Reactions of Complex Ligands, LXXV[◇]

Chiral Metal Carbene Modified [2.2]Metacyclophanes: Synthesis, Structure, and Chiroptic Properties

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Received February 24, 1997

Keywords: Carbene complexes / Chromium / Cyclophanes / Chirality

Pentacarbonyl{4-[2.2]metacyclophanyl(methoxy)carbene}-chromium(0) (**6**) was prepared according to the Fischer route from 4-bromo[2.2]metacyclophane. Aminolysis with non-chiral and chiral amines affords aminocarbene complexes **7**–**12**. X-Ray structure analyses for **6** and its aminocarbene analogs **7** and **8** indicate that the incorporation of the chromium–carbene fragment has no significant influence on the deformation of the [2.2]metacyclophane skeleton.

In the recent past various types of metal coordinated cyclophanes have become accessible, and further studies have focussed on their chemical properties and conformational effects[1]. Among them tricarbonyl chromium complexes have received most attention: The $Cr(CO)_3$ group is a potent acceptor which is as easily introduced as removed; it increases the acidity of aromatic and benzylic hydrogen atoms and it activates the benzene ligand towards nucleophilic attack[2]. Following the synthesis of the [2.2]paracyclophane $Cr(CO)_3$ complex in the early 1960's[3] the $Cr(CO)_3$ route has been exploited in substitution reactions of [2.2]metacyclophanes[4]; for instance, it has been used for the synthesis of *syn*-[2.2]metacyclophanes which are not accessible via other routes[5]. Due to their rigid conformation [2.2]metacyclophanes are well-suited for stereochemical investigations[6]. Unsymmetric substitution of either the benzene rings or the ethylene bridge reduces the symmetry and – as a consequence of the high inversion barrier of the cyclophane skeleton – allows the formation of enantiomers[7].

Results and Discussion

We now report on a novel approach to transition metal modified cyclophanes[1,8] bearing an electrophilic metal carbene moiety[9]. Chromium carbenes are known to undergo a variety of either metal-centered or ligand-centered cycloaddition reactions[10] which might be exploited in further functionalization and asymmetrization of the cyclophane skeleton.

Pentacarbonyl{4-[2.2]metacyclophanyl(methoxy)carbene}-chromium(0)

We aimed at the incorporation of the pentacarbonylchromium carbene moiety into the 4-position of the [2.2]metacyclophane skeleton, and thus first concentrated on the synthesis of the 4-bromo derivative which is accessible via ring contraction of the dithiacyclophane[11], and which – after halogen/lithium exchange – is expected to allow a metal carbene functionalization following the Fischer route[12]. Cyclization of 2,4-bis(bromomethyl)bromobenzene (**1**) and 1,3-bis(mercaptomethyl)benzene (**2**) under dilution principle conditions[13] yields 5-bromo-2,11-dithia[3.3]metacyclophane (**3**) in modest yield. Oxidation of the disulfide **3** with hydrogen peroxide generates the disulfone **4** which undergoes flash vacuum pyrolysis[11] to give 4-bromo[2.2]metacyclophane (**5**) in good yields. Bromine/lithium exchange in **5** using *n*-butyllithium at −30°C followed by addition to hexacarbonyl chromium affords the pentacarbonyl acyl chromate which undergoes alkylation by trimethyloxonium tetrafluoroborate to give a 84% yield of the cyclophanyl-(methoxy)carbene complex **6** (Scheme 1).

Heteroatom-stabilized metal carbenes exhibit considerable π-bonding of the carbene carbon to heteroatom bond which allows to detect (*E*) and (*Z*) isomers in their NMR spectra[14]. At 40°C the rotation around the carbene carbon to oxygen bond in **6** is fast with respect to the NMR time scale, and thus a sharp singlet is observed for the methoxy group in the ^{1}H-NMR spectrum. If the sample is cooled down to room temperature this signal broadens and finally, at −50°C, splits into a double set of signals indicating a lifetime of (*E*) and (*Z*) isomers of **6** sufficiently long for observation by NMR. The (*E*/*Z*) ratio is solvent-dependent: At −50°C it increases from 1:1 to 3:1 if $CDCl_3$ is replaced by deuterated toluene. This is in contrast to the parent

[◇] Part LXXIV: K. H. Dötz, S. Siemoneit, F. Hohmann, M. Nieger, *J. Organomet. Chem.*, in press.

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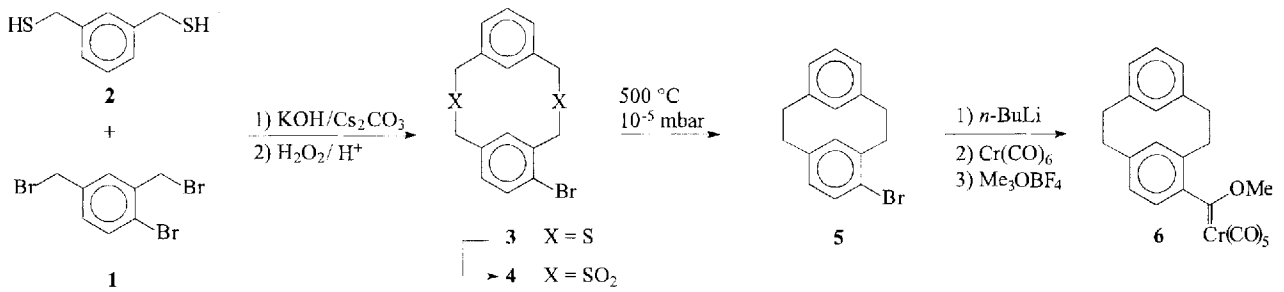
Scheme 1. Synthesis of methoxycarbene complex **6**



methoxy(phenyl)carbene complex of chromium for which the (*Z*) configuration has been reported to be favoured both in solution and in the solid state[15]. The configuration of both isomers has been assigned on the basis of solvent-induced shifts of the methoxy hydrogen atoms observed in isotropic and anisotropic solvents[16,17]. The temperature of coalescence observed for the methoxy function of the cyclophanyl(methoxy)carbene complex **6** (−10 ± 1°C) corresponds to a barrier of rotation of 52.6 ± 0.2 kJ/mol. Similar barriers of rotation have been reported for methoxycarbene complexes bearing less heavily substituted C-carbene side chains which indicates that the [2.2]metacyclophane skeleton does not hamper significantly the rotation around the carbene carbon to oxygen bond[17].

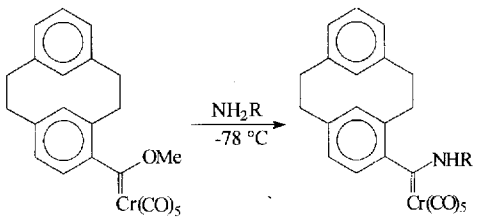
Aminolysis Reactions

Although aminolysis is generally a straightforward reaction of metal alkoxycarbenes; however, it may fail if sterically congested secondary amines are used[18]. Our first attempts indicated that the reaction rate of the aminolysis of **6** depends both on the temperature and on the steric demand of the amine. Following the increasing bulk of the amine the reaction rate decreases in the order of ammonia, allylamine, *sec*-butylamine, and phenylethylamine. According to the kinetics reported for the aminolysis – increasing reaction rate with decreasing temperature[19] – the aminolysis works best at −78°C (Scheme 2). If, however, the amine is generated in situ from the hydrochloride precursor an increase of the temperature to 30°C is required for solubility reasons; even under these conditions the aminolysis takes about two weeks to go to completion.

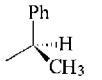
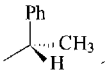
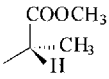
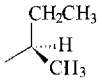
In comparison with alkoxycarbene complexes the rotational barrier around the $C_{carbene}$–N bond is distinctly higher, and both rotamers can be detected and separated as configurationally stable isomers[17,18].

The configuration across the $C_{carbene}$–N bond has been determined by methods reported in the literature[16,18]. Starting with aminocarbene complex **8** we found that the solvent effect on the chemical shift of the N–H protons is more significant than that of the N–CH_2 hydrogen atoms. Due to the geometry of the complex the N–H proton should be influenced by the aromatic ring current of the cyclophane deck, and thus the N–H hydrogen of the (*Z*) isomer may be expected to resonate at higher field than that of the (*E*) isomer. An assignment of configuration based on

Scheme 2. Synthesis of aminocarbene complexes **7**–**12**



6 **7-12**

	7	8	9	10	11	12
R	H					

this argument is supported by solvent-dependent chemical shifts. If $CDCl_3$ is replaced by the typical anisotropic solvent C_6D_6 a more pronounced upfield shift is observed for the N–H hydrogen atoms in the (*Z*) isomers than in the (*E*) analogs[20]. Based on the chemical shift of the N–H protons we assume the same configuration for complexes **9**–**12**. X-Ray studies indicate that in the solid state bulky substituents at the carbene carbon tend to favour the (*E*) isomer whereas the (*Z*) isomer predominates in less hindered complexes[20] in which the steric interaction between the N substituent and the *cis* CO ligands becomes less important.

Comparative X-Ray Studies on Methoxy- and Aminocarbene Complexes

The chromium carbene bond can be described as a carbon-to-metal single bond with an only weak additional π-back donation[21]. An increasing donor ability of the heteroatom shortens the carbene–heteroatom bond and increases the bond order as indicated by restricted rotation documented by temperature-dependent NMR spectroscopy (see above). Since the π-donor capacity of nitrogen exceeds that of oxygen the back donation in aminocarbene complexes is less effective than in their alkoxycarbene analogs; this results in longer metal–carbene bond lengths for chro-

mium aminocarbenes **7** [208.1(3) pm] and **8** [208.3(3) pm] compared with their alkoxycarbene precursor **6** [201.6(3) pm] (Figures 1–3). Complexes **6** and **8** adopt the (*E*) configuration across the heteroatom–carbene bond. In all complexes the carbene plane and the $C_{carbene}$–X–C(H) plane are nearly coplanar; this conformation allows an efficient conjugation across the chromium carbene carbon-heteroatom fragment. X-Ray structures on a series of chromium carbenes indicate that the angle between adjacent equatorial carbonyl ligands is bisected by the carbene plane. In our case, however, the bulky cyclophane substituent forces the carbene plane and two of the *cis*-CO ligands to adopt an eclipsed conformation. Compared with the unsubstituted [2.2]metacyclophane **13**[1,22,23] the carbena-metal fragment does not influence significantly the deformation of the cyclophane skeleton (Figure 4).

Very recently, investigations on hydrogen bonding in transition metal carbonyl complexes revealed an interaction between the CO ligands and C–H groups[24]. Although N–H groups are expected to be more potent hydrogen donors an only weak intermolecular N–H···O interaction can be deduced for the chromium aminocarbenes **7** and **8** from H···O distances (**7**: 267 pm, **8**: 252 pm) and N–H···O bond angles (**7**: 147°, **8**: 136°).

Figure 1. Molecular structure of **6**

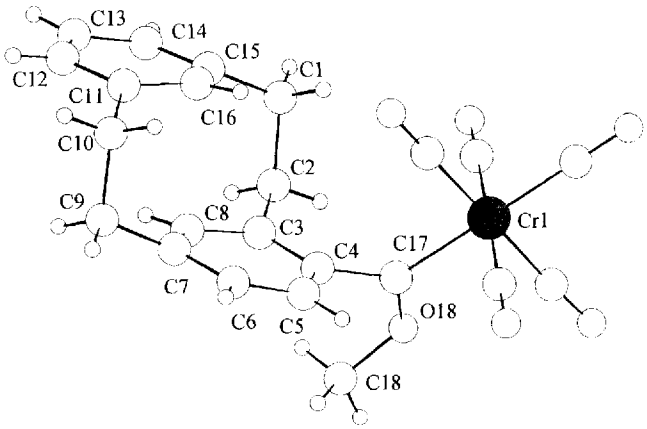
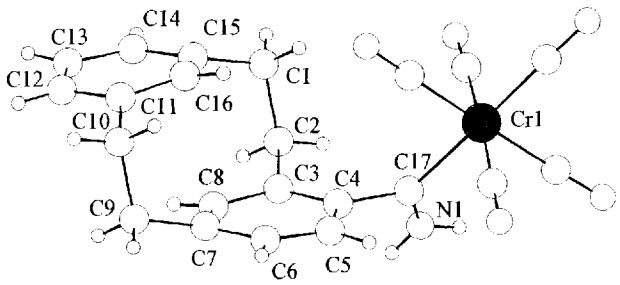


Figure 2. Molecular structure of **7**



Optically Active Cyclophane–Metal Carbene Complexes

An access to enantiopure cyclophanylcarbene complexes can be envisaged by aminolysis using optically active amines. Generally, this approach is complicated by the formation of a mixture of (*E*)- and (*Z*)-isomers which may result

Figure 3. Molecular structure of **8**

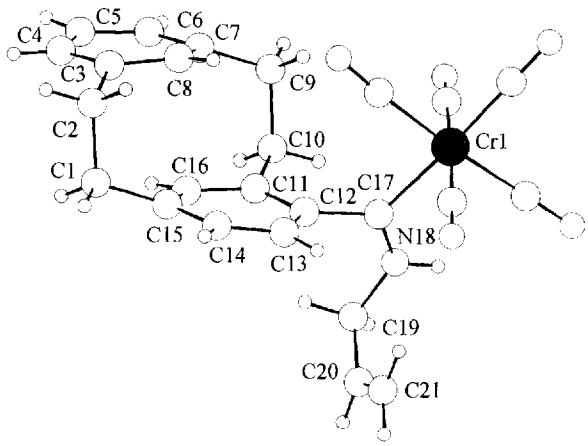
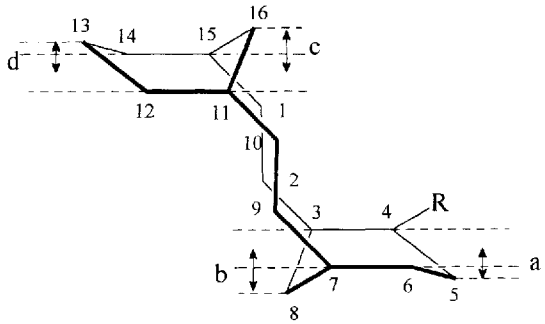


Figure 4. Deformation of the cyclophane skeleton (in pm)



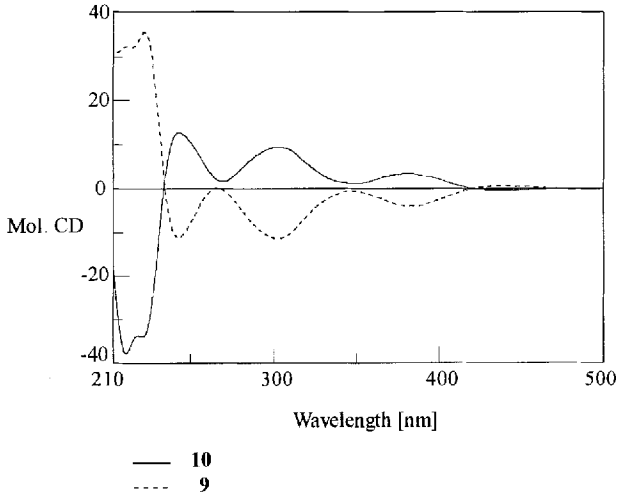
	6	**7**	**8**	**13**(293 K)[22]	**13**(113 K)[23]
a	-3.2	-3.4	-5.3	-4.2	-5
b	-10.5	-11.0	-11.3	-14.3	-11
c	12.0	-11.0	10.8	14.3	11
d	4.5	-5.8	4.7	4.2	5
C-8···C-16	262	264	262	269	263
$Cr\text{-}(CO)_{trans}$	188.6 (4)	186.5 (3)	187.4 (3)		
$Cr\text{-}(CO)_{cis}$	189.5 (5)	188.9 (6)	190 (1)		
$Cr\text{-}C_{carbene}$	201.6 (3)	208.1 (2)	208.3 (3)		
$C_{carbene}\text{-}X$	131.7 (4)	130.1 (3)	130.8 (3)		
$C_{carbene}\text{-}C\text{-}4$	148.7 (4)	149.4 (3)	150.0 (3)		

in four isomers. For instance, the reaction of methoxycarbene complex **6** with (*S*)-alanine methyl ester or (*R*)-*sec*-butylamine gave diastereomeric mixtures of (*E*)-**11** or (*E*)-**12** which could not be separated by chromatography or crystallization. Aminolysis with (*R*)- and (*S*)-phenylethylamine also afforded a diastereomeric mixture of (*E*)-**9** and (*E*)-**10**, respectively, from which, however, single diastereomers could be obtained after recrystallization. Since both enantiomers of phenylethylamine are readily available, this route provides a straightforward access to optically active [2.2]metacyclophanes bearing a metal carbene moiety.

We speculated whether the means of circular dichroism can be applied to establish the absolute configuration of the cyclophane skeleton in the aminocarbene complexes **9** and **10**. As depicted in Figure 5 their CD spectra are symmetric

indicating that both compounds are enantiomers. A comparison with CD spectra of cyclophane derivatives bearing no metal containing functional groups reveals that the bands at 300 and 380 nm are caused by the carbena pentacarbonylchromium fragment which is in agreement with UV data previously reported for metal carbenes[17,25]. The absorptions up to 250 nm recorded for carbene complex **10** resemble those observed for (−)-4-[2.2]metacyclophane carboxamide[26] suggesting that both compounds may have the same R_P configuration with respect to the cyclophane skeleton.

Figure 5. CD spectra of **9** and **10**



Support by the *Deutsche Forschungsgemeinschaft* (SFB 334), the *Graduiertenkolleg "Spektroskopie isolierter und konensierter Moleküle"* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental Section

General: All operations including organometallics were carried out under argon. Solvents were dried by using standard methods, distilled, saturated and stored under argon. Merck silica gel 60 (0.063−0.200 mm) was used for column chromatography. − ^{1}H and ^{13}C NMR: Bruker AM-400, AM-250 and DRX-500. − FT-IR: Nicolet Magna 550. − Elemental analysis: Heraeus CHN-O-Rapid. − MS (EI, 70 eV): Kratos MS 50. − CD: JASCO 720. − 2,4-Bis(brommethyl)brombenzene[27], trimethyloxonium tetrafluoroborate[28], and 1,3-bis(mercaptomethyl)benzene[29] were prepared according to methods reported in the literature.

5-Bromo-2,11-dithia[3.3]metacyclophane (**3**): A solution of 100 mg of caesium carbonate in 300 ml of ethanol and 300 ml of toluene was filled into a two-component dilution apparatus which was fitted with a dropping funnel for each component. Solution A, consisting of 6.86 g (20 mmol) of 2,4-bis(bromomethyl)bromobenzene (**1**) in 80 ml of toluene and solution B, consisting of 3.4 g (20 mmol) of 1,3-bis(mercaptomethyl)benzene (**2**) in 20 ml of toluene and of a solution of 2.24 g (40 mmol) of potassium hydroxide in 2 ml of water and 38 ml of ethanol, were added synchronously within 5 h and the mixture was refluxed for 1 h. After evaporation of the solvent the residue was extracted with trichloromethane, the solution was concentrated and purified by column chromatography (petroleum ether, b.p. 40−60°C/trichloromethane, 1:1) affording a yellow oil which gave 1.4 g (20%) of **3** as a white solid from trichloromethane. R_f = 0.6 (petroleum ether, b.p. 40−60°C/trichloromethane, 1:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 [s, 2H, 3,3′-H], 3.75 [s, 2H, 10,10′-H], 3.80 [s, 4H, 12,12′-H), 1,1′-H], 6.75 [s, 2H, aryl H], 6.95 [s, 3H; aryl H], 7.10−7.20 [m, 2H, aryl H]. − ^{13}C NMR (400 MHz, $CDCl_3$): δ = 36.7, 37.9, 38.1, 38.2 (C-1,3,10,12), 121.7 (C-5), 126.9 (C-7), 127.4 (C-15), 128.4, 128.6 (C-14, C-16), 131.8 (C-18), 132.3 (C-9), 133.1 (C-6), 135.4 (C-8), 136.5 (C-4), 136.9, 137.0 (C-13, C-17). − MS (EI): *m/z* (%): 352 (75) [M^+], 271 (50) [M^+ − Br], 183 (15) [$M^+ - C_8H_9S_2$], 167 (8) [$M^+ - C_8H_8Br$], 137 (58) [$M^+ - C_8H_8BrS$], 105 (100) [$M^+ - C_8H_7BrS_2$]. − $C_{16}H_{15}BrS_2$ (351.3): calcd. C 54.70, H 4.30; found C 54.88, H 4.42. − HR-MS [^{81}Br]: calcd. 351.9778; found 351.9784.

5-Bromo-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetraoxide (**4**): 5.38 g (15 mmol) of 5-bromo-2,11-dithia[3.3]metacyclophane (**3**) was dissolved in 50 ml of toluene and 100 ml of glacial acetic acid at 70°C. Then 50 ml of hydrogen peroxide (35%) were added and the reaction mixture was heated to reflux for 5 h. The solution was cooled to room temperature, the resulting precipitate was filtered off and washed with water, ethanol, and trichloromethane. The product was dried in vacuo to give 5.4 g (86%) of **4**. − IR (KBr): $\tilde{\nu}$ = 1310 cm^{-1}, 1110 (SO_2). − ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.60 [br, 4H, CH_2], 4.70 [br, 4H, CH_2], 6.95 [d, *J* = 8.2 Hz, 1H, 1-H], 7.05 [m, 2H, aryl H], 7.20 [d, *J* = 6.8 Hz, 1H, aryl H], 7.30 [d, *J* = 8.2 Hz, 1H, 6-H], 7.70 [s, 2H, 9-H, 18-H]. − MS (EI): *m/z* (%): 414 (1) [M^+], 286 (1) [$M^+ - 2\ SO_2$], 258 (1) [$M^+ - 2\ SO_2 - CH_2$], 207 (100) [$M^+ - 2\ SO_2$ − Br], 179 (19) [$M^+ - 2\ SO_2$ − Br − $2\ CH_2$], 104 (14) [$M^+ - 2\ SO_2 - C_8H_7Br$]. − $C_{16}H_{15}BrO_4S_2$ (415.3): calcd. C 46.27, H 3.64; found C 46.22, H 3.67. − HR-MS [^{79}Br]: calcd. 413.9595; found 413.9598.

4-Bromo[2.2]metacyclophane (**5**): 5.30 g (12.7 mmol) of 5-bromo-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (**4**) was transferred in 200-mg portions to a quartz-pyrolysis apparatus, sublimed at 240°C, and pyrolyzed at 500°C and 10^{-5} mbar. The product condensed behind the pyrolysis zone and was dissolved in trichloromethane. The solvent was evaporated and the residue subjected to column chromatography (petroleum ether, b.p. 40−60°C) to give 2.3 g (63%) of **5**. R_f = 0.5 (petroleum ether, b.p. 40−60°C). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.95 [td, *J* = 12.3 Hz, 3.4 Hz, 1H, 2-H_{ax}], 2.00−2.05 [m, 2H, benzyl H_{ax}], 2.20 [td, *J* = 12.3 Hz, 3.3 Hz, 1H, benzyl H_{ax}], 3.00−3.10 [m, 3H, benzyl H_{eq}], 3.60 [dt, *J* = 12.4 Hz, 3.4 Hz, 1H, 2-H_{eq}], 4.25 [d, *J* = 1.8 Hz, 8-H], 4.35 [s, 1H, 16-H], 6.90 [dd, *J* = 8 Hz, 1.8 Hz, 1H, 6-H], 7.00 [d, *J* = 7.4 Hz, 1H, aryl H], 7.05 [d, *J* = 7.4 Hz, 1H, aryl H], 7.30 [t, *J* = 7.4 Hz, 1H, 13-H], 7.47 [d, *J* = 8 Hz, 1H, 5-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 38.6, 40.6, 40.9, 41.1 (C-1,2,9,10), 120.8 (C-4), 125.6 (C-12), 125.9 (C-14), 127.4 (C-6), 129.4 (C-13), 132.5 (C-5), 136.4 (C-16), 137.7 (C-8), 138.1, 138.4, 138.7, 138.9 (aryl C). − MS (EI): *m/z* (%): 286 (25) [M^+], 258 (10) [$M^+ - CH_2CH_2$], 207 (100) [M^+ − Br], 179 (28) [M^+ − Br − CH_2CH_2], 165 (20) [M^+ − Br − CH_2CH_2 − CH_2], 103 (20) [M^+ − Br − C_8H_8]. − $C_{16}H_{15}Br$ (287.2): calcd. C 66.91, H 5.26; found C 66.75, H 5.33. − HR-MS [^{79}Br]: calcd.: 286.0357; found 286.0359.

Pentacarbonyl{4-[2.2]metacyclophanyl(methoxy)carbene}chromium(0) (**6**): 4.5 ml (7.2 mmol) of *n*-butyllithium (1.6 mol/l in hexane) were added drop by drop to a solution of 2.01 g (7 mmol) of **5** in 20 ml of diethyl ether at −30°C. The solution was stirred for 30 min at −30°C and 30 min at room temperature, and then was added at −30°C to a suspension of 1.54 g (7 mmol) of hexacarbonylchromium in 20 ml of diethyl ether. The reaction mixture was allowed to reach room temperature and stirred for 3 h. The deep yellow solution was evaporated and the residue was dissolved in 30 ml of dichloromethane. At −20°C 1.24 g (8.4 mmol) of trimethyl-

oxonium tetrafluoroborate were added, and the mixture was warmed to room temperature. After removal of the solvent and chromatography of the residue on silica gel (eluent: petroleum ether, b.p. 40–60°C/diethyl ether 5:1) 2.6 g (84%) of **6** were isolated as a red solid which was recrystallized from hexane. R_f = 0.5 (petroleum ether, b.p. 40–60°C/diethyl ether, 5:1). – IR (hexane): $\tilde{\nu}_{CO}$ = 2064 cm^{-1} (m, A_1), 1990 (w, B_1), 1963 (s, A_1), 1954 (vs, E), 1946 (sh, E). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.95–2.30 [m, 4H, benzyl H_{ax}], 2.80 [dt, *J* = 12.4 Hz, 3.2 Hz, 1H, benzyl H_{eq}], 3.00–3.20 [m, 3H, benzyl H_{eq}], 4.00 [s, 1H, 16-H], 4.30–4.60 [br. 3H, OCH_3], 4.70 [s, 1H, 8-H], 7.00 [d, *J* = 7.7 Hz, 1H, 12-H], 7.10 [m, 2H, aryl H], 7.15 [d, *J* = 7.7 Hz, 1H, 14-H], 7.30 [t, *J* = 7.7 Hz, 1H, 13-H]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.1, 40.5, 40.7, 40.9 (C-1,2,9,10), 123.1 (C-3), 125.5 (C-5, C-6), 125.6 (C-14, C-12), 127.2 (C-7), 129.4 (C-13), 136.9 (C-16), 137.1 (C-8), 138.6, 138.7, 138.9 (aryl C), 216.1 (*cis* CO), 224.2 (*trans* CO), 359.2 (carbene C). – MS (EI): *m/z* (%): 442 (1) [M^+], 414 (5) [M^+ – CO], 386 (6) [M^+ – 2 CO], 358 (6) [M^+ – 3 CO], 302 (100) [M^+ – 5 CO]. – $C_{23}H_{18}CrO_6$ (442.4): calcd. C 62.45, H 4.10; found C 62.38, H 4.13. – HR-MS: calcd.: 442.0508; found 442.0534.

Pentacarbonyl{amino-4-[2.2]metacyclophanylcarbene}chromium(0) (**7**): A weak flow of gaseous ammonia was bubbled through a solution of 221 mg (0.5 mmol) of **6** in 20 ml of THF at –78°C until the colour changed from dark red to yellow. After 30 min the reaction mixture was allowed to warm to room temperature. The solvent was removed at reduced pressure, and the residue was purified by column chromatography (petroleum ether, b.p. 40–60°C/dichloromethane, 1:1) to give 200 mg of **7** as a yellow solid. R_f = 0.6 (petroleum ether, b.p. 40–60°C/dichloromethane, 1:1). – IR (hexane): $\tilde{\nu}_{CO}$ = 2056 cm^{-1} (m, A_1), 1978 (w, B_1), 1949 (vs, E), 1944 (sh, E), 1923 (s, A_1). – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.00–2.20 [m, 4H, benzyl H_{ax}], 3.00–3.20 [m, 4H, benzyl H_{eq}], 4.15 [s, 1H, 16-H], 4.55 [s, 1H, 8-H], 7.00–7.15 [m, 4H, aryl H], 7.30 [t, *J* = 7.4 Hz, 1H, 13-H], 8.30 [s, 1H, NH], 9.10 [s, 1H, NH]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.1, 40.0, 40.5, 40.6 (C-1,2,9,10), 122.8 (C-3), 125.5 (C-12), 125.5 (C-14), 126.6 (C-7), 127.6 (C-8), 129.4 (C-13), 136.7 (C-16), 137.5 (C-6), 138.2 (C-11), 138.4 (C-5), 138.8 (C-15), 150.8 (C-4), 217.0 (*cis* CO), 222.9 (*trans* CO), 294.9 (carbene C). – MS (EI): *m/z* (%): 427 (2) [M^+], 399 (6) [M^+ – CO], 371 (7) [M^+ – 2 CO], 343 (1) [M^+ – 3 CO], 315 (17) [M^+ – 4 CO], 287 (100) [M^+ – 5 CO]. – $C_{22}H_{17}CrNO_5$ (427.4): calcd. C 61.83, H 4.01, N 3.28; found C 61.92, H 4.01, N 3.06. – HR-MS: calcd. 427.0512; found 427.0525.

(E)- and (Z)-Pentacarbonyl{4-[2.2]metacyclophanyl[(2-propenylamino)carbene]}chromium(0) (**8**): At –78°C 0.2 ml (2.67 mmol) of allylamine were added to a solution of 100 mg (0.23 mmol) of **6** in 10 ml of THF, and the resulting yellow solution was stirred for 15 min at this temperature. Evaporation of the solvent gave a 7:5 mixture of (*E*) and (*Z*) isomers. Column chromatography (petroleum ether, b.p. 40–60°C/diethyl ether, 3:1) yielded 40 mg (37%) of pure (*E*) isomer which was isolated as yellow crystals after recrystallization from hexane. The (*Z*) isomer could not be obtained as a pure substance. – R_f = 0.6 (*Z*), 0.7 (*E*) (petroleum ether, b.p. 40–60°C/dichloromethane, 2:1). – (*E*)- isomer: IR (hexane): $\tilde{\nu}_{CO}$ = 2056 cm^{-1} (m, A_1), 1973 (w, B_1), 1940 (vs, E), 1917 (s, A_1). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.97 [td, *J* = 12.3 Hz, 3.8 Hz, 1H, benzyl H_{ax}], 2.08 [td, *J* = 12.1 Hz, 3.5 Hz, 1H, benzyl H_{ax}], 2.17 [td, *J* = 12.9 Hz, 3.7 Hz, 1H, benzyl H_{ax}], 2.52 [td, *J* = 12.4 Hz, 3.5 Hz, 1H, benzyl H_{ax}], 2.88 [dt, 12.5 Hz, 3.5 Hz, 1H, benzyl H_{eq}], 3.05–3.12 [m, 2H, benzyl H_{eq}], 3.17 [dt, *J* = 11.8 Hz, 3.3 Hz, 1H, benzyl H_{eq}], 3.70 [m, 1H, NCH_2], 3.86 [m, 1H, NCH_2], 3.98 [s, 1H, 16-H], 4.94 [s, 1H, 8-H], 5.24 [d, *J* = 17.1 Hz, 1H, =CHH_{cis}], 5.28 [d, *J* = 10.3 Hz, 1H, =CHH_{trans}], 5.75 [m, 1H, =CH], 7.01 [d, *J* = 7.7 Hz, 1H, 5-H], 7.10 [m, 2H, 12-H, 14-H], 7.20 [d, *J* = 7.7 Hz, 1H, 6-H], 7.33 [t, *J* = 7.5 Hz, 1H, 13-H], 9.10 [br. 1H, NH]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.6, 38.4, 40.3, 40.6 (C-1,2,9,10), 52.7 (NCH_2), 119.8 (CH_2=CH), 122.3 (C-5), 125.3, 125.6 (C-12, C-14), 126.4 (C-6), 126.7 (C-7), 129.3 (C-13), 130.7 (CH=CH_2), 136.5 (C-16), 137.0 (C-3), 137.7 (C-8), 138.8, 138.9 (C-11, C-15), 145.3 (C-4), 217.4 (*cis* CO), 222.4 (*trans* CO), 284.7 (carbene C). – MS (EI): *m/z* (%): 467 (4) [M^+], 439 (7) [M^+ – CO], 411 (10) [M^+ – 2 CO], 383 (7) [M^+ – 3 CO], 355 (21) [M^+ – 4 CO], 327 (100) [M^+ – 5 CO], 286 (18) [M^+ – 5 CO – C_3H_5], 275 (22) [M^+ – $Cr(CO)_5$]. – $C_{25}H_{21}CrNO_5$ (467.4): calcd. C 62.24, H 4.53, N 3.00; found C 61.99, H 4.63, N 2.76. – HR-MS: calcd. 467.0825; found 467.0820.

General Procedure for the Aminolysis with Enantiopure Phenylethylamine: At –78°C 0.6 ml (4.78 mmol) of (*R*)- and (*S*)-phenylethylamine, respectively, were added to a solution of 20 mg (0.5 mmol) of **6** in 10 ml of THF, and the solution was stirred for 6 h at this temperature. Evaporation of the solvent gave 1:1 mixture of two diastereomers from which 40 mg (15%) of one (*E*) isomer were obtained as a yellow solid after recrystallization from hexane.

Pentacarbonyl{4-[2.2]metacyclophanyl(E-(R)-2'-phenylethylamino)carbene}chromium(0) (**9**): R_f = 0.4 (petroleum ether, b.p. 40–60°C/dichloromethane, 2:1). – IR (hexane): $\tilde{\nu}_{CO}$ = 2056 cm^{-1} (m, A_1), 1980 (w, B_1), 1944 (vs, E), 1922 (s, A_1). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.55 [d, *J* = 6.9 Hz, 3H, CH_3], 2.00–2.15 [m, 3H, benzyl H_{ax}], 2.55 [m, 1H, 2-H_{ax}], 2.95–3.15 [m, 4H, benzyl H_{eq}], 4.00 [s, 1H, 16-H], 4.70 [m, 1H, CH], 4.95 [s, 1H, 8-H], 6.75 [d, *J* = 7.6 Hz, 1H, aryl H], 6.95 [m, 2H, aryl H], 7.10 [m, 3H, aryl H], 7.20–7.35 [m, 4H, aryl H], 9.25 [br, 1H, NH]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7 (CH_3), 37.8, 38.6, 40.4, 40.7 (C-1,2,9,10), 59.2 (CH), 121.9, 125.5, 125.7, 126.3 (aryl CH), 126.5 (aryl C), 128.2, 129.0, 129.4, 129.4 (aryl CH), 136.6 (C-16), 136.7 (aryl C), 137.9 (aryl CH), 138.9, 139.1, 139.9 (aryl C), 145.8 (C-4), 217.5 (*cis* CO), 222.5 (*trans* CO), 283.0 (carbene C). – MS (EI): *m/z* (%): 531 (2) [M^+], 503 (3) [M^+ – CO], 475 (4) [M^+ – 2 CO], 447 (2O) [M^+ – 3 CO], 419 (18) [M^+ – 4 CO], 391 (100) [M^+ – 5 CO], 339 (20) [M^+ – $Cr(CO)_5$]. – $C_{30}H_{25}CrNO_5$ (531.5): calcd. C 67.79, H 4.74, N 2.64; found C 67.53, H 4.74, N 2.47. – HR-MS: calcd. 531.1138; found 531.1151.

Pentacarbonyl{4-[2.2]metacyclophanyl(E-(S)-2'-phenylethylamino)carbene}chromium(0) (**10**): R_f = 0.4 (petroleum ether, b.p. 40–60°C/dichloromethane, 2:1). – IR (hexane): $\tilde{\nu}_{CO}$ = 2056 cm^{-1} (m, A_1), 1980 (w, B_1), 1944 (vs, E), 1922 (s, A_1). – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.55 [d, *J* = 6.9 Hz, 3H, CH_3], 2.00–2.15 [m, 3H, benzyl H_{ax}], 2.55 [td, *J* = 12.4 Hz, 3.5 Hz, 1H, 2-H_{ax}], 3.00 [dt, *J* = 12.4 Hz, 3.4 Hz, 1H, benzyl H_{eq}], 3.05 [dt, *J* = 11.8 Hz, 3.0 Hz, 1H, benzyl H_{eq}], 3.10 [dt, *J* = 12.5 Hz, 3.6 Hz, 1H, benzyl H_{eq}], 3.15 [dt, *J* = 11.9 Hz, 3.5 Hz, 1H, benzyl H_{eq}], 4.00 [s, 1H, 16-H], 4.70 [m, 1H, CH], 5.00 [s, 1H, 8-H], 6.70 [d, *J* = 7.75 Hz, 1H, aryl H], 6.95 [m, 2H, aryl H], 7.05 [d, *J* = 7.75 Hz, 1H, aryl H], 7.10 [m, 2H, aryl H], 7.25 [m, 3H, aryl H], 7.30 (t, *J* = 7.45 Hz, 1H, aryl H], 9.25 [br, 1H, NH]. – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.7 (CH_3), 37.8, 38.6, 40.4, 40.7 (C-1,2,9,10), 59.2 (CH), 121.9, 121.9, 125.5, 125.7, 125.7, 126.3 (aryl CH), 126.5 (aryl C), 128.2, 129.0, 129.4, 136.6 (aryl CH), 136.7 (aryl C), 137.9 (aryl CH), 138.9, 139.1, 139.9 (aryl C), 145.8 (C-4), 217.5 (*cis* CO), 222.5 (*trans* CO), 283.0 (carbene C). – MS (EI): *m/z* (%): 531 (3) [M^+], 503 (3) [M^+ – CO], 475 (4) [M^+ – 2 CO], 447 (20) [M^+ – 3 CO], 419 (20) [M^+ – 4 CO], 391 (100) [M^+ – 5 CO], 339 (8) [M^+ – $Cr(CO)_5$]. – $C_{30}H_{25}CrNO_5$ (531.5): calcd. C 67.79, H 4.74, N 2.64; found C 67.49, H 4.79, N 2.53. – HR-MS: calcd. 531.1138; found 531.1151.

Pentacarbonyl{4-[2.2]metacyclophanyl-(E-(S)-1-carbomethoxyethylamino)carbene}chromium(0) (**11**): 150 mg (1.4 mmol) of alanine methyl ester hydrochloride and 1 ml of triethylamine were added to a solution of 150 mg (0.34 mmol) of **6** in 10 ml of dichloromethane. The reaction mixture was cooled to −30°C and stirred for 2 weeks at this temperature. The solvent was removed, and the residue was purified by column chromatography (petroleum ether, b.p. 40−60°C/diethyl ether, 2:1) to give 110 mg (63%) of a yellow solid which contains an inseparable mixture of two (*Z*) diastereomers (ratio 2:1). − R_f = 0.6 (petroleum ether, b.p. 40−60°C/diethyl ether, 2:1). − IR (KBr): $\tilde{\nu}_{CO}$ = 2055 cm^{-1} (m, A_1), 1980 (w, B_1), 1933 (s, A_1), 1921 (vs, E), 1906 (sh, E), 1752 (w). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 [d, *J* = 7.2 Hz, 3H, CH_3], 1.45 [d, *J* = 7.2 Hz, 3H*, CH_3], 1.90 [td, *J* = 12.5 Hz, 4.1 Hz, 1H, benzyl H_{ax}], 2.00−2.20 [m, 2H, + 3H*, benzyl H_{eq}], 2.50 [td, *J* = 12.5 Hz, 3.5 Hz, 1H, benzyl H_{ax}], 2.55 [td, *J* = 12.3 Hz, 3.3 Hz, 1H*, benzyl H_{ax}], 2.80 [dt, *J* = 12.5 Hz, 3.3 Hz, 1H, benzyl H_{eq}], 2.90 [dt, *J* = 12.5 Hz, 3.3 Hz, 1H*, benzyl H_{eq}], 3.00−3.20 [m, 3H, 3H*, benzyl H_{eq}]#, 3.65 [s, 3H*, OCH_3], 3.80 [s, 3H, OCH_3], 3.90 [s, 1H*, 16-H], 3.95 [s, 1H, 16-H], 4.1 [dq, *J* = 8.5 Hz, 8.3 Hz, 1H*, CH], 4.30 [dq, *J* = 8.3 Hz, 7.3 Hz, 1H, CH], 4.90 [s, 1H, 8-H], 4.95 [s, 1H*, 8-H-], 6.85 [d, *J* = 7.7 Hz, 1H*, 5-H], 7.03 [d, *J* = 7.75 Hz, 1H, 5-H], 7.05 [m, 1H, 1H*, 12-H]#, 7.10 [m, 1H, 1H*, 6-H]#, 7.15 [d, *J* = 7.75 Hz, 1H*, 12-H], 7.20 [d, *J* = 7.5 Hz, 1H, 14-H], 7.30 [t, *J* = 7.5 Hz, 1H, 13-H], 7.32 [t, *J* = 7.75 Hz, 1H*, 13-H], 9.50 [br, 1H*, NH], 9.70 [br, 1H, NH]. − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.9 (CH_3), 19.9 (CH_3)*, 38.0 (CH_2), 38.7 (CH_2)*, 39.1 (CH_2), 39.2 (CH_2)*, 41.0 (CH_2)*, 41.1 (CH_2), 41.2 (CH_2)#, 53.7 (NCH)*, 53.8 (NCH), 57.2 (OCH_3), 57.8 (OCH_3)*, 121.9 (C-5)*, 123.3 (C-5), 126.2 (C-12)#, 126.4 (C-14)#, 126.9 (C-7), 127.2 (C-7)*, 127.3 (C-6)#, 130.2 (C-13)#, 137.5 (C-16)*, 137.6 (C-16), 137.7 (C-3)*, 138.0 (C-3), 138.5 (C-8), 138.6 (C-8)*, 139.4 (C-11)*, 139.5 (C-11), 139.6 (C-15), 139.7 (C-15)*, 145.3 (C-4), 145.9 (C-4)*, 171.3 (*C*O-OCH_3)*, 171.8 (*C*OOCH$_3$), 217.9 (*cis* CO)*, 218.0 (*cis* CO), 222.3 (*trans* CO)#, 287.5 (carbene C), 298.8 (carbene C)*. − MS (EI): *m/z* (%): 513 (4) [M$^+$], 485 (2) [M$^+$ − CO], 457 (2) [M$^+$ − 2 CO], 429 (5) [M$^+$ − 3 CO], 401 (20) [M$^+$ − 4 CO], 373 (100) [M$^+$ − 5 CO]. − $C_{26}H_{23}CrNO_7$ (513.5): calcd. C 60.82, H 4.51, N 2.73; found C 60.74, H 4.60, N 2.59. − HR-MS: calcd. 513.0879; found 513.0872. (*refers to the minor diastereomer, # refers to both diastereomers.)

Pentacarbonyl{4-[2.2]metacyclophanyl(E-(R)-2'-butylamino)carbene}chromium(0) (**12**): At −78°C 0.1 ml (1 mmol) of (*R*)-2-butylamine were added to a solution of 100 mg (0.23 mmol) of **6** in 10 ml of THF. After 30 min. the solvent was evaporated. Column chromatography (petroleum ether, b.p. 40−60°C/dichloromethane, 2:1) afforded 100 mg (90%) of a 1:1 mixture of two diastereomers. R_f = 0.68 (petroleum ether, b.p. 40−60°C/dichloromethane, 2:1). − IR (hexane): $\tilde{\nu}_{CO}$ = 2054 cm^{-1} (m, A_1), 1980 (w, B_1), 1921 (s, A_1), 1894 (vs, E). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 [t, *J* = 7.35 Hz, 3H, CH_2CH_3], 0.95 [t, *J* = 7.45 Hz, 3H, CH_2CH_3], 1.02 [d, *J* = 6.6 Hz, 3H, CH_3], 1.20 [t, *J* = 6.6 Hz, 3H, CH_3], 1.45 [quin, *J* = 7.35 Hz, 2H, CH_2], 1.50−1.70 [m, 2H, CH_2], 2.00 [2 td, *J* = 12.4 Hz, 3.5 Hz, *J* = 12.3, 3.4 Hz, 2H, benzyl H_{ax}], 2.10 [m, 2H, benzyl H_{eq}], 2.20 [td, *J* = 12 Hz, 3.4 Hz, 2H, benzyl H_{ax}], 2.60 [td, *J* = 12.4 Hz, 3.2 Hz, 2H, benzyl H_{ax}], 2.97 [m, 2H, benzyl H_{eq}], 3.10 [m, 4H, 2 benzyl H_{ax}, 2 benzyl H_{eq}], 3.18 [m, 2H, benzyl H_{eq}], 3.50 [m, 1H, CH], 3.52 [m, 1H, CH], 3.98 [s, 2H, 16-H], 5.00 [s, 1H, 8-H], 5.05 [s, 1H, 8-H], 6.97 [d, *J* = 7.7 Hz, 1H, 5-H], 7.00 [d, *J* = 7.7 Hz, 1H, 5-H], 7.10 [m, 4H, aryl H], 7.20 [d, *J* = 7.7 Hz, 2H, 14-H], 7.35 [t, *J* = 7.7 Hz, 2H, 13-H], 8.80 [br, 1H, NH], 8.95 [br, 1H, NH]. − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.7, 10.9 (CH_2CH_3), 20.4, 21.1 (CH_3); 29.3, 30.4 (CH_2), 38.1, 38.3, 38.8, 39.0, 40.8, 40.8, 41.1, 41.1 (C-1,2,9,10), 58.4, 58.9 (NCH), 121.9, 122.5 (C-5), 125.8, 125.9 (C-12), 126.1, 126.1 (C-14), 126.6, 126.7 (C-6), 126.8, 127.2 (C-7), 129.8, 129.9 (C-13), 136.9 (C-4)#, 137.0 (C-3)# (C-16), 137.1 (C-16), 138.3, 138.4 (C-8), 139.3, 139.4 (C-15), 139.5, 139.5 (C-11), 218.1, 218.1 (*cis* CO), 223 (*trans* CO)#, 280.9, 282.1 (carbene C). − MS (EI): *m/z* (%): 483 (3) [M$^+$], 455 (4) [M$^+$ − CO], 427 (5) [M$^+$ − 2 CO], 399 (4) [M$^+$ − 3 CO], 371 (10) [M$^+$ − 4 CO], 343 (100) [M$^+$ − 5 CO]. − $C_{26}H_{25}CrNO_5$ (483.5): calcd. C 64.59, H 5.21, N 2.90; found C 64.35, H 5.16, N 2.88. − HR-MS: calcd. c 483.1144; found 483.1141 (# refers to both diastereomers).

X-ray Crystallographic Studies of **6** *and* **8**[30]: The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. In **6** and **8** an absorption correction was applied on the basis of Ψ-scans (**6**: $T_{min./max.}$ = 0.361/0.881, **7**: $T_{min./max.}$ = 0.526/0.956, **8**: $T_{min./max.}$ = 0.495/1.000), and an extinction correction was applied in **8**. Details of data collection and refinement are given in Table 1. Programs used: SHELXTL-Plus, G. M. Sheldrick, University of Göttingen, Germany (1993).

Table 1. Crystallographic data and summary of data collection and refinement

compound	**6**	**7**	**8**
crystal data			
formula	$C_{23}H_{18}CrO_6$	$C_{22}H_{17}CrNO_5$	$C_{25}H_{21}CrNO_5$
M	442.4	427.4	467.4
colour	orange	yellow	yellow
dimensions [mm]	0.22×0.25×0.33	0.45×0.23×0.10	0.08×0.25×0.43
crystal system	triclinic	orthorhombic	monoclinic
space group	*P*−1 (No.2)	*Pbca* (No.61)	$P2_1/c$ (No.14)
a [Å]	9.774(2)	11.949(1)	12.176(1)
b [Å]	10.462(1)	14.363(1)	14.163(1)
c [Å]	10.653(1)	23.929(1)	13.155(1)
α [°]	107.71(1)	90	90
β [°]	98.16(1)	90	99.43(1)
γ [°]	91.24(1)	90	90
V [Å^3]	1024.8(3)	4106.8(5)	2237.9(3)
Z	2	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.43	1.38	1.39
μ [mm^{-1}]	4.92	4.87	4.51
F(000)	456	1760	968
structure solution and refinement			
full-matrix least-squares refinement on	F^2	F^2	F^2
parameter/restraints	272/0	268/2	293/1
measured reflections	3230	5992	3489
unique reflections used in refinement	3025	3881	3314
wR2	0.137	0.115	0.120
R_1 [for $I>2\sigma(I)$]	0.047	0.041	0.043
largest diff. peak and hole [eÅ^{-3}]	0.37/−0.51	0.34/−0.49	0.46/−0.63
data collection parameter			
diffractometer: Enraf-Nonius	-CAD4	-MACH3	-CAD4
radiation	Cu-*K*α	Cu-*K*α	Cu-*K*α
λ [Å]	1.54178	1.54178	1.54178
T [K]	208(2)	293(2)	200(2)
2 $\theta_{max.}$ [°]	120	140	120
	$-10 \le h \le 0$	$-2 \le h \le 14$	$0 \le h \le 13$
	$-11 \le k \le 11$	$-17 \le k \le 2$	$-15 \le k \le 0$
	$-11 \le l \le 11$	$-2 \le l \le 29$	$-14 \le l \le 14$

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[30] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100 202. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambrige CB2 1EZ, UK (fax: int. code +(1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk).

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