dimethyl fumarate, −78 to 0 °C, 89%.

[34, 35]. These ketone complexes are promising substrates for nucleophilic addition reactions. It was expected that the conformational rigidity of their organic ligands in combination with the steric bulk of the metal fragment would lead to substituted hydroxybenzocyclobutene complexes with high diastereoselectivity. Moreover, the planarity of the benzocyclobutene ligand permits an ideal transfer of the electron density to the metal causing a considerable activation of the keto groups towards nucleophilic reagents [34, 35].

1-Hydroxybenzocyclobutene complexes are of particular interest as it has been reported [34, 39–41] that the alcoholate of the 1-hydroxybenzocyclobutene complex **2** undergoes a ring opening reaction leading to an *ortho*-quinodimethane intermediate under very mild conditions, which could be trapped with various dienophiles to yield 1-tetralol complexes such as **3** [42–45] (Scheme 1).

Addition reactions of nucleophiles containing a dienophile moiety to **1** should thus lead to compounds that are educts for ring opening/intramolecular cycloaddition reactions finally leading to interesting polycyclic systems. This is especially important in the light of the chirality of the intermediate *ortho*-quinodimethane in these reactions. Here we report on addition reactions of carbon nucleophiles to **1** and on some reactions of the resulting 1-hydroxybenzocyclobutene complexes in which an unexpected opening of the four-membered ring is observed. This ring opening is compared with similar reactions of diketone **25**. The material presented in this paper has in part been the subject of a preliminary communication [46].

Experimental

All operations are performed in an argon atmosphere in flame dried reaction vessels. M.p. (uncorrected): Büchi SMP-20, determined in sealed glass capillaries in an argon atmosphere. IR: Nicolet 7199 FT-IR. ^1H NMR: Bruker WH 400 (400.1 MHz), AM 200 (200.1 MHz). ^{13}C NMR: Bruker WH 400 (100.6 MHz), WM 300 (75.5 MHz), AM 200 (50.3 MHz); signal multiplicities are determined either by inspection of gated spectra 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 311 A. HRMS: Finnigan MAT 820. DSC: DuPont TA 9900. Elemental analyses: Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim an der Ruhr.

General procedure for aqueous workup

After addition of an aqueous solution to the reaction mixture, the organic layer is diluted with diethyl ether and the layers are separated. The aqueous phase is extracted with diethyl ether until the extract remains colourless. The combined organic phases are washed with water (three times) and dried over $MgSO_4$. After filtration the volatile components are evaporated under reduced pressure to give the crude product. All chromatographic separations are carried out using silica gel.

Tricarbonyl(η⁶-1-endo-hydroxy-1-exo-methylbenzocyclobutene)chromium(0) (4)

A solution of 834 mg (3.28 mmol) of **1** in 60 ml diethyl ether/THF (2:1) is added dropwise to 14.6 ml (13.1 mmol) of a 0.9 M solution of methyl magnesium chloride in THF at −78 °C over a period of 2 h. The resulting yellow solution is stirred overnight at −78 °C and hydrolysed with 2 M aqueous hydrochloric acid at −78 °C. After workup, **4** is obtained as yellow powder (871 mg (3.22 mmol), 98%). M.p. 107 °C. IR (THF) (cm^{-1}): ν 1966 (s, CO), 1890 (s, CO). ^1H NMR (200 MHz, [D_6]acetone): δ 1.60 (s, 3H, CH_3), 3.06 (d, 1H, *endo*-2-H or *exo*-2-H, $^2J = -14.0$ Hz), 3.13 (d, 1H, *endo*-2-H or *exo*-2-H), 4.47 (s, 1H, OH), 5.13 (dd, 1H, 4-H or 5-H, $^3J = 6.1$ Hz, $^3J = 6.1$ Hz), 5.48 (dd, 1H, 4-H or 5-H, $^3J = 6.1$ Hz, $^3J = 6.1$ Hz), 5.55 (d, 1H, 3-H or 6-H, $^3J = 6.1$ Hz), 5.79 (d, 1H, 3-H or 6-H, $^3J = 6.1$ Hz). ^{13}C NMR (50 MHz, [D_6]acetone): δ 26.8 (q, CH_3), 47.8 (t, C2), 76.8 (s, C1), 89.4 (d, C_{arom}), 89.8 (d, C_{arom}), 90.7 (d, C_{arom}), 95.8 (d, C_{arom}), 114.4 (s, C6a), 124.6 (s, C2a), 234.6 (s, CO). MS: *m/z* (%) 270 (17) [M^+], 214 (4) [$M^+ - 2CO$], 186 (43) [$M^+ - 3CO$], 184 (18), 168 (16), 52 (100) [^{52}Cr]. *Anal.* Calc. for $C_{12}H_{10}CrO_4$: C, 53.34; H, 3.73; Cr, 19.24. Found: C, 53.28; H, 3.82; Cr, 19.21%.

Tricarbonyl(η⁶-1-endo-hydroxy-1-exo-vinylbenzocyclobutene)chromium(0) (5)

Following the same procedure as described for **4**, 34 ml (34.0 mmol) of a 1 M solution of vinyl magnesium bromide are treated with 1.81 g (7.1 mmol) of **1** in 330 ml diethyl ether. The crude product is recrystallised from pentane to give 1.92 g (6.8 mmol, 96%) of **5** as yellow needles. M.p. 81 °C. IR (THF) (cm^{-1}): ν 1967 (s, CO), 1890 (s, CO). ^1H NMR (200 MHz, [D_8]THF): δ 3.13 (d, 1H, *endo*-2-H or *exo*-2-H, $^2J = -13.6$ Hz),

3.21 (d, 1H, *endo*-2-H or *exo*-2-H), 4.99 (s, 1H, OH), 5.06 (dd, 1H, 4-H or 5-H, ^3J=6.3 Hz, ^3J=6.1 Hz), 5.11 (dd, 1H, *E*-8-H, $^2J_{E\text{-}8,\,Z\text{-}8}$= −1.3 Hz, $^3J_{cis}$=10.4 Hz), 5.38 (dd, 1H, *Z*-8-H, $^3J_{trans}$=17.2 Hz), 5.41 (dd, 4-H or 5-H, ^3J=6.3 Hz, ^3J=6.1 Hz), 5.49 (dd, 1H, 3-H or 6-H, ^3J=6.1 Hz), 5.69 (dd, 1H, 3-H or 6-H, ^3J=6.3 Hz), 6.14 (dd, 1H, 7-H). ^{13}C NMR (50 MHz, [D$_8$]THF): δ 47.4 (t, C2), 78.8 (s, C1), 88.6 (d, C3 or C6), 89.1 (d, C4 or C5), 90.7 (d, C4 or C5), 95.1 (d, C3 or C6), 114.0 (t, C8), 114.0 (s, C6a), 122.4 (s, C2a), 141.6 (d, C7), 234.2 (s, CO). MS (70 eV): *m/z* (%) 282 (18) [M^+], 254 (1) [M^+ −CO], 226 (10) [M^+ −2CO], 198 (37) [M^+ −3CO], 180 (24), 129 (11), 128 (17), 52 (100) [^{52}Cr]. *Anal.* Calc. for $C_{13}H_{10}CrO_4$: C, 55.32; H, 3.57; Cr, 18.42. Found: C, 55.44; H, 3.54; Cr, 18.36%.

Tricarbonyl[η^6-1-exo-(5-hexenyl)-1-endo-hydroxybenzocyclobutene]chromium(0) (6)

Following the same procedure as described for **4**, 996 mg (3.9 mmol) of **1** in 200 ml diethyl ether are added to 19 ml (19.0 mmol) of 5-hexenyl-1-magnesium bromide (1 M solution in diethyl ether). After chromatography of the crude product (20×300 mm, pentane, diethyl ether), **6** is obtained as orange oil (1.23 g (3.6 mmol), 93%). IR (THF) (cm^{-1}): ν 1964 (s, CO), 1888 (s, CO). ^{1}H NMR (200 MHz, [D$_8$]THF): δ 1.34–1.65 (m, 4H, 7-H, 8-H), 1.83 (m, 2H, 9-H), 2.07 (m, 2H, 10-H), 3.00 (d, 1H, *endo*-2-H or *exo*-2-H, ^2J= −13.8 Hz), 3.10 (d, 1H, *endo*-2-H or *exo*-2-H), 4.32 (s, 1H, OH), 4.96 (m, 2H, 12-H), 5.05 (dd, 1H, 4-H), 5.40 (dd, 1H, 5-H), 5.46 (d, 1H, 3-H or 6-H), 5.73 (d, 1H, 3-H or 6-H), 5.80 (tdd, 1H, 11-H, $^3J_{trans}$=17.1 Hz, $^3J_{cis}$=10.0 Hz, $^3J_{11,\,10}$=6.7 Hz). ^{13}C NMR (50 MHz, [D$_8$]THF): δ 25.1 (t, C10), 30.0 (t, C9), 34.5 (t, C8), 40.4 (t, C7), 46.6 (t, C2), 79.3 (s, C1), 88.6 (d, C$_{arom}$), 89.0 (d, C$_{arom}$), 90.4 (d, C$_{arom}$), 95.1 (d, C$_{arom}$), 114.2 (s, C6a), 114.7 (t, C12), 124.0 (s, C2a), 139.4 (d, C11), 234.3 (s, CO). MS (70 eV): *m/z* (%) 338 (7) [M^+], 310 (4) [M^+ −CO], 282 (7) [M^+ −2CO], 254 (37) [M^+ −3CO], 252 (26), 186 (19), 162 (16), 144 (24), 143 (22), 52 (100) [^{52}Cr]. *Anal.* Calc. for $C_{17}H_{18}CrO_4$: C, 60.35; H, 5.36; Cr, 15.37. Found: C, 60.43, H, 5.48, Cr, 15.19%.

Tricarbonyl[η^6-1-exo(tert-butyldimethylsilyloxy)butyl-1-endo-hydroxybenzocyclobutene]chromium(0) (7)

Following the same procedure as described for **4**, 1.32 g (5.2 mmol) of **1** in 150 ml diethyl ether/THF (2:1) are added to 47.2 ml (26.0 mmol) of a 0.55 M solution of 1-(tert-butyldimethylsilyloxy)butyl magnesium chloride in THF. Chromatography of the crude product (30×100 mm) gives 1.06 g (2.4 mmol, 46%) of **7** as yellow oil (ethyl acetate/pentane 1:4), 300 mg (1.2 mmol, 23%) of **2** as a yellow solid (diethyl ether, first fraction) and 515 mg (1.6 mmol, 30%) of **13** as a yellow solid (diethyl ether, second fraction). IR (THF) (cm^{-1}): ν 1966 (s, CO), 1889 (s, CO). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ 0.04 (s, 6H, Si(CH$_3$)$_2$), 0.88 (s, 9H, C(CH$_3$)$_3$), 1.56 (m, 4H, 8-H, 9-H), 1.91 (t, 2H, 7-H, ^3J=7.4 Hz), 3.07 (d, 1H, *endo*-2-H or *exo*-2-H, ^2J= −13.6 Hz), 3.20 (d, 1H, *endo*-2-H or *exo*-2-H), 3.63 (m, 2H, 10-H), 5.18 (dd, 1H, 4-H or 5-H, ^3J=6.0 Hz, ^3J=6.0 Hz), 5.60 (d, 1H, 3-H or 6-H, ^3J=6.0 Hz), 5.67 (dd, 4-H or 5-H, ^3J=6.0 Hz, ^3J=6.0 Hz), 5.85 (d, 1H, 3-H or 6-H, ^3J=6.0 Hz). ^{13}C NMR (50 MHz, [D$_6$]acetone): δ= −5.2 (q, SiCH$_3$), 18.7 [s, *C*(CH$_3$)$_3$], 21.9 (t, C8 or C9), 26.2 [q, C(*C*H$_3$)$_3$], 33.6 (t, C8 or C9), 40.0 (t, C7), 46.4 (t, C2), 63.3 (t, C10), 79.5 (s, C1), 89.2 (d, C3 or C6), 89.5 (d, C4 or C5), 91.1 (d, C4 or C5), 95.8 (d, C3 or C6), 114.8 (s, C6a), 124.0 (s, C2a), 234.5 (s, CO). MS (70 eV): *m/z* (%) 442 (9) [M^+], 414 (1) [M^+ −CO], 386 (5) [M^+ −2CO], 359 (35) [M^+ −3CO, ^{53}Cr], 358 (100) [M^+ −3CO, ^{52}Cr], 301 (22), 299 (11), 238 (26), 143 (17), 127 (19), 126 (31), 75 (15), 73 (11), 52 (34) [^{52}Cr]. *Anal.* Calc. for $C_{21}H_{30}CrO_5Si$: C, 56.98; H, 6.85; Cr, 11.74; Si, 6.35. Found: C, 57.10; H, 6.93; Cr, 11.84; Si, 6.29%.

Tricarbonyl(η^6-1-endo-trimethylsilyloxy-1-exo-vinylbenzocyclobutene)chromium(0) (8)

A solution of 961 mg (3.4 mmol) of **5** in 25 ml dichloromethane is cooled to 0 °C and treated with 435 mg (4.0 mmol) of chlorotrimethylsilane and 405 mg (4.0 mmol) of triethylamine. The orange solution is stirred for 18 h at 25 °C. After addition of 200 ml ice-cold water and following aqueous workup, the crude product is dissolved in a minimum amount of acetone. After storage at −30 °C, 895 mg (2.52 mmol, 74 %) of **8** are obtained as yellow crystals. M.p. 92 °C. IR (THF) (cm^{-1}): ν 1968 (s, CO), 1892 (s, CO). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ 0.20 (s, 9H, CH$_3$), 3.23 (d, 1H, *endo*-2-H or *exo*-2-H, ^2J= −13.7 Hz), 3.36 (d, 1H, *endo*-2-H or *exo*-2-H), 5.21 (dd, 1H, 4-H or 5-H, ^3J=6.1 Hz, ^3J=6.4 Hz), 5.22 (dd, 1H, *E*-8-H, $^3J_{cis}$=10.2 Hz, $^2J_{E\text{-}8,\,Z\text{-}8}$= −1.1 Hz), 5.35 (dd, 1H, *Z*-8, $^3J_{trans}$=17.1 Hz), 5.55 (dd, 1H, 4-H or 5-H, ^3J=6.1 Hz, ^3J=6.4 Hz), 5.63 (d, 1H, 3-H or 6-H, ^3J=6.4 Hz), 5.87 (d, 1H, 3-H or 6-H, ^3J=6.4 Hz), 6.27 (dd, 1H, 7-H). ^{13}C NMR (50 MHz, [D$_6$]acetone): δ 1.7 (q, CH$_3$), 47.6 (t, C2), 80.7 (s, C1), 89.1 (d, C3 or C6), 89.9 (d, C4 or C5), 91.1 (d, C4 or C5), 95.5 (d, C3 or C6), 114.2 (s, C6a), 115.5 (t, C8), 121.6 (s, C2a), 141.1 (d, C7), 234.3 (s, CO). MS (70 eV): *m/z* (%) 354 (25) [M^+], 298 (5) [M^+ −2CO], 270 (66) [M^+ −3CO], 256 (24), 255 (81), 129 (10), 128 (16), 127 (30), 126 (100), 52 (40) [^{52}Cr]. *Anal.* Calc. for $C_{16}H_{18}CrO_4Si$: C, 54.22; H, 5.13; Cr, 14.67; Si, 7.93. Found: C, 54.20; H, 5.12; Cr, 14.61; Si, 8.11%.

Crystal structure analysis of 8

Molecular formula $C_{16}H_{18}CrO_4Si$, molecular weight 354.4 g mol^{-1}, crystal colour yellow, crystal size

$0.28 \times 0.46 \times 0.49$ mm, $a = 8.693(1)$, $b = 9.490(1)$, $c = 11.063(1)$ Å, $\alpha = 97.51(1)$, $\beta = 110.32(1)$, $\gamma = 95.38(1)°$, $V = 838.9$ Å^3, $T = 293$ K, $D_{calc} = 1.40$ g cm^{-3}, $\mu = 7.47$ cm^{-1}, $Z = 2$, triclinic, space group $P\bar{1}$ (No.2), Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω–2θ, 12 144 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]_{max}$ 0.75 Å^{-1}, 5809 independent reflections, 4609 observed reflections ($I > 2\sigma(I)$), structure solved by heavy atom method, H atom positions calculated and fixed in the final refinement stages, $R = 0.037$, $R_w = 0.052$ for 199 refined parameters, residual electron density 0.46 e Å^{-3}. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table 1.

Computer programs used: data reduction: DATAP [47]; structure solution: SHELXS-86 [48]; structure refinement: GFMLX, a modified version of ORFLS [49]; molecular diagram (50% thermal ellipsoids): ORTEP [50]. Computer: VAX 4000-300. Scattering factors: from ref. 51.

*Tricarbonyl(η^6-1-endo-tert-butyldimethylsilyloxy-1-exo-vinylbenzocyclobutene)chromium(0) (**9**)*

A solution of 3.54 g (21.5 mmol) of chloro-tert-butyldimethylsilane and 1.48 g (21.7 mmol) of imidazole in 20 ml of DMF is added to 758 mg (2.7 mmol) of **5**. After stirring for 41 h at 25 °C, the solution is cannulated into 100 ml of ice-cold water and worked up to give a crude product, which is chromatographed (30×200 mm, diethyl ether/pentane 2:1) to yield 842 mg (2.1 mmol, 78%) of **9** as a yellow oil. IR (THF) (cm^{-1}): ν 1967 (s, CO), 1888 (s, CO). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ 0.18 (s, 3H, SiCH$_3$), 0.20 (s, 3H, SiCH$_3$), 0.95 (s, 9H, C(CH$_3$)$_3$), 3.24 (d, 1H, *endo*-2-H or *exo*-2-H, $^2J = -14.0$ Hz), 3.43 (d, 1H, *endo*-2-H or *exo*-2-H), 5.17 (dd, 1H, 4-H or 5-H, $^3J = 5.8$ Hz, $^3J = 6.0$ Hz), 5.21 (dd, 1H, *E*-8-H, $^3J_{cis} = 10.6$ Hz, $^2J_{E\text{-}8,\,Z\text{-}8} = -0.8$ Hz), 5.36 (dd, 1H, *Z*-8-H, $^3J_{trans} = 17.2$ Hz), 5.56 (d, 1H, 3-H or 6-H, $^3J = 6.0$ Hz), 5.61 (dd, 1H, 4-H or 5-H, $^3J = 6.0$ Hz, $^3J = 5.8$ Hz), 5.93 (d, 1H, 3-H or 6-H, $^3J = 6.0$ Hz), 6.31 (dd, 1H, 7-H). ^{13}C NMR (50 MHz, [D$_6$]acetone): δ −2.5 (q, SiCH$_3$), −2.3 (q, SiCH$_3$), 18.7 (s, *C*(CH$_3$)$_3$), 26.2 (q, C(*C*H$_3$)$_3$), 47.2 (t, C2), 80.4 (s, C1), 88.1 (d, C3 or C6), 88.7 (d, C4 or C5), 91.7 (d, C3 or C6), 96.4 (d, C4 or C5), 114.9 (s, C6a), 115.5 (t, C8), 120.9 (s, C2a), 141.3 (d, C7), 234.9 (s, CO). MS (70 eV): *m/z* (%) 396 (10) [M^+], 340 (1) [$M^+ - 2$CO], 312 (28) [$M^+ - 3$CO], 257 (11), 256 (36), 255 (27), 241 (13), 127 (28), 126 (100), 112 (10), 52 (45) [^{52}Cr]. *Anal.* Calc. for $C_{19}H_{24}CrO_4Si$: C, 57.55; H, 6.11; Cr, 13.11; Si, 7.08. Found: C, 57.38; H, 6.55; Cr, 13.01; Si, 6.94%.

TABLE 1. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) with e.s.d.s in parentheses[a]

Atom	*x*	*y*	*z*	U_{eq}
Cr	0.2709(1)	0.7903(1)	0.0167(1)	0.037(1)
Si	0.1529(1)	0.7485(1)	0.4074(1)	0.040(1)
O	0.1535(1)	0.6482(1)	0.2732(1)	0.037(1)
O(1)	−0.0615(2)	0.8185(2)	0.0336(2)	0.070(1)
O(2)	0.3931(2)	1.0757(2)	0.1936(2)	0.074(1)
O(3)	0.1774(3)	0.9388(2)	−0.2149(2)	0.076(1)
C(1)	0.0648(2)	0.8065(2)	0.0267(2)	0.046(1)
C(2)	0.3477(3)	0.9666(2)	0.1252(2)	0.048(1)
C(3)	0.2127(3)	0.8828(2)	−0.1253(2)	0.050(1)
C(4)	0.4458(2)	0.6885(2)	0.1642(2)	0.042(1)
C(5)	0.5264(2)	0.7351(2)	0.0825(2)	0.051(1)
C(6)	0.4459(3)	0.6845(2)	−0.0519(2)	0.055(2)
C(7)	0.2902(3)	0.5938(2)	−0.1030(2)	0.049(1)
C(8)	0.2069(2)	0.5530(2)	−0.0221(2)	0.041(1)
C(9)	0.2906(2)	0.6022(2)	0.1133(2)	0.035(1)
C(10)	0.2850(2)	0.5926(2)	0.2492(2)	0.036(1)
C(11)	0.4607(2)	0.6943(2)	0.3053(2)	0.048(1)
C(12)	0.2952(3)	0.4416(2)	0.2769(2)	0.050(1)
C(13)	0.1886(3)	0.3632(2)	0.3092(3)	0.064(2)
C(14)	0.2933(3)	0.6898(3)	0.5551(2)	0.073(2)
C(15)	0.2137(4)	0.9426(2)	0.4130(3)	0.074(2)
C(16)	−0.0643(3)	0.7197(3)	0.3957(3)	0.073(2)

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$

*Tricarbonyl[η^6-1-(2-oxo-7-octenyl)benzene]chromium(0) (**12**)*

The yellow solution of 1.11 g (3.3 mmol) of **6** in 65 ml THF is cooled to −78 °C and treated with 2.23 ml (3.6 mmol) of n-butyllithium in hexane (1.6 M). The solution is allowed to warm to 25 °C over 16 h, thereby changing its colour to a deep red. After recooling to −78 °C, the mixture is hydrolysed with 10 ml of a saturated aqueous solution of NH_4Cl and worked up. The crude product is chromatographed (25×400 mm, diethyl ether/pentane 1:1) to give 911 mg (2.7 mmol, 83%) of **12** as a yellow oil. IR (THF) (cm^{-1}): ν 1965 (s, CO), 1888 (s, CO), 1719 (w, ketone). ^{1}H NMR (200 MHz, [D$_8$]THF): δ 1.29–1.65 (m, 4H, 10-H, 11-H), 2.04 (m, 2H, 12-H), 2.47 (t, 9-H), 2.88 (s, 2H, 7-H), 4.90 (dd, 1H, *E*-14-H, $^2J_{E\text{-}14,\,Z\text{-}14} = -1.6$ Hz, $^3J_{cis} = 10.5$ Hz), 4.97 (dd, 1H, Z-14-H, $^3J_{trans} = 17.2$ Hz), 5.36 (d, 2H, 2(6)-H, $^3J = 6.4$ Hz), 5.37 (dd, 1H, 4-H, $^3J = 6.4$ Hz), 5.53 (d, 2H, 3(5)-H), 5.79 (dd, 1H, 13-H). ^{13}C NMR (75 MHz, [D$_8$]THF): δ 23.8 (t, C10), 29.2 (t, C11), 34.2 (t, C12), 42.8 (t, C9), 48.4 (t, C7), 92.4 (d, C4), 95.0 [d, C3(5)], 95.4 [d, C2(6)], 106.8 (s, C1), 114.8 (t, C14), 139.2 (d, C13), 205.5 (s, C8), 234.0 (s, CO). MS (70 eV): *m/z* (%) 338 (7) [M^+], 310 (8) [$M^+ - $CO], 282 (6) [$M^+ - 2$CO], 254 (55) [$M^+ - 3$CO], 253 (10), 252 (32), 186 (25), 163 (21), 144 (34), 143 (28), 91 (10), 52 (100) [^{52}Cr]. *Anal.* Calc. for $C_{17}H_{18}CrO_4$: C, 60.34; H, 5.37; Cr, 15.37. Found: C, 60.40; H, 5.48; Cr, 15.25%.

*Tricarbonyl[η^6-1-endo-hydroxy-1-exo(4-hydroxy)benzocyclobutene]chromium(0) (**13**)*

A solution of 825 mg (1.66 mmol) of **7** in 25 ml THF is cooled to −5 °C and treated with 5 ml of aqueous hydrofluoric acid (35%). After stirring for 1 h at 25 °C, 30 ml of water are added and the mixture worked up. The crude product is chromatographed (30×90 mm, diethyl ether) to yield 450 mg (1.37 mmol, 74%) of **13** as a yellow solid, m.p. 99 °C. IR (THF) (cm^{-1}): ν 1972 (s, CO), 1897 (s, CO). ^1H NMR (200 MHz, [D_6]acetone): δ 1.57 (m, 4H, 8-H, 9-H), 1.91 (t, 2H, 7-H, $^3J_{7,8}=6.8$ Hz), 3.06 (d, 1H, *endo*-2-H or *exo*-2-H, $^2J=-13.7$ Hz), 3.21 (d, 1H, *endo*-2-H or *exo*-2-H), 3.54 (t, 2H, 10-H, $^3J_{10,9}=5.4$ Hz), 4.39 (s, OH), 5.19 (dd, 1H, 4-H or 5-H, $^3J=6.0$ Hz, $^3J=6.2$ Hz), 5.59 (dd, 4-H or 5-H, $^3J=6.0$ Hz, $^3J=6.2$ Hz), 5.61 (d, 3-H or 6-H, $^3J=6.2$ Hz), 5.87 (d, 3-H or 6-H, $^3J=6.0$ Hz). ^{13}C NMR (50 MHz, [D_6]acetone): δ 21.8 (t, C8 or C9), 33.5 (t, C8 or C9), 40.0 (t, C7), 46.3 (t, C2), 62.0 (t, C10), 79.3 (s, C1), 89.2 (d, C3 or C6), 89.5 (d, C4 or C5), 91.1 (d, C4 or C5), 95.7 (d, C3 or C6), 114.8 (s, C6a), 124.0 (s, C2a), 234.5 (s, CO). MS (70 eV): *m/z* (%) 328 (24) [M^+], 300 (1) [M^+-CO], 272 (7) [M^+-2CO], 244 (46) [M^+-3CO], 226 (21), 196 (14), 168 (27), 129 (14), 119 (12), 91 (12), 69 (11), 52 (100) [^{52}Cr]. *Anal.* Calc. for $C_{15}H_{16}CrO_5$: C, 54.87; H, 4.92; Cr, 15.84. Found: C, 54.71; H, 4.84; Cr, 15.73%.

*Tricarbonyl{[η^6-1-(6-tert-butyldimethylsilyloxy)-2-oxohexyl]benzene}chromium(0) (**14**)*

A solution of 240 mg (0.54 mmol) of **7** in 8 ml THF is cooled to 0 °C and treated with 224 mg (0.71 mmol) of tetrabutylammonium fluoride trihydrate (TBAF·$3H_2O$) in 3 ml THF. After stirring for 15 min, 10 ml of water and of diethyl ether are added and the mixture is worked up. The crude product is chromatographed (20×100 mm, ethyl acetate/pentane 1:5) yielding 153 mg (0.35 mmol, 64%) of **14** as a yellow oil. IR (THF) (cm^{-1}): ν 1966 (s, CO), 1886 (s, CO), 1720 (m, ketone-CO). ^1H NMR (200 MHz, [D_6]acetone): δ 0.04 (s, 6H, $SiCH_3$), 0.88 (s, 9H, $C(CH_3)_3$), 1.42–1.68 (m, 4H, 10-H, 11-H), 2.64 (t, 2H, 9-H, $^3J_{9,10}=7.0$ Hz), 3.62 (t, 2H, 12-H, $^3J_{12,11}=3.0$ Hz), 3.62 (s, 2H, 7-H), 5.49 (d, 2H, 2(6)-H, $^3J=5.6$ Hz), 5.52 (dd, 1H, 4-H, $^3J=6.4$ Hz), 5.68 (dd, 2H, 3(5)-H). ^{13}C NMR (50 MHz, [D_6]acetone): δ −5.5 (q, $SiCH_3$), 18.7 (s, $C(CH_3)_3$), 20.6 (t, C10 or C11), 26.2 (q, $C(CH_3)_3$), 32.8 (t, C10 or C11), 42.5 (t, C7 or C9), 48.3 (t, C7 or C9), 63.2 (t, C12), 92.9 (d, C4), 95.7 (d, C2(6)), 96.0 (d, C3(5)), 107.8 (s, C1), 206.4 (s, C8), 234.5 (s, CO). MS (70 eV): *m/z* (%) 442 (2) [M^+], 386 (13) [M^+-2CO], 358 (84) [M^+-3CO], 302 (28), 238 (32), 143 (24), 127 (37), 126 (62), 91 (24), 75 (60), 52 (100) [^{52}Cr].

*Tricarbonyl[η^6-1-hydroxy-1-(5-hexenyl)-1,2,3,4-tetrahydro-2,3-di(methoxycarbonyl)naphthalene]-chromium(0) (**18**)*

A solution of 771 mg (2.28 mmol) of **6** in 45 ml THF is cooled to −78 °C and treated with 1.57 ml (2.52 mmol) of n-butyllithium in hexane (1.6 M). After stirring for 1 h at −78 °C a solution of 675 mg (4.69 mmol) of dimethyl fumarate in 5 ml THF is added and the mixture is allowed to warm up to 25 °C over 16 h. Hydrolysis with a saturated aqueous solution of NH_4Cl at −78 °C and work up lead to an orange oil, which is chromatographed (25×400 mm, diethyl ether/pentane 5:1). 674 mg (1.40 mmol, 61%) of **18** are obtained as a mixture of diastereomers (purity 70% (NMR)). IR (THF) (cm^{-1}): ν 1968 (s, CO), 1894 (s, CO), 1742 (m, ester-CO). ^1H NMR (200 MHz, [D_6]acetone, main fraction ($R_f=0.32$)): δ 1.10–1.46 (m, 8H, 9-H, 10-H, 11-H, 12-H), 2.74–2.93 (m, 4H, 2-H, 3-H, 4-H), 3.62 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 4.91 (d, 1H, *E*-14-H, $^3J_{cis}=10.0$ Hz), 4.95 (d, *Z*-14-H, $^3J_{trans}=18.4$ Hz), 5.60–5.98 (m, 4H, 5-H, 6-H, 7-H, 8-H), 6.06 (dd, 1H, 13-H).

*Tricarbonyl[η^6-(1-ethyl-2-oxo-7-octenyl)benzene]-chromium(0) (**19**)*

A solution of 680 mg (2.01 mmol) of **6** in 40 ml THF is cooled to −78 °C and treated with 1.40 ml (2.24 mmol) of n-butyllithium in hexane (1.6 M solution). The mixture is allowed to warm up to 25 °C over 16 h and then recooled to −78 °C, then 3.26 ml (40.4 mmol) of ethyl iodide is added. After warming to room temperature and stirring for 3 h at 25 °C, 50 ml of water is added and the mixture is worked up. The crude product is purified by column chromatography (400×25 mm, diethyl ether/pentane = 1:1) to yield 630 mg (1.72 mmol, 86%) of **19** as a yellow oil. IR (THF) (cm^{-1}): ν 1966 (s, CO), 1890 (s, CO), 1716 (w, ketone-CO). ^1H NMR (200 MHz, [D_8]THF): δ 1.11 (t, 3H, CH_3, $^3J=7.6$ Hz), 1.29–1.45 (m, 2H, 10-H or 11-H), 1.51–1.69 (m, 2H, 10-H or 11-H), 2.03 (td, 2H, 12-H, $^3J_{12,11}=7.7$ Hz), 2.56 (m, 2H, CH_2CH_3), 2.74 (t, 2H, 9-H), 3.45 (m, 1H, 7-H), 4.89 (dd, 1H, *E*-14-H, $^2J_{E\text{-}14,Z\text{-}14}=-2.0$ Hz, $^3J_{cis}=10.4$ Hz), 4.97 (dd, 1H, *Z*-14-H, $^3J_{trans}=17.0$ Hz), 5.37 (dd, 2H, 3-H, 5-H, $^3J=6.6$ Hz), 5.55 (dd, 2H, 2-H, 6-H, $^3J=7.4$ Hz), 5.69 (dd, 1H, 4-H), 5.77 (dd, 1H, 13-H). ^{13}C NMR (50 MHz, [D_8]THF): δ 12.6 (q, CH_3), 23.4 (t, C10), 28.9 (t, C11 or CH_2CH_3), 29.2 (t, C11 or CH_2CH_3), 34.4 (t, C12), 43.9 (t, C9), 57.4 (d, C7), 92.3 (d, C_{arom}) 92.4 (d, C_{arom}), 95.5 (d, C_{arom}), 95.9 (d, C_{arom}), 96.3 (d, C_{arom}), 110.0 (s, C1), 114.8 (t, C14), 139.3 (d, C13), 208.6 (s, C8), 234.0 (s, CO). MS (70 eV): *m/z* (%) 366 (6) [M^+], 338 (4) [M^+-CO], 310 (5) [M^+-2CO], 282, (47) [M^+-3CO], 281 (19), 280 (37), 214 (23), 170 (26), 164 (14), 162 (11), 91 (17), 55 (15), 52 (100) [^{52}Cr]. *Anal.* Calc. for

$C_{19}H_{22}CrO_4$: C, 62.28; H, 6.06; Cr; 14.19. Found: C, 62.30; H, 6.10; Cr, 14.25%.

1-Hydroxy-1-(5-hexenyl)benzocyclobutene (21)

24.4 ml (24.4 mmol) of a 1 M solution of 5-hexenyl-1-magnesium bromide in diethyl ether are treated with 961 mg (8.1 mmol) of **20** in 20 ml diethyl ether and the mixture is refluxed for 2 h. After hydrolysis with 10 ml of aqueous hydrochloric acid (2 M solution) and work up the crude product is purified by Kugelrohr distillation to give 1.417 g (7.0 mmol, 86%) of **21** as a colourless liquid, b.p. 155 °C/10^{-2} mbar. IR (neat) (cm^{-1}): ν 3528 (m, br, OH), 3073 (m), 3021 (w), 2928 (s), 2856 (m), 1641 (m), 1600 (m), 1458 (m), 1417 (w), 1263 (w), 1216 (w), 1179 (w), 1152 (w), 1138 (w), 1053 (w), 994 (m), 910 (m), 756 (m), 715 (m), 632 (w, br). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28–1.56 (m, 4H, 7-H, 8-H), 1.73–1.82 (m, 2H, 9-H), 2.02 (td, 2H, 10-H, $^3J_{10,9}=6.8$ Hz, $^3J_{10,11}=7.0$ Hz) 3.02 (d, 1H, 2-H or 2′H, $^2J_{2,2'}=-14.2$ Hz), 3.23 (d, 1H, 2-H or 2′-H), 4.91 (tdd, 1H, *E*-12-H, $^2J_{E\text{-}12,Z\text{-}12}=-1.9$ Hz, $^3J_{cis}=10.0$ Hz, $^4J_{E\text{-}12,10}=1.6$ Hz), 4.97 (tdd, 1H, *Z*-12-H, $^3J_{trans}=16.8$ Hz), 5.78 (tdd, 1H, 11-H), 7.05–7.24 (m, 4H, H_{arom}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.3 (t, C10), 29.0 (t, C9), 33.6 (t, C8), 38.7 (t, C7), 46.4 (t, C2), 80.6 (s, C1), 114.2 (t, C12), 120.9 (d, C_{arom}), 123.6 (d, C_{arom}), 126.8 (d, C_{arom}), 128.9 (d, C_{arom}), 138.7 (d, C11), 141.3 (s, C2a), 150.3 (s, C6a). MS (70 eV): *m/z* (%) 202 (2) [M^+], 119 (100) [$C_8H_7O^+$], 91 (37), 65 (11). *Anal.* Calc. for $C_{14}H_{18}O$: C, 83.11; H, 8.99. Found: C, 83.19; H, 9.08%.

2-Methyl-1-(1-oxo-6-heptenyl)benzene (22)

Following the procedure as described for **12**, a solution of 756 mg (3.7 mmol) of **21** in 75 ml THF is treated with 2.57 ml (4.1 mmol) of n-butyllithium in hexane (1.6 M solution). The crude product is purified by Kugelrohr distillation to give 565 mg (2.8 mmol, 75%) of **22** as a colourless liquid, b.p. 135 °C/10^{-2} mbar. IR (neat) (cm^{-1}): ν 3074 (w), 3022 (w), 2858 (m), 1687 (s, ketone), 1641 (m), 1600 (w), 1572 (w), 1486 (w), 1456 (m), 1441 (w), 1381 (w), 1350 (w), 1286 (w), 1259 (w), 1224 (w), 1194 (w), 1048 (w), 993 (w), 910 (m), 754 (m), 693 (w). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.47 (m, 2H, 9-H or 10-H), 1.72 (m, 2H, 9-H or 10-H), 2.08 (ttd, 2H, 11-H, $^3J_{11,10}=7.2$ Hz, $^3J_{11,12}=1.4$ Hz, $^4J_{11,13}=1.6$ Hz), 2.47 (s, 3H, CH_3), 2.87 (t, 2H, 8-H, $^3J_{8,9}=7.4$ Hz), 4.94 (tdd, 1H, *E*-13-H, $^2J_{E\text{-}13,Z\text{-}13}=-2.1$ Hz, $^3J_{cis}=10.4$ Hz), 5.00 (tdd, 1H, *Z*-13-H, $^3J_{trans}=17.0$ Hz), 5.79 (tdd, 1H, 12-H), 7.17–7.37 (m, 4H, H_{arom}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.0 (q, CH_3), 23.7 (t, C9), 28.4 (t, C10), 33.4 (t, C11), 41.2 (t, C8), 114.5 (t, C13), 125.5 (d, C3 or C6), 128.1 (d, C4 or C5), 130.9 (d, C3 or C6), 131.7 (d, C4 or C5), 137.7 (s, C1 or C2), 138.1 (s, C1 or C2), 138.3 (d, C12), 204.4 (s, C7). MS (70 eV): *m/z* (%) 202 (8) [M^+], 119 (100) [$C_8H_7O^+$], 91 (35), 65 (11). *Anal.* Calc. for $C_{14}H_{18}O$: C, 83.11; H, 8.99. Found: C, 82.94; H, 9.05%.

Tricarbonyl{η^6-N[(1S)-1-(2-hydroxyethyl)-2-methyl]phenylacetamide}chromium(0) (23)

A solution of 282 mg (1.1 mmol) of **1** is treated dropwise with 114 mg (1.1 mmol) of L-valinol. After stirring for 1 h at 25 °C a yellow solid begins to precipitate. The suspension is stirred for additional 16 h, the yellow solid is isolated and washed twice with cold diethyl ether and three times with pentane. The solid is resolved in a minimum quantity of THF and a four-fold volume of pentane is added. After storage at −30 °C, 245 mg (0.68 mmol, 62%) of **23** are obtained as a yellow solid, m.p. 134 °C. IR (THF) (cm^{-1}): ν 1963 (s, CO), 1887 (s, CO), 1682 (m, amide-CO). ^{1}H NMR (200 MHz, [D_8]THF): δ 0.88 (d, 3H, CH_3), 0.92 (d, 3H, CH_3), 1.89 (m, 1H, $CH(CH_3)_2$), 3.22 (s, 7-H), 3.51 (m, 2H, CH_2OH), 3.65 (m, 1H, $CHCH_2OH$), 3.62 (s, br, 2H, OH a. NH), 5.35 (dd, 1H, H_{arom}), 5.57 (m, 4H, H_{arom}). ^{13}C NMR (50 MHz, C_6D_6): δ 19.0 (q, CH_3), 20.0 (q, CH_3), 29.8 (d, $CH(CH_3)_2$), 42.6 (t, C7), 57.5 (d, $CHCH_2OH$), 63.0 (t, CH_2OH), 92.2 (d, C_{arom}), 95.1 (d, C_{arom}), 95.2 (d, C_{arom}), 95.2 (d, C_{arom}), 109.1 (s, C1), 169.1 (s, CONH), 234.3 (CO). MS (70 eV): *m/z* (%) 329 (2) [M^+], 301 (30) [M^+-2CO], 273 (100) [M^+-3CO], 255 (23), 190 (24), 160 (44), 91 (44), 72 (55), 60 (19), 52 (22) [^{52}Cr]. *Anal.* Calc. for $C_{16}H_{19}CrNO_5$: C, 53.78; H, 3.36; Cr, 14.55; N, 3.92. Found: C, 53.92; H, 5.32; N, 3.98; Cr, 14.61%.

Tricarbonyl(η^6-N((S)phenylethyl)phenylacetamide)-chromium(0) (24)

A solution of 1.00 g (3.9 mmol) **1** in 50 ml diethyl ether is treated dropwise with 377 mg (3.99 mmol) of 1-(*S*)-phenylethylamine. After stirring for 5 days in the dark, an orange solid starts to precipitate. The suspension is allowed to stir for additional 3 days, and the orange solid is collected. The crude product is dissolved in a minimum amount of diethyl ether and treated with a five-fold quantity of pentane. After storage at −30 °C, 956 mg (2.6 mmol, 65%) of **24** are obtained as yellow needles, m.p. 137 °C. IR (THF) (cm^{-1}): ν 1970 (s, CO), 1895 (s, CO), 1683 (m, amide-CO). ^{1}H NMR (200 MHz, [D_8]THF): δ 1.29 (d, 3H, CH_3), 3.06 (s, 2H, 7-H), 4.92 (dd, 1H, H_{arom}), 5.24 (d, 1H, H_{arom}), 5.33 (m, 4H, H_{arom} a. CH), 7.0–7.3 (m, 5H, phenyl-H). ^{13}C NMR (50 MHz, [D_8]THF): δ 22.3 (q, CH_3), 42.5 (t, C7), 49.6 (d, CH), 92.5 (d, C_{arom}), 95.3 (d, C_{arom}), 95.4 (d, C_{arom}), 108.9 (C1), 127.2 (d, C_{phenyl}), 127.8 (d, C_{phenyl}), 129.3 (d, C_{phenyl}), 129.5 (d, C_{phenyl}), 145.2 (s, C_{phenyl}), 168.5 (s, CONH), 234.3 (s, CO). MS (70 eV): *m/z* (%) 375 (19) [M^+], 319 (14) [M^+-2CO], 291 (98) [M^+-3CO], 263 (29), 239 (12), 187 (40), 143 (44), 105

(57), 91 (12), 79 (13), 52 (100) [^{52}Cr]. *Anal.* Calc. for $C_{19}H_{17}CrNO_4$: C, 60.80; H, 4.57; Cr, 13.85; N, 3.73. Found: C, 60.77; H, 4.51; Cr, 13.78; N, 3.82%.

Tricarbonyl[η^6-(ethyl)phenylglyoxylate)chromium(0) (26)

A solution of 105 mg (1.55 mmol) of sodium ethanolate in 15 ml THF is cooled to −78 °C and treated dropwise with 276 mg (1.03 mmol) of **25** in 120 ml diethyl ether. The solution is stirred for 1 h, hydrolysed with 5 ml of aqueous hydrochloric acid (2 M) at −78 °C and worked up. The crude product is chromatographed (200×30 mm, diethyl ether/pentane 1:1) to yield 276 mg (0.88 mmol, 85%) **26** as a red solid, m.p. 85 °C. IR (THF) (cm^{-1}): ν 1984 (s, CO), 1917 (s, CO), 1733 (m, ester-CO), 1684 (ketone-CO). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ 1.37 (t, 3H, CH_3, ^3J=7.1 Hz), 4.41 (q, 2H, CH_2), 5.63 (dd, 2H, 3(5)-H, ^3J=6.2 Hz, ^3J=6.5 Hz), 6.15 (dd, 1H, 4-H), 6.42 (d, 2H, 2(6)-H). ^{13}C NMR (50 MHz, [D$_6$]acetone): δ 14.1 (q, CH_3), 63.3 (t, CH_2), 90.9 [d, C2(6)], 91.0 (s, C1), 97.1 [d, C3(5)], 98.3 (d, C4), 162.7 (s, C8), 184.0 (s, C7), 231.7 (s, CO). MS (70 eV): *m/z* (%) 314 (15) [M^+], 258 (21) [M^+-2CO], 230 (32) [M^+-3CO], 159 (23), 158 (100) [$C_7H_6CrO^+$], 129 (20), 52 (69) [^{52}Cr]. *Anal.* Calc. for $C_{13}H_{10}CrO_6$: C, 49.69; H, 3.21; Cr, 16.55. Found: C, 49.20; H, 3.31; Cr, 16.45%.

Tricarbonyl[η^6-5,6-dihydro-3-phenylpyrazin-2(1)-one]chromium(0) (27) and 1,2-bis-[tricarbonyl(η^6-phenylglyoxylamide)chromium(0)]ethane (28)

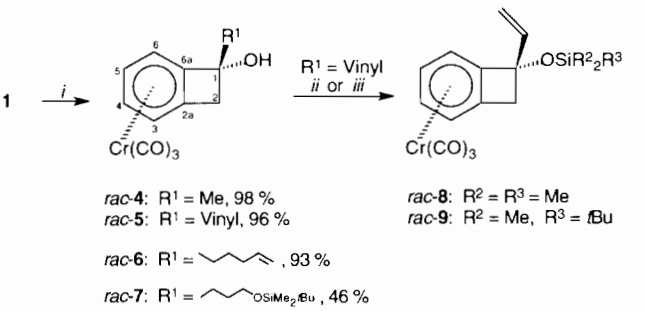
A solution of 350 mg (1.32 mmol) of **25** in 70 ml diethyl ether/THF (1:1) is added to 733 mg (13.2 mmol) of ethylenediamine in 10 ml diethyl ether at −78 °C. The resulting solution is stirred for 16 h at −78 °C, treated with 10 ml of aqueous hydrochloric acid (1 M) and worked up. The crude product is extracted with 5 ml dichloromethane. 20 mg (0.03 mmol) of **28** remain as dark red solid. The extract is chromatographed (200×30 mm, ethyl acetate/diethyl ether 5:1) to give 319 mg (1.00 mmol, 75%) of **27** as an orange solid. **27**: m.p. 146 °C. IR (THF) (cm^{-1}): ν 1970 (s, CO), 1897 (s, CO), 1689 (m, amide-CO), 1599 (m, C=N). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ 3.45 (t, 2H, CH_2, ^3J=5.9 Hz), 3.89 (t, 2H, CH_2), 5.63 (dd, 2H, *m*-H, ^3J=6.4 Hz, ^3J=6.0 Hz), 5.78 (dd, 1H, *p*-H), 6.66 (d, 2H, *o*-H), 7.61 (s, br, 1H, NH). ^{13}C NMR (50 MHz, [D$_6$]acetone): δ 39.2 (t, CH_2), 49.2 (t, CH_2), 93.0 (d, *o*-C), 95.8 (d, *p*-C), 96.1 (d, *m*-C), 101.2 (s, *ipso*-C), 157.0 (s, C2 or C3), 158.3 (s, C2 or C3), 233.8 (s, CO). MS (70 eV): *m/z* (%) 310 (10) [M^+], 282 (4) [M^+-CO], 254 (11) [M^+-2CO], 226 (100) [M^+-3CO], 52 (68) [^{52}Cr]. *Anal.* Calc. for $C_{13}H_{10}CrN_2O_4$: C. 50.32; H, 3.26; N, 9.03; Cr, 16.76. Found: C, 50.28; H, 3.35; N, 8.96; Cr, 16.59%. **28**: m.p. 215 °C (decomp.). IR (KBr) (cm^{-1}): ν 3400 (w, NH), 3100 (w), 2963 (w), 2930 (w), 1978 (s, CO), 1897 (s, CO), 1674 (s, amide-CO), 1648 (s, amide-CO), 1592 (w), 1535 (w), 1449 (w), 1408 (w), 1150 (m, br), 849 (w), 652 (m), 616 (m), 528 (w). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ 3.41 (m, 4H, CH_2), 5.52 (dd, 4H, *m*-H, ^3J=6.6 Hz, ^3J=6.6 Hz), 6.05 (dd, 2H, *p*-H), 6.65 (d, 4H, *o*-H), 8.95 (m, 2H, NH). ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ 37.8 (t, CH_2), 89.0 (d, *o*-C or *m*-C), 91.3 (s, *ipso*-C), 97.2 (d, *o*-C or *m*-C), 97.3 (d, *p*-C), 161.5 (s, CONH), 184.8 (s, *C*OCONH), 230.8 (s, CO). MS (FAB, matrix: 3,4-dimethoxybenzyl alcohol): *m/z* 597 [M^++H].

Results and discussion

Nucleophilic addition

The reaction of the monoketo complex **1** with various Grignard reagents proceeds at −78 °C in very good to quantitative yield to give the 1-hydroxybenzocyclobutene complexes **4–7** (Scheme 2). In all cases, ^{1}H NMR spectra of the crude products show the presence of only one diastereomer. The comparably low yield for the formation of **7** (46%) can be explained by taking into account that **13** is formed as a side product (30%) by hydrodesilylation and **2** by a Grignard reduction (23%). It is thought in analogy to the 1-indanone and 1-tetralone homologues [15–18] that the attack of the Grignard reagents takes place from the uncomplexed *exo* face of complex **1** leading to 1-*endo*-hydroxybenzocyclobutene complexes. In contrast to the higher homologues, nucleophilic additions to **1** occur at temperatures which are nearly 100 °C below those used for the 1-indanone and 1-tetralone complexes. This highlights once more the remarkable activation of the keto functionality in **1** towards nucleophilic additions resulting from the electron withdrawal by the tricarbonylchromium group via the conjugated π-system of the ligand.

Characteristic NMR signals of the alcohol complexes **4–7** are the AB spin system for the methylene protons of the four-membered ring with a ^2J(H,H) coupling



Scheme 2. Reagents and conditions: *i*: R^1MgBr, −78 °C, d.e. ≥ 90%; *ii*: $ClSiMe_3$, NEt_3, 75%; *iii*: $ClSiMe_2tBu$, imidazol, DMF, 79%.

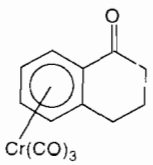
constant of *c.* −14 Hz. The chemical shift of C2 ($\delta = 47$) also indicates the presence of the four-membered ring.

Reactivity of vinyl derivative 5

The vinyl substituted complex **5** was synthesised with the aim of performing a two-step transformation consisting of a ring opening of the corresponding alcoholate and subsequent cyclisation reaction to give the 1-tetralone complex **10** (Scheme 3). This so-called vinyl cyclobutane rearrangement is widely used in the uncomplexed case for the synthesis of anthracyclines [52–54]. Alkoxy initiated and therefore charge accelerated reactions of this type are also known [55].

To our disappointment, treatment of **5** at −78 °C with a stoichiometric as well as with a catalytic amount of n-butyllithium leads only to a complicated mixture of various compounds. This can be understood by taking into account the large number of possible reaction pathways by which the alkoxide can be transformed (e.g. proximal or distal ring opening followed by intra- or intermolecular Michael reactions).

In order to more finely tune the reactivity it was decided to silylate the alcohol group in **5** with the hope of obtaining a better control of the vinyl cyclobutane rearrangement by generating low concentrations of alcoholate from a silyl ether [56]. Thus **5** was converted into the trimethylsilyl ether **8** in good yield under mild basic conditions in order to prevent a ring opening reaction. For the introduction of the sterically more bulky tert-butyldimethylsilyl group, an excess of the silylating reagent was necessary owing to the assumed *endo* configuration of the alcohol group in **5**. Silyl ether **9** was obtained in 79% yield under these conditions. Treatment of the silyl ethers **8** and **9** with tetrabutyl ammonium fluoride trihydrate (TBAF·$3H_2O$) in a temperature range of −78 to 25 °C does not lead to a better control of the product distribution. A similarly complicated mixture of several compounds was obtained as was found for the reaction of **5** with n-butyllithium. The desired complex **10** could only be detected in traces by TLC during the reaction of **8** with TBAF. However, a more useful cyclisation reaction might be possible by changing the counterion of the alcoholate. It has recently been demonstrated that the ring opening temperature of the alcoholate of **2** increases when using zinc instead of lithium as the counterion. Possibly an analogous strategy can be used in the desired cyclisation reaction of **5**.



10

Scheme 3.

X-ray structure analysis of 8

The relative configuration at C1 with respect to the $Cr(CO)_3$ group in complexes **2** and **4–7** has hitherto not thoroughly been established. An NOE experiment performed with a derivative of **2** in which one carbonyl ligand was substituted with triphenylphosphine was not fully conclusive. An X-ray analysis was undertaken to establish the relative configuration at C1. Suitable crystals of the trimethylsilyl ether **8** were obtained by recrystallisation from a concentrated acetone solution.

The results of the crystal structure analysis of **8** are summarised in Fig. 1 and confirm the assumed *endo* configuration, with the silyloxy substituent at C1 oriented towards the tricarbonylchromium fragment and proves that the attack of the nucleophile from the uncoordinated face of the organic ligand has occurred. The benzocyclobutene skeleton is completely planar [35, 41], and the C10–C11 bond length of 1.600(3) Å is long for a normal single bond between sp^3-hybridised carbon atoms [57]. The *anti* conformation of the tricarbonyl chromium group reveals a steric repulsion between the silyl group and the carbonyl ligands in the solid state. The lengths of the aromatic π-bonds show a small alternation with the π-bonds in *trans* position to the carbonyl ligands slightly shorter than the other aromatic bonds as a consequence of the strong d–π^* backbonding between chromium and the carbon monoxide ligands. The molecular structure of **8** in the solid state is thus comparable with those of other corresponding (η^6-arene)tricarbonylchromium(0) complexes [58, 59].

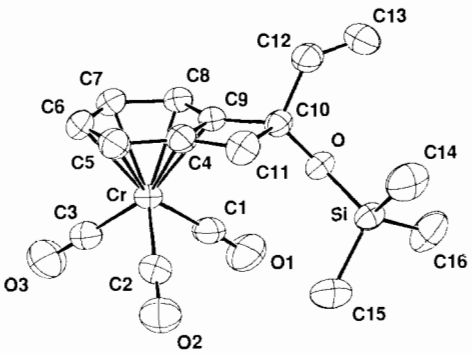
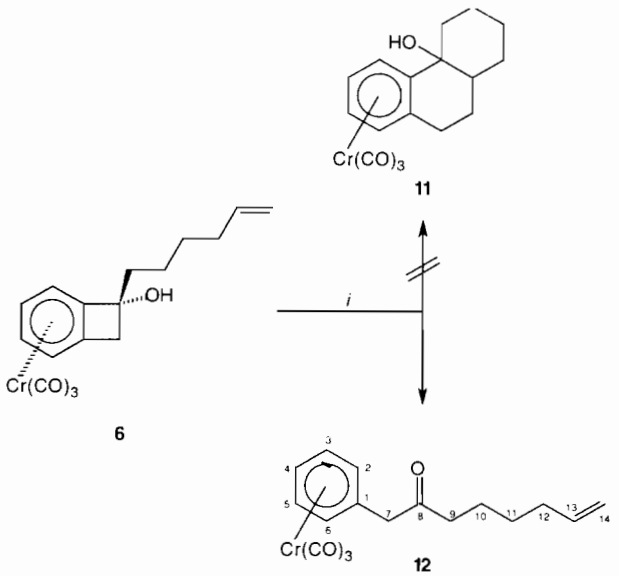


Fig. 1. Molecular structure of **8**. Selected distances (Å) and angles (°): Si–O 1.658(1), O–C10 1.394(2), C4–C5 1.411(3), C4–C9 1.398(3), C4–C11 1.514(3), C5–C6 1.400(4), C6–C7 1.421(3), C7–C8 1.401(3), C8–C9 1.410(3), C9–C10 1.535(3) C10–C11 1.600(3), C10–C12 1.509(3), C12–C13 1.308(3), C11–C4–C9 94.2(2), C10–C9–C4 93.4(2), C11–C10–C9 85.8(1), C10–C11–C4 86.6(2), C12–C10–O 112.1(2).

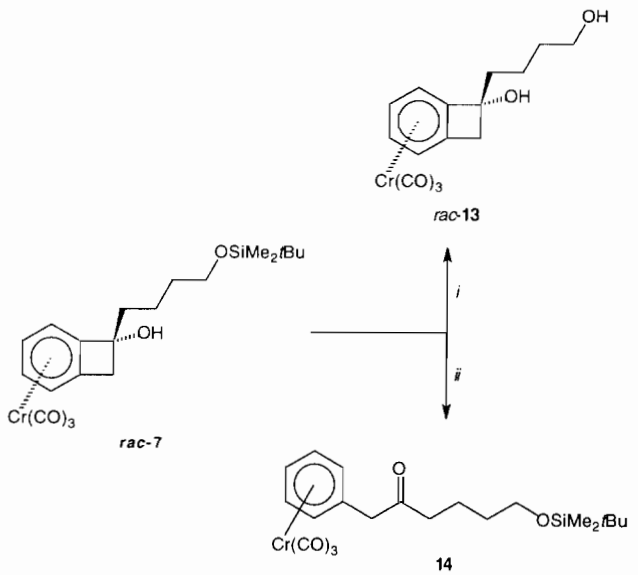
Proximal ring opening reactions of 1-substituted 1-hydroxybenzocyclobutene complexes

As shown in Scheme 1, ring opening of the alcoholate of **2** proceeds under very mild reaction conditions leading to an *ortho*-quinodimethane intermediate, which can be converted into the tetralol complex **3** by a highly stereoselective intermolecular cycloaddition reaction. In the view of the importance of intramolecular cycloaddition reactions, which have been widely used in syntheses of complicated carbon skeletons [42, 60, 61], examination of an intramolecular version of the ring opening/cycloaddition protocol appears necessary. A suitable starting material to perform this type of reaction at a coordinated benzocyclobutene has to bear an alcohol function at the four-membered ring rendering the anion-driven ring opening reaction favourable. Furthermore, a side chain incorporated dienophile moiety is also a prerequisite. Therefore, it might be expected that the alcoholate of the hexenyl derivative **6** can be converted to the tricyclic complex **11** by a reaction sequence consisting of ring opening and intramolecular [4+2] cycloaddition.

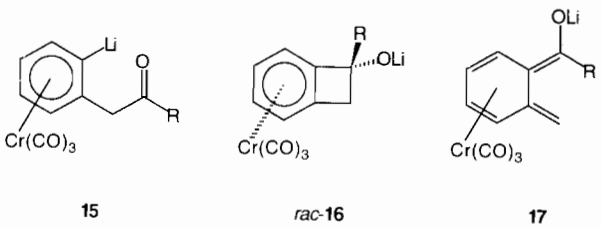
Treatment of **6** with n-butyllithium at −78 °C gave the orange solution of the corresponding alkoxide, which was allowed to warm up to 25 °C over 16 h. After hydrolysis and aqueous workup the ring opened chain product **12** was obtained in 83% yield instead of the expected cycloadduct **11** (Scheme 4). The formation of **12** can be explained by the opening of the proximal bond of the four-membered ring instead of the distal one, thus preventing the following cycloaddition. Remarkably, a similar reaction can be observed by trying to deprotect the primary alcohol group in **7** (Scheme 5). Treatment of the silyl ether **7** with TBAF·$3H_2O$



Scheme 4. Reagents and conditions: *i*: n-BuLi, −78 to 25 °C, 83%.



Scheme 5. Reagents and conditions: *i*: HF·aq (35%), 74%; *ii*: TBAF·$3H_2O$, 64%.

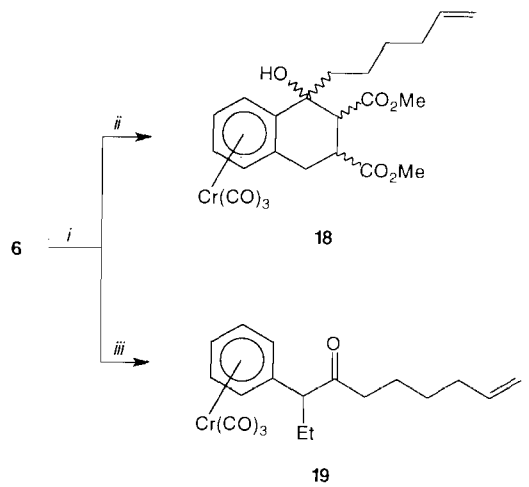


Scheme 6.

under aprotic conditions led to the ring opened product **14** in which the primary alcohol group remained protected. To prevent the basic conditions, aqueous hydrofluoric acid was used for the deprotection and yielded the benzocyclobutene complex **13** in 74% yield.

The alcoholate **16** was considered as a key intermediate for the explanation of this unexpected proximal ring opening reaction. Distal ring opening as observed for the alcoholate of **2** leads to the *ortho*-quinodimethane complex **17** as a highly reactive intermediate. In contrast, the proximal ring opening of **16** (R = hexenyl) yields the aryllithium complex **15** [62]. This kind of anion is also accessible by the deprotonation of an arene complex at −78 °C and is known to be stabilised by the electron withdrawing tricarbonylchromium moiety [7]. Considering the small structural differences between **2** and **6** it was assumed that the three species **15**–**17** are in equilibrium (Scheme 6).

Treatment of **6** with n-butyllithium and an excess of dimethyl fumarate yielded the cycloadduct **18** as mixture of numerous stereoisomers (Scheme 7), confirming the presence of distal ring opening product **17**. The decrease in stereoselectivity of the cycloaddition reaction can be interpreted as a consequence of a non-torquoselective



Scheme 7. Reagents and conditions: *i*: n-BuLi, −78 °C; *ii*: dimethyl fumarate, −78 to 25 °C, 61%; *iii*: EtI, −78 to 25 °C, 86%.

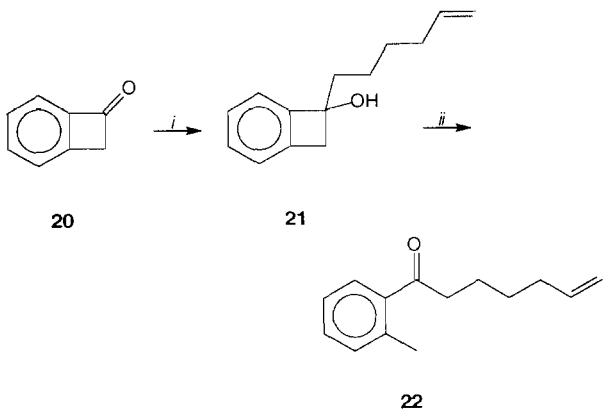
[63] ring opening leading to an *ortho*-quinodimethane, with an undefined double bond configuration.

To furnish evidence that the aromatic anion **15** is the primary product of a proximal ring opening reaction, **6** was treated with n-butyllithium and ethyl iodide in the temperature range from −78 to 25 °C. However, the monosubstituted derivative **19** was obtained in 86% yield instead of an *ortho* disubstituted benzene complex. The formation of **19** can be understood by taking into account the fact that ethyl iodide is not reactive enough for alkylations below −10 °C. It was shown by Semmelhack *et al.* [7] that at temperatures above −10 °C benzylic protons are more acidic than the protons attached directly to the aromatic nucleus. As a result, the ethyl group is found attached to the benzylic position of **15**.

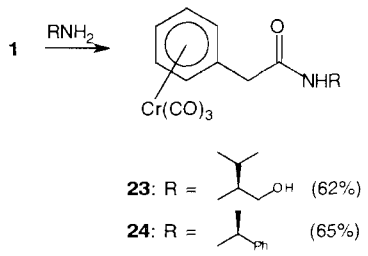
The alkoxy-initiated proximal ring opening reaction is unusual in the chemistry of 1-hydroxybenzocyclobutenes [64] and apparently is a special feature of the tricarbonylchromium complexes. In a control experiment **21**, the organic ligand of **6**, which can be obtained from 1-oxobenzocyclobutene (**20**) and 1-hexenyl magnesium bromide in 86% yield, was treated with n-butyllithium. Here the usual distal ring opening takes place leading to the *ortho* disubstituted benzene derivative **22**. In addition, the experiment demonstrates that the dienophile fragment in the side chain of **21** is not reactive enough to undergo cycloaddition reactions at the temperature of the ring opening reaction (Scheme 8).

Reactions of 1 and 25 with organic bases

If one wishes to take advantage of the stereoselective cycloaddition chemistry of 1-hydroxybenzocyclobutene complexes derived from **1** by reduction or nucleophilic addition, **1** has to be applied in enantiomerically pure form [41]. In an attempt to separate its enantiomers



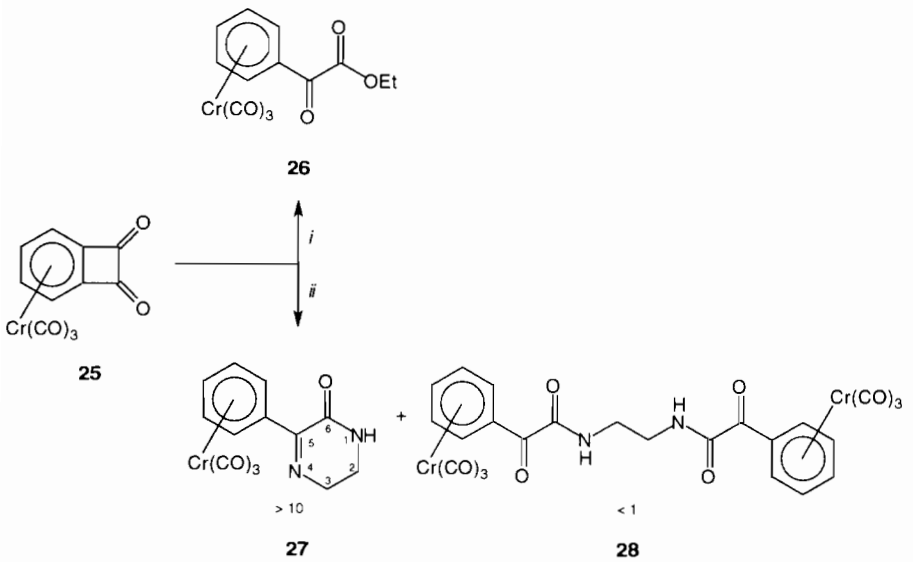
Scheme 8. Reagents and conditions: *i*: 5-hexenyl magnesium bromide, 86%; *ii*: n-BuLi, −78 to 25 °C, 75%.



Scheme 9.

1 was treated with chiral primary amines like L-valinol and (*S*)-(1-phenylethyl)amine [46]. The reaction unexpectedly yielded proximal ring opened products **23** and **24** (Scheme 9). It should be noted that the reaction rate as compared to that of the reaction of **6** with n-butyllithium is much lower. Apparently the amine attacks the keto group with formation of an adduct containing an alcoholate functionality, which induces the following proximal ring opening reaction.

Another complex in the series which is highly reactive towards nucleophiles is tricarbonyl(η^6-1,2-dioxobenzocyclobutene)chromium(0) (**25**). We recently reported [35, 41] that this complex undergoes a double addition of vinyl lithium derivatives followed by a double anionic oxy-Cope rearrangement as a sequential transformation at −78 °C. In the course of this reaction, the distal bond of the four-membered ring opens very cleanly. We have found that in contrast, when using bases like alcoholates or amines, the opening of the proximal bond proceeds under comparably mild reaction conditions. Thus treatment of **25** with sodium ethanolate at −78 °C gives the α-oxoester **26** in 85% yield. With 1,2-diaminoethane, formation of the heterocyclic compound **27** can be observed as product of a nucleophilic addition, proximal ring opening and intramolecular condensation of the remaining amino function with the resulting ketone. The dimeric complex **28** was formed in traces and was fully characterised (Scheme 10).



Scheme 10. Reagents and conditions: *i*: NaOEt, −78 °C, 85%; *ii*: $H_2NCH_2CH_2NH_2$, −78 °C, 75%.

In conclusion, we have presented a number of reactions in which a proximal bond of the anellated ring in benzocyclobutene complexes is opened. In several cases it was shown that this reactivity differs from that of the uncoordinated ligand. The possibility of proximal ring opening reactions of benzocyclobutene complexes has to be taken into account when the extremely valuable distal ring opening reactions (followed by a [4+2] cycloaddition or in connection with double anionic oxy-Cope rearrangements) are to be exploited in synthesis.

Supplementary material

Further details of the crystal structure investigation (listings of hydrogen atom positional parameters, anisotropic thermal parameters, distances and angles) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-57960, the names of the authors and the journal citation.

Acknowledgements

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