Reactions of Complex Ligands, LXXVII[◇]

Axial-Chiral Metal Carbenes: Synthesis and Structure of 1,1-Binaphthyl-Derived Carbonyl-Carbene Complexes of Chromium

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Axial-chiral mono- and biscarbene complexes of chromium containing the 1,1-binaphthyl skeleton have been obtained in both racemic and enantiopure forms in a one-pot reaction starting from lithiated 2,2-dimethoxy-1,1-binaphthyl (**1**) and hexacarbonyl chromium via the Fischer route. An X-ray structure analysis of the biscarbene complex **2** reveals that the biscarbene functionalization significantly increases the dihedral angle defined by the biaryl planes. The enantiopure complexes have been characterized by CD spectroscopy.

Introduction

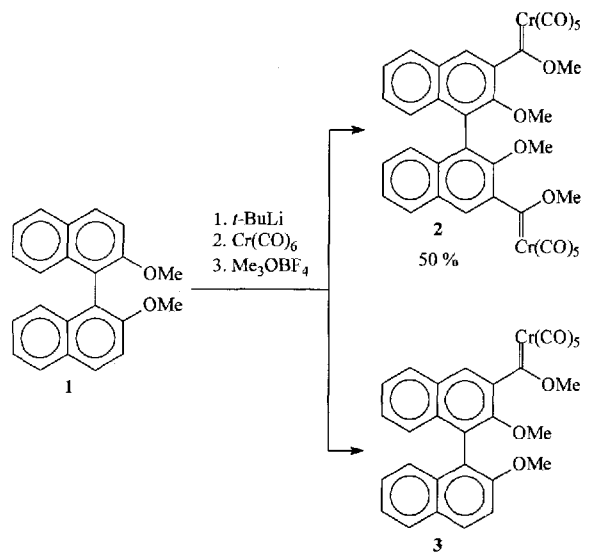
Fischer-type carbene complexes have become valuable reagents in stereoselective organic synthesis as a result of their potential in both metal and ligand-centered C–C bond formation[2]. A chiral modification of this class of compounds may be based on either the incorporation of chiral information into the carbene ligand, the coligand sphere or on a chiral metal center[3]. So far, synthetic efforts have focussed on optically active alkoxy- and aminocarbene complexes bearing a chiral center in the *heteroatom* carbene side chain[4]. In contrast, examples of a chiral-modified *carbon* carbene side chain are rare[5]. Applications in diastereoselective synthesis include aldol and Michael addition[6], benzannulation[4][7] and photochemical cycloaddition reactions[8].

As part of our ongoing series of studies of stereoselective syntheses we became interested in optically active metal carbenes bearing an axis of chirality. We concentrated on the 1,1′-binaphthyl skeleton which has been the subject of an increasing amount of interest in stereoselective synthesis and asymmetric catalysis during the past two decades[9], and we now report on its metal–carbene functionalization.

Synthesis of Binaphthyl Chromium Carbenes

In order to incorporate the 1,1′-binaphthyl skeleton into the carbene side chain we focussed on the Fischer route. Lithiation of racemic 2,2′-dimethoxy-1,1′-binaphthyl (**1**) using *n*-butyllithium at room temperature in the presence of TMEDA has been reported in the literature[10]; however, we found that an unsatisfactory mixture of mono- and bismetalated products was obtained under these conditions. Thus, it was necessary to further optimize the reaction in order to improve the yield of the desired *bis*-lithiated 2,2′-dimethoxy-1,1′-binaphthyl and to reduce the formation of the *mono*-lithiated counterpart. Best results on a 5 mmol scale were obtained using an excess of *tert*-butyllithium at −40 °C over 6 hours which allowed up to 63% bismetalation as indicated by quenching experiments with trimethylsilyl chloride[11]. Addition of hexacarbonyl chromium to a solution containing the lithiated binaphthyls generated the acyl chromate intermediates which underwent alkylation

Scheme 1. Preparation of biscarbene complex **2** and monocarbene complex **3**



[◇] Part XXVI: Ref.[1].

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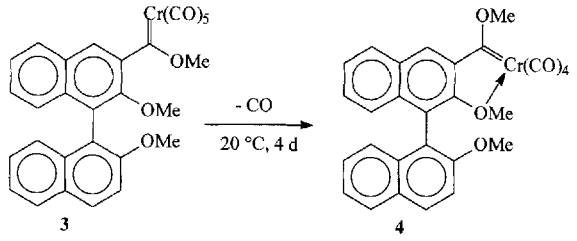
with trimethyloxonium tetrafluoroborate at ambient temperature to give the methoxycarbene complexes **2** and **3** in moderate yields.

Under these conditions and during the chromatographic workup a partial decarbonylation of the monocarbene complex **3** occurred which resulted in concomitant formation of the carbene-chelate complex **4**. Whereas column chromatography afforded pure biscarbene complex **2**, carbene chelate **4** (which is less soluble than **3**) was isolated as a black solid by crystallization from petroleum ether/diethyl ether.

Scheme 2. Decarbonylation of monocarbene complex **3** to monocarbene chelate complex **4**



3 4

36 %

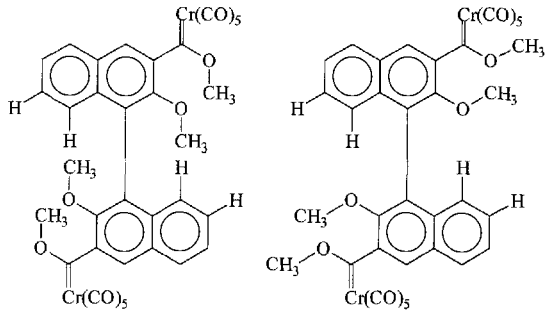
Temperature-Dependent NMR Studies

The ^{1}H-NMR spectrum of the biscarbene complex **2** shows broad signals for the methoxy groups attached to the aromatic system and the carbene atom and also for the aromatic protons in the positions 7, 7′, 8 and 8′. This observation may be explained in terms of a hindered rotation of the carbene methoxy group around the $C_{carbene}-O$ bond which evidently influences both the aromatic methoxy groups and the aromatic 7, 7′, 8, 8′-hydrogen atoms. We suggest that the orientation of the carbene methoxy group controls the conformation of the aromatic methoxy group in such a way that it interferes with the aromatic protons 7 and 8 of the neighboring binaphthyl system as demonstrated for the *E* and the *Z* configuration of the $C_{carbene}-O$ bond (Figure 1).

To further investigate this problem we extended our studies to temperature-dependent ^{1}H-NMR measurements. When the temperature was raised to 323 K the methoxy and the aromatic hydrogen signals of biscarbene complex **2** became sharp, whereas lowering the temperature to 233 K lead to a clean double set of signals for the aromatic and the carbene methoxy groups combined with an additional complex signal system arising from the aromatic protons. This result is in agreement with the idea that an *E*/*Z* isomerization across the $C_{carbene}-O$ bond is responsible for the cooperative mobility within the molecule. By variation of the temperature in steps of 3 K the coalescence temperature for the *E*/*Z* isomeration of the carbene methoxy group was determined to be 295 K which corresponds to a free enthalpy of activation of 55.4 kJ/mol[12].

Support for such a cooperative mobility is provided by the ^{13}C-NMR spectrum which at 298 K exhibits only seven rather broad signals in the range between δ = 134 and 122 for the aromatic carbon atoms. Lowering the temperature to 273 K revealed a complex system of signals between δ = 134 and 122; two pairs of additional signals between δ = 148 and 144 may be assigned to the methoxy-substituted aromatic carbon atoms. The cooperative mechanism described above obviously leads to a broadening of the signals if the ^{13}C-NMR spectrum is recorded close to the temperature of coalescence and thus prevents the detection of the remaining signals of the binaphthyl system at 298 K.

Figure 1. Cooperative mobility of methoxy groups and interaction with aromatic hydrogen atoms in complex **2**



Molecular Structure of Biscarbene Complex 2

The molecular structure of the racemic biscarbene complex **2** was established by X-ray analysis (Figure 2) in order to determine the conformational preference of the carbene methoxy group and to quantify the dihedral angle between the naphthyl groups.

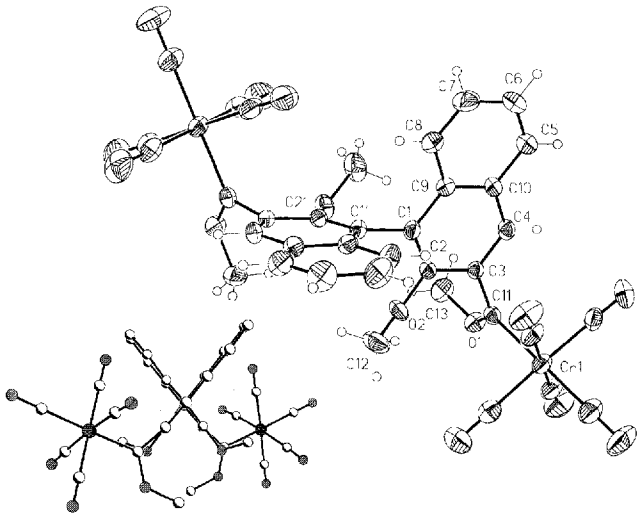
In the solid state both carbene methoxy groups adopt the *E* configuration with respect to the $C_{carbene}-O$ bond. While the oxygen atom of the aromatic methoxy group lies in the plane of the naphthyl group the $C_{carbene}-C(3)$ axis deviates by 10° from the plane [C(1)–C(2)–C(3)]. Compared with 2,2′-dimethoxy-1,1′-binaphthyl (**1**)[13] the torsion angle between the aromatic methoxy group and the naphthylene plane increases from 15° to 56° [C(1)–C(2)–O(2)–C(12)]. The aromatic and the carbene methoxy groups occupy opposite sides of the naphthyl system which is indicative of the steric interaction between these groups described above. On the other hand, the exocyclic angle C(1)–C(2)–O(2) increases to 124° reflecting the steric interaction to the neighboring naphthyl half.

In comparison with the racemic 2,2′-dimethoxy-1,1′-binaphthyl (**1**) the dihedral angle 0 between the two binaphthyl systems [C(2)–C(1)–C(1′)–C(2′)] is reduced from 110° to 75°. We suggest that this result reflects the balance of steric interactions between the bulky metal-carbonyl moieties on one side and between both naphthyl ring systems on the other side. In addition, the C(1)–C(1′) bond connecting both naphthyl units is slightly, though not significantly, lengthened to 1.507(6) Å when compared with the nonmetalated binaphthyl precursor **1** [1.488 (7) Å].

Optical Properties of Complexes 2 and 4

To explore the optical properties imposed by the chiral axis of the biaryl skeleton we extended our studies to the enantiopure analogs. As described above for the racemic

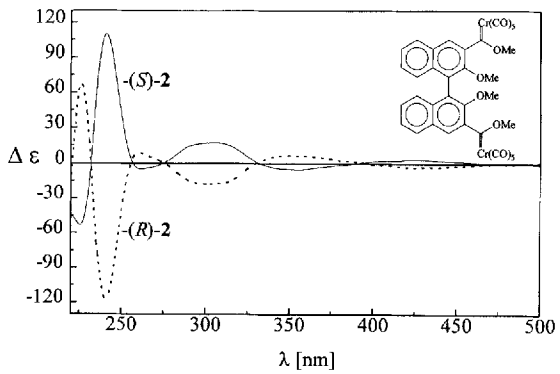
Figure 2. Molecular structure of (*R,S*)-**2**[a]; thermal ellipsoids are drawn at the 30% probability level



[a] Selected bond lengths [Å] and angles [°]: C(1)–C(1′) 1.507(6), Cr(1)–C(11) 2.011(3), C(1)–C(2)–O(2) 124.3(3), C(3)–C(2)–O(2) 114.2(3), C(9)–C(1)–C(1′)–C(9′) 75.07(3), C(2)–C(3)–C(11)–O(1) 78.71(3), C(1)–C(2)–C(3)–C(11) 169.6(3), C(1)–C(2)–O(2)–C(12) 56.1(3).

series, (*R*)- and (*S*)-2,2′-dihydroxy-1,1′-binaphthyl have been modified into optically active biscarbene and monocarbene chelate complexes **2** and **4**. The CD spectra recorded for both the (*R*) and the (*S*) enantiomers of biscarbene complex **2** and monocarbene complex **4** represent accurate mirror images in both the form and intensity of the signals (Figure 3).

Figure 3. CD-spectra of (*R*)- and (*S*)-biscarbene complex **2** and (*R*)- and (*S*)-monocarbene chelate complex **4**



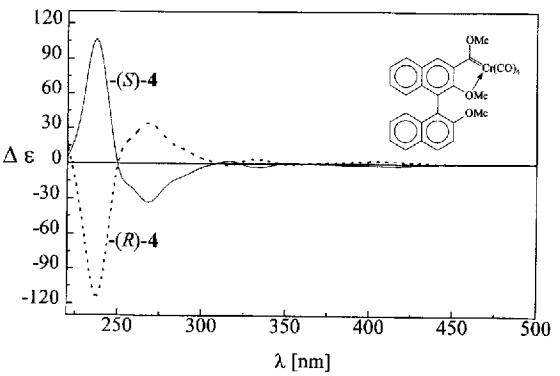
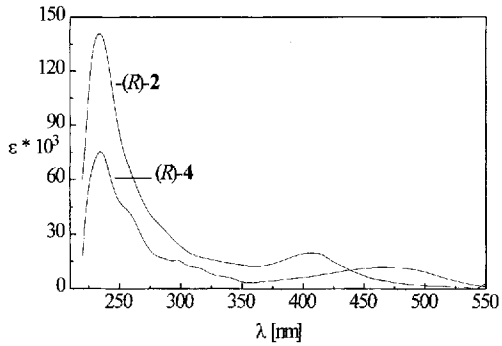


Figure 4. UV/VIS-spectra of (*R*)-biscarbene complex **2** and (*R*)-monocarbene chelate complex **4**



In order to localize the energetic position of the ^1B_b electronic transition of the naphthalene chromophore we recorded UV/VIS-spectra of the (*R*)-biscarbene complex **2** and (*R*)-monocarbene chelate complex **4** and we found absorption maxima at 234 nm for complex **2** and at 235 nm for complex **4**. The absorption maxima for the metal-ligand charge-transfer transition (MLCT) are at 406 nm for (*R*)-**2** and 468 nm for (*R*)-**4** (Figure 4)[14].

The CD spectrum of the symmetric (*R*)-bischromium-biscarbene **2** reveals a negative exciton CD couplet originating from the ^1B_b electronic transition which, together with the solid-state structure of the racemic component, is compatible with a cisoid conformation ($\theta < 100°$)[15]. In contrast, the nonsymmetrical (*R*)-monocarbene chelate complex **4** shows a positive couplet ($\theta > 110°$) indicating a transoid conformation. The energy for this transition observed in (*R*)-biscarbene complex **2** resembles that observed for the nonmetalated precursor **1** whereas the transition in (*R*)-monocarbene chelate complex **4** is shifted to lower energy (Table 1). Only a weak CD effect was detected for (*R*)-**2** and (*R*)-**4** in the MLCT range.

We have demonstrated that metal-carbene-modified binaphthyls reveal unexpected spectroscopic properties in the solid state and in solution which reflect the interaction between the bulky metal–carbonyl fragments. Benzannulation studies directed towards densely functionalized biphenanthrenyls are underway and will be reported in due course.

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Table 1. CD data of (*R*)-**1**, (*R*)-**2** and (*R*)-**4** in $CHCl_3$

Compound	Circular dichroism $\Delta\varepsilon_{max}$ [dm^{-3} mol^{-1} cm^{-1}] (λ_{max})[nm]
(*R*)-**1**	+ 84 (227); −161 (241); + 14 (289); + 9 (323)
(*R*)-**2**	+ 67 (226); −117 (241); + 9 (260); −18 (299); + 6 (348); −3 (425)
(*R*)-**4**	−114 (238); + 34 (268); −1.5 (316); + 4 (332); + 2 (405)

skopie isolierter und kondensierter Moleküle" and the *Fonds der Chemischen Industrie* is gratefully acknowledged. We further thank *Merck AG* for providing us with enantiopure (*R*)- and (*S*)-1,1-dihydroxybinaphthyl.

Experimental Section

General: All operations were performed under argon. Solvents were dried by distillation from sodium-potassium or sodium hydride; petroleum ether 40−60 °C. − ^{1}H and ^{13}C NMR: Bruker DRX 500. Chemical shifts refer to those of residual solvent signals based on δ_{TMS} = 0.00. − FT-IR: Nicolet Magna 550. − MS: Kratos 1H Concept. − Melting points: Büchi SMP 20, uncorrected. − Elemental analyses: Heraeus CHN-O-Rapid. − CD and UV/VIS: 0.02 cm path-length cell, Jasco J-720 spectropolarimeter.

3,3'-[(R,S)-2,2'-Dimethoxy-1,1'-binaphthyldiyl]bis(methoxycarbene)bis[pentacarbonylchromium(0)] (**2**) *and 3-[(R,S)-2,2'-dimethoxy-1,1'-binaphthyl](methoxycarbene)tetracarbonylchromium(0)* (**4**): 20 ml THF was added to a solution of 15 ml (25.5 mmol) 1.7 M *tert*-butyllithium in hexane at −78 °C. The mixture was stirred for 15 min, and then added to a solution of 2.0 g (6.4 mmol) (*R,S*)-2,2'-dimethoxy-binaphthyl in 70 ml THF at −40 °C and stirred for 6 h. After addition of 8.4 g (38.25 mmol) of hexacarbonyl chromium, suspended in 20 ml of THF, the suspension was stirred for 5 h at −40 °C and for an additional 15 h at 0 °C. The solvent was removed in vacuo, the mixture dissolved in 70 ml of dichloromethane and 5.6 g (38 mmol) of trimethyloxonium tetrafluoroborate were added. The mixture was stirred for 1 h at 0 °C and for another 1 h at 20 °C. The solution was filtered and the solvent was removed in vacuo. Chromatography (250 g of silica gel 20 × 6 cm, 10 °C, petroleum ether/diethyl ether, 5:1) of the deep red residue yielded first the biscarbene complex **2** as a red solid followed by a mixture of the pentacarbonyl monocarbene complex **3** and the tetracarbonyl monocarbene chelate complex **4**. The mixture was dissolved in 20 ml of petroleum ether/diethyl ether (5:1); black crystals of the carbene chelate complex **4** were obtained after the solution was allowed to stand for several days at 20 °C.

The enantiopure 3,3'-[(*R*) and (*S*)-2,2'-dimethoxy-1,1'-binaphthyldiyl]bis(methoxycarbene)bis[pentacarbonylchromium(0)] and (*R*)- and (*S*)-2,2'-dimethoxy-1,1'-binaphthyl)(methoxycarbene)-tetracarbonylchromium(0) were prepared from (*R*)- and (*S*)-2,2'-dimethoxy-1,1'-binaphthyl by following the same procedure.

(R,S)-2,2'-Dimethoxy-1,1'-binaphthyl (**1**): The compound was prepared according to ref.[10]. − ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 3.76 (s, 6 H, OCH_3), 7.10 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, 8-H), 7.20 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.4 Hz, 2 H, 7-H), 7.31 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 2 H, 6-H), 7.46 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, 3-H), 7.86 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 5-H), 7.97 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, 4-H).

3,3'-[(R,S)-2,2'-Dimethoxy-1,1'-binaphthyldiyl]bis(methoxycarbene)bis[pentacarbonylchromium(0)] (**2**): Yield 2.5 g (3.2 mmol, 50%), m.p. 170 °C (dec.), R_f = 0.52 (petroleum ether/diethyl ether, 5:1), red crystals. − IR (petroleum ether): $\tilde{\nu}$ = 2064 cm^{-1} (m, A_1^1; C=O), 1953 (s, A_2^1, E; C=O). − ^{1}H NMR (500.13 MHz, $CDCl_3$, 323 K): δ = 3.23 (s, 6H, $OCH_{3arom.}$), 4.40 (s, 6 H, $OCH_{3carbene}$), 7.20 (d, br, $^3J_{HH}$ = 8.4 Hz, 2 H, 8-H and 8'-H), 7.30 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, 7-H and 7'-H), 7.45 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.1 Hz, 2 H, 6-H and 6'-H), 7.55 (s, 2 H, 4-H and 4'-H), 7.92 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 5-H and 5'-H). − ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 60.41 ($OCH_{3arom.}$), 65.69 ($OCH_{3carbene}$), 134.13, 129.48, 128.76, 127.68, 125.81, 125.38, 122.60 (br, C_{aryl}), 216.28 ($C{=}O_{cis}$), 224.23 ($C{=}O_{trans}$), 352.93 (br, Cr=C). − MS (FAB); *m/z* (%): 781.9 (15) [M^+], 669.9 (89) [M^+ − 4 CO], 641.9 (100) [M^+ − 5 CO], 614.0 (25) [M^+ − 6 CO], 586.0 (45) [M^+ − 7 CO], 558.0 (87) [M^+ − 8 CO], 530.0 (42) [M^+ − 9 CO], 502.0 (24) [M^+ − 10 CO]. − $C_{36}H_{22}O_{14}Cr_2$ (782.55): calcd. C 55.25, H 2.83; found C 55.29, H 2.89.

3-[(R,S)-2,2'-Dimethoxy-1,1'-binaphthyl](methoxycarbene)-tetracarbonylchromium(0) (**4**): Yield 1.2 g (2.3 mmol, 36%), R_f = 0.41 (petroleum ether/diethyl ether, 5:1), black solid. − IR (diethyl ether): $\tilde{\nu}$ = 2017 cm^{-1} (s, A_1^1; C=O), 1945 (s, A_2^1; C=O), 1917 (vs, B_1; C=O), 1862 (s, B_2; C=O). − ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 3.42 (s, 3 H, $OCH_{3arom.-C2'}$), 3.87 (s, 3 H, $OCH_{3carbene}$), 5.00 (s, 3 H, $OCH_{3arom.-C2}$), 7.09 (d, $^3J_{HH}$ = 8 Hz, 1 H, 8'-H), 7.13 (d, $^3J_{HH}$ = 8 Hz, 1 H, 3'-H), 7.31 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, 2 H, 6-H and 6'-H), 7.38 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, 1 H, 7-H), 7.42 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, 1 H, 7'-H), 7.48 (d, $^3J_{HH}$ = 8 Hz, 1 H, 8-H), 7.90 (d, $^3J_{HH}$ = 8 Hz, 1 H, 4'-H), 8.01 (d, $^3J_{HH}$ = 8 Hz, 1 H, 5'-H), 8.05 (s, 1 H, 4-H), 8.06 (d, $^3J_{HH}$ = 8 Hz, 1 H, 5-H). − ^{13}C-NMR (125.76 MHz, $CDCl_3$): δ = 56.25 ($OCH_{3arom.-C2'}$), 67.94 ($OCH_{3carbene}$), 72.31 ($OCH_{3arom.-C2}$), 113.08, 115.78, 116.94, 120.46, 124.12, 124.66, 125.75, 125.99, 127.51, 128.28, 128.82, 128.99, 130.36, 131.11, 131.36, 133.23, 133.62, 135.87 (C_{aryl}), 154.88 (C-2'), 160.40 (C-2), 215.20, 215.52 ($C{=}O_{cis}$), 231.82, 232.06 ($C{=}O_{trans}$), 337.23 (C=Cr). − MS (FAB); *m/z* (%): 520.1 (17) [M^+], 464.1 (31) [M^+ − 2 CO], 436.1 (100) [M^+ − 3 CO], 408.1 (70) [M^+ − 4 CO]. − $C_{28}H_{20}O_7Cr$ (520.46): calcd. C 64.62, H 3.87; found C 63.84, H 4.02. The enantiopure complexes gave spectroscopic data identical with those listed above for the racemic compounds.

Crystallographic Data for **2**[16]: Formula $C_{36}H_{22}O_{14}Cr_2$, molecular mass 782.6, orthorhombic, space group *Pccn* (no. 56), Z = 4, a = 2530.3 (6), b = 823.2 (2), c = 1687.6(4) pm, V = 3.554 (2) nm^3, $\rho_{calcd.}$ = 1.46 Mg/m^{-3}, μ(Mo-K_α) = 0.68 mm^{-1}, crystal dimensions 0.45 × 0.40 × 0.15 mm, 4022 reflections (3136 unique; R_{int} = 0.036) were measured with a Nicolet R3m diffractometer with graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) at room temperature, $2\Theta_{max}$ = 50° ($-1 \le h \le 30$, $-1 \le k \le 9$, $-1 \le l \le 20$). The structure was solved by direct methods (SHELXTL-Plus[16]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-93[17]). All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were refined by using a riding model. R values: R_1 = 0.041 [for $I > 2\sigma(I)$], wR_2 = 0.095 for 3136 reflections with 237 parameters. Largest difference peak 0.196 e $nm^{-3} \cdot 10^3$, largest difference hole −0.221 e $nm^{-3} \cdot 10^3$.

The labelling of the atoms used in the publication varies from the original labelling as follows (original first): C10→C1, C11→C2, C2→C3, C3→C4, C4→C10, C1→C11.

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