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Enantioselective Chromatography of Chiral Chalcon-Tricarbonylchromium Complexes and Their Use in Stereoselective Michael Addition

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Summary. The enantiomeres of the title compounds **1–8** could be separated by enantioselective chromatography on microcrystalline triacetylcellulose in ethanol. A high stereoselectivity of the Michael addition of dimethylmalonate was observed only for the *ortho*-substituted complexes **1**, **2** and **3**, while the selectivity decreased with *meta*-substituted substrates. A synthesis of 3-(*ortho*-dimethylaminophenyl)-tricarbonylchromium-1-phenyl-2-propenone (**4**) and 3-(*meta*-dimethylaminophenyl)-tricarbonylchromium-1-phenyl-2-propenone (**8**) is described. Methods for the estimation of diastereomeric excess (d.e.) and – after decomplexation – enantiomeric excess (e.e.) are compared. The absolute chiralities of complexes were determined by optical comparison and by chemical correlation.

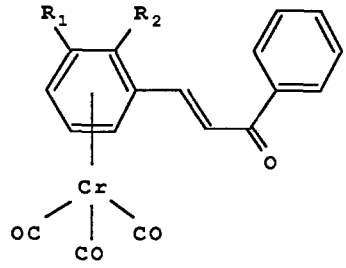
Keywords. Circular dichroism; Chemical and chiroptical correlation; Cyclic chromatography; Optical resolution; Triacetylcellulose; 3-(*ortho*-Dimethylaminophenyl)-tricarbonylchromium-1-phenyl-2-propenone; 3-(*meta*-Dimethylaminophenyl)-tricarbonylchromium-1-phenyl-2-propenone.

Enantioselektive Chromatographie von chiralen Chalcon-tricarbonylchrom-Komplexen und ihre Verwendung in stereoselektiven Michael-Additionen

Zusammenfassung. Die Enantiomeren der im Titel genannten Verbindungen **1–8** wurden durch enantioselektive Chromatographie an mikrokristalliner Triacetylcellulose in Ethanol getrennt. Die Michael-Addition von Malonsäuredimethylester an die *ortho*-substituierten Komplexe **1**, **2** und **3** verläuft stereospezifisch, während aus den *meta*-substituierten Komplexen Gemische der Diastereomeren erhalten werden. Die Darstellung von 3-(*ortho*-Dimethylaminophenyl)-tricarbonylchrom-1-phenyl-2-propenon (**4**) und 3-(*meta*-Dimethylaminophenyl)-tricarbonylchrom-1-phenyl-2-propenon (**8**) wird beschrieben. Methoden zur Bestimmung des diastereomeren Überschusses (d.e.) und – nach Dekomplexierung – des enantiomeren Überschusses (e.e.) werden einer kritischen Bewertung unterzogen. Die chiroptischen Eigenschaften und die Absolutkonfigurationen der Komplexe wurden bestimmt; letztere durch optischen Vergleich und/oder chemische Korrelation.

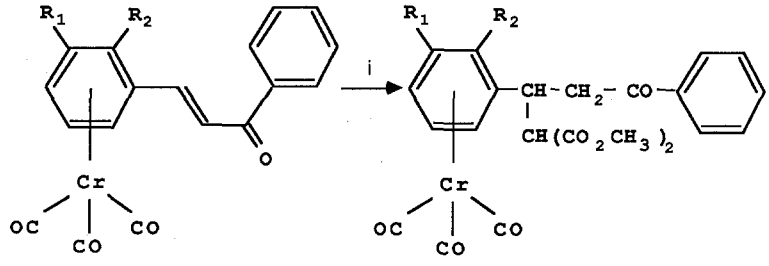
Introduction

Arene-tricarbonylchromium complexes have become popular in organic synthesis for various reasons: A number of them is easily accessible by standard procedures [1]. These complexes show increased reactivity for nucleophilic substitution and

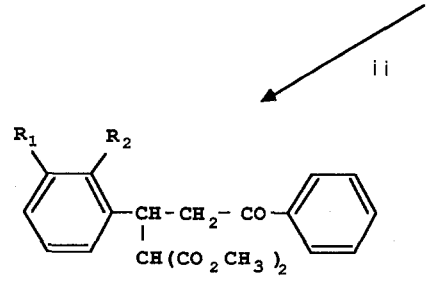


Comp.	R_1	R_2
1	H	CH_3
2	H	OCH_3
3	H	OCH_2CH_3
4	H	$N(CH_3)_2$
5	H	Cl
6	CH_3	H
7	OCH_3	H
8	$N(CH_3)_2$	H
9	Cl	H

Scheme 1



1 - 4 and **6 - 8** **1M - 4M** and **6M - 8M**



1L - 4L and **6L - 8L**

i: $CH_2(CO_2CH_3)_2$ / NaH /MeOH, 20°C

ii: hv

Scheme 2

after the transformation the auxiliary $Cr(CO)_3$ might be removed chemically or photochemically [2]. Moreover, $Cr(CO)_3$ can also be used as a stereochemical protecting group for optically labile compounds (atropisomerism) [3], or to decrease temporarily the symmetry ($\rightarrow C_1$ when complexing an asymmetric *ortho-* or *meta*-disubstituted arene) [4]. After resolution of the racemate, the enantiomeric complexes can be used for diastereoselective syntheses. Subsequent decomplexation destroys the original chiral moiety and leaves a product with a single chiral center. Its enantiomeric purity is directly proportional to the diastereoselectivity of the syntheses. As prochiral substituents CO and C=C are of importance. Especially reactions which result in an asymmetric C−C bond formation can be of high synthetic value [5]. From this point of view the Michael addition applied to chiral chalcon-tricarbonylchromium complexes (see Scheme 1) offers an access to optically stable centrochiral compounds without benzylic OH at the chiral center (see Scheme 2).

Results and Discussion

Preparation of N,N-Dimethylamino − Substituted Benzaldehyde-Tricarbonylchromium Complexes

Both complexes are accessible in good yield via the Fukui-method [6], with slight modifications, by the metallation of N,N-dialkyl substituted amines using *DMF* as the electrophile. When the metallation was carried out with an equimolar quantity of N,N,N′,N′-tetramethylethylenediamine (*TMEDA*) and 3 equivalents of *n-Bu*Li, the combined yield of *o-* and *m*-(N,N-dimethylaminobenzaldehyde)tricarbonylchromium reached 80% (based on recovered starting material). The *o*/*m*-ratio was found to be approximately 1 : 1. Traces of the *para*-isomer could also be isolated. Its structure was proved via the corresponding chalcon which was prepared alternatively by complexation of 3-(*p*-dimethylaminophenyl)-1-phenyl-2-propenone with $Cr(CO)_6$.

Attempts have been made to rise the yields of *o-* and *m*-dimethylaminobenzaldehyde-$Cr(CO)_3$ complexes when employing an up to seven-fold excess of *n-Bu*Li, but only complex mixtures could be obtained. The metallation without *TMEDA* afforded exclusively the *meta*-isomer, but in very low yield.

Preparation of Chalcone-Tricarbonylchromium Complexes

All complexes were prepared by base-catalyzed condensations of appropriate substituted benzaldehyde tricarbonylchromium and acetophenone. The condensations usually proceeded smoothly.

Some complications were observed in the preparation of **4** and **8**. Highly purified dimethylaminobenzaldehyde-$Cr(CO)_3$, freshly distilled acetophenone and carefully purified and dried ethanol had to be used. Otherwise no chalcon complexes could be isolated.

In a similar way it was tried to prepare *ortho*-fluorochalcon-$Cr(CO)_3$ by condensation of *ortho*-fluorobenzaldehyde-$Cr(CO)_3$ and acetophenone in ethanol. But during this reaction a nucleophilic substitution of fluorine by an ethoxy-group took place [7]. The course of this and of similar reactions is under investigation.

Chromatographic Separation of Enantiomeric Tricarbonylchromium Complexes on Triacetylcellulose

The limiting factor for this kind of asymmetric synthesis is given by the economy of producing enantio-pure substrates. There are several possibilities to achieve this: Resolution of the appropriate aldehydes via diastereoisomeric semioxamazones [8], followed by the condensation with acetophenone. More convenient is the direct resolution of the substrates by enantioselective chromatography on triacetylcellulose [9] (see Table 1).

Even in the cases of small separation factors ($\alpha \leqslant 1.10$) complete separations could be achieved by a "recycling-technique" [10]. Semipreparative quantities of **2**, **3** and **6** could be isolated (20–40 mg of pure enantiomers on a column 300 × 25 mm). For **1** a conventional optical resolution had to be performed to obtain pure enantiomers, because of the small separation factor [8]. The results are summarized in Table 1. For the elution order a clear trend is found: with a single exception (**5**) compounds of the same configuration are eluted preferentially

Table 1. Chromatographic separation of chalcon-tricarbonylchromium complexes **1–9** on microcrystalline triacetylcellulose[a]

Comp.	k'[b]	a[c]	$[\alpha]_D^{20}$	e.e.[d]	Config.[e]
1	1.52	< 1.06	+24°	~1%[f]	(+)S
			−9°	~0.5%	(−)R
2	1.56	1.5	+1 352°	100%	(+)R
	2.35		−1 404°	100%	(−)S
3	1.28	6.8	+1 628°	100%	(+)R
	8.64		−1 611°	100%	(−)S
4	1.22	1.03	+1 020°	?	(+)R
	1.26		−870°	?	(−)S
5	1.36	1.10	−1 470°	90%	(−)S
	1.49		+776°	40–50%	(+)R
6	1.38	1.24	−177°	100%	(−)S
	1.71		+161°	90%	(+)R
7	1.81	1.07	−255°	90%	(−)R
	1.94		+259°	90%	(+)S
8	1.59	⩽	[g]	?	(−)R
			+213°	?	(+)S
9	1.67	0	–	–	–

[a] Conditions: column (30 × 2.5 cm), packed with micro crystalline triacetylcellulose; particle size: 20–30 μm; solvent: ethanol (96%); flow rate 70–80 ml/h; temperature: 40 °C; detection: UV (254 nm); sample size: 1–2 mg/ml in analytical runs, up to 80 mg/5 ml in preparative runs. For a more detailed description refer to [9].

[b] Capacity ratio: $k' = (V - V_0)/V_0$.

[c] Separation factor: $a = k_2'/k_1'$.

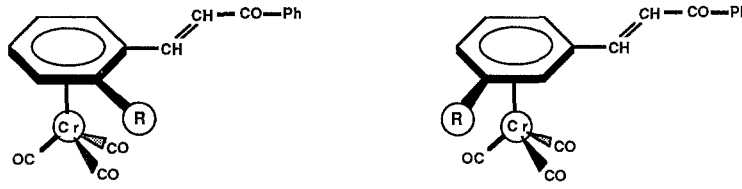
[d] Estimated from the peak shape.

[e] **1** and **6** are chemically correlated with the corresponding aldehydes, **2**, **3**, **4**, and **5** with **1**, and **7** and **8** with **6** by optical comparison (see Figs. 1, 2).

[f] For an optical pure sample: $[\alpha]_D^{20} = 1\,992° \pm 20°$.

[g] Not estimated.

Configurations of preferrently eluted enantiomeres of **1** - **4** and **6** - **8**



R = CH_3 (**1** and **6**), OCH_3 (**2** and **7**), OCH_2CH_3 (**3**), $N(CH_3)_2$ (**4** and **8**) **Scheme 3**

(see Scheme 3 and Table 1). At the present no detailed interpretation of this behavior can be given but it seems of interest that a similar trend can be observed also with other arene-tricarbonylchromium complexes (Ref. [4]).

Chiroptical Properties and Absolute Chiralities

For the chalcon-tricarbonylchromium complexes under investigation the chiroptical properties are presented in Table 1 and Figs. 1 and 2, except for **9** where no detectable separation could be realized. The chiralities as given in Table 1 were established

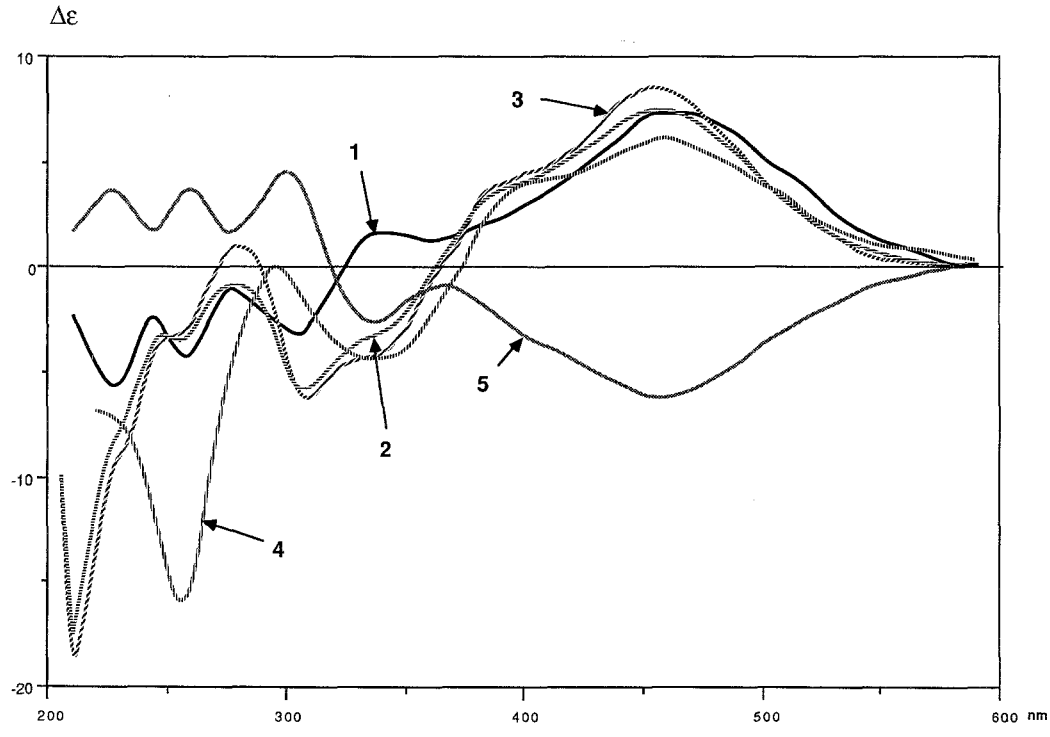


Fig. 1. CD spectra of chalcon-tricarbonylchromium complexes **1–5**

either by optical comparison and/or by synthesis from the optically active aldehydes of known absolute configuration [11].

Michael Additions

Chalcon-tricarbonylchromium-complexes are suitable substrates for Michael additions. These proceed smoothly at ambient temperature with high regioselectivity (Scheme 2) [12]. The reaction is influenced by steric factors in the cases of *ortho*-substitution, while *meta*-substituents do not seem to have a dramatic effect. Thus

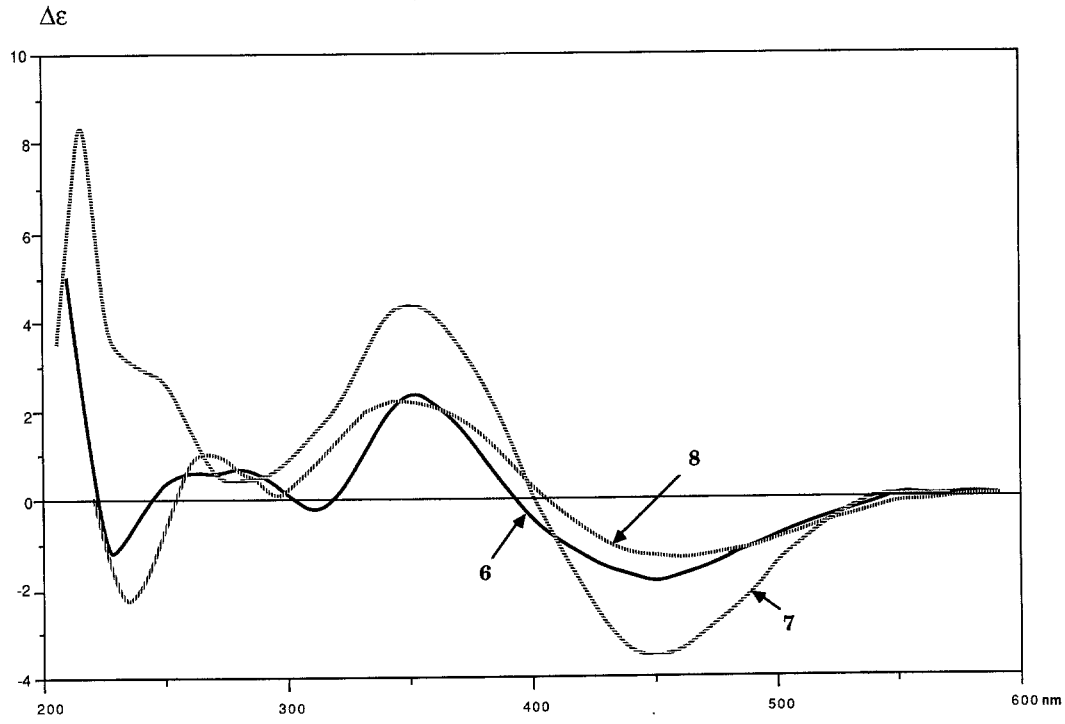


Fig. 2. CD spectra of chalcon-tricarbonylchromium complexes **6–8**

Table 2. UV spectra of chalcones **1–9**

Compound		Conc.	λ_{max} (ε)			
o-CH_3	**1**	$3.36 \cdot 10^{-4}$		274 (20 870)	331 (7 680)	463 (5 680)
o-OCH_3	**2**	$3.48 \cdot 10^{-5}$	207 (37 000)	282 (18 800)		456 (6 200)
o-OC_2H_5	**3**	$1.17 \cdot 10^{-3}$		290 (23 420)		458 (8 060)
o-$N(CH_3)_2$	**4**	$6.34 \cdot 10^{-4}$	217 (39 160)	261 (28 030)	321 (14 660)	460 (6 880)
o-Cl	**5**	$7.27 \cdot 10^{-5}$		272 (21 440)	339 (7 650)	462 (5 310)
m-CH_3	**6**	$3.16 \cdot 10^{-4}$		274 (22 820)	331 (7 420)	461 (5 060)
m-OCH_3	**7**	$2.78 \cdot 10^{-5}$	206 (42 000)	274 (23 100)	332 (5 970)	462 (4 350)
m-$N(CH_3)_2$	**8**	$2.95 \cdot 10^{-4}$	218 (37 900)	259 (25 900)	335 (6 110)	471 (4 140)
m-Cl	**9**	$2.64 \cdot 10^{-4}$		269 (23 600)	336 (7 580)	456 (4 550)

for **4**, where a severe steric interaction has to be expected, the yield was decreased due to the occurrence of unidentified sideproducts.

From the expected two diastereoisomers only one could be detected in the case of *ortho*-substituted compounds (**1–4**) by ^{1}H NMR analysis (see Table 3). For **1** we employed a shift reagent [Eu(*fod*)$_3$], but no trace of a second diastereoisomer could be detected. The same is true for **2** and **3** but the reliability of the integration is unclear because of excessive peak overlapping. As expected, the selectivity was almost lost for the *meta*-substituted complexes **6**, **7** and **8**. From ^{1}H NMR integration an appr. 42 : 58 (**6**), and 50 : 50 (?) (**7**) and 60 : 40 (**8**) ratio was found for the diastereoisomers. As described for **2** and **3**, peak overlapping was a serious problem in the case of **7**. The use of a shift reagent did not give any improvement. Therefore, other methods were applied in order to obtain more accurate values for d.e.:

Photochemical decomplexation of the optically active Michael addition products was easily accomplished by irridation of the cooled solution with a photolamp (2000 W) for about 20 min.

After filtration of the colorless solution, the optical rotation of the free ligand was measured or, alternatively, chromatographic separation of the enantiomers was performed on triacetylcellulose. The former usually gives less accurate results, since the absolute rotation lies in the range of 10–20° only, and often shows no linear relation with concentration. Moreover, if the concentration is estimated by UV, a typical error of at least ± 5% must be considered. At the other hand, e.e. – when obtained from the integration ratio of baseline separated enantiomeric peaks – is only influenced by the reliability of the integrator and the error never exceeds 2%. Therefore several methods have been applied simultaneously whenever it was possible to reach a higher precision. As a typical example the results for **2** are outlined below:

(−)-**2** (~ 30 mg) was obtained by Michael addition of dimethylmalonate to (+)-**2**, which in turn was accessible in an optically pure form by chromatography. Photochemical decomplexation of a cooled ethanolic solution afforded the optically active ligand: $[\alpha]_D$ + 11°, CD 253 (− 1.04), 272 (− 0.54). This was subjected to chromatography on a triacetylcellulose column under standard conditions, but even after repetitive cycles no trace of a second enantiomer could be detected. With an authentic racemate of the ligand (prepared by Michael addition to the uncomplexed chalcon) a sufficient chromatographic separation of the enantiomers could be achieved (13 cycles, $\alpha = 1.06$) to give (−)-**2L**: $[\alpha]_D$ − 13°, CD 251 (+ 1.01), 272 (+ 0.57) and (+)-**2L**: $[\alpha]_D$ + 12°, CD 250 (− 0.99), 271 (− 0.58). These results indicate a high stereoselectivity of the addition in this case with the exclusive formation of a single stereoisomere.

The most reliable d.e.-values are summarized below:

Comp. (d.e.): **1** (~ 100%), **2** (~ 100%), **3** (~ 100%), **4** (> 90%), **6** (16%), **7** (~ 0%), **8** (20%). The chloro compounds **5** and **9** have been excluded from these investigations because of their extreme sensitivity.

Experimental

UV: Perkin-Elmer, Spectrometer Lambda-7; ^{1}H NMR: Bruker WP-250 (250 MHz), recorded in $CDCl_3$, with *TMS* as internal standard; CD: Jobin-Yvon, Dichrograph Mark-III, recorded in ethanol (96%); optical rotations: Perkin-Elmer Polarimeter 241, 1 dm-cell, at 20 ± 0.1 °C; melting points were determined on a Kofler-apparatus and are uncorrected.

All the synthetic experiments were carried out under an atmosphere of purified argon, while the reaction vessel was protected from light. All solvents (analytical grade) were dried and degassed prior use.

For the synthesis of **1–3**, **5–7**, and **9** refer to [12].

Table 3. ^{1}H-NMR spectra of tricarbonylchromium complexes

Comp.	CH_3[a]	CH=CH	$C_6H_4-Cr(CO)_3$	C_6H_5
1	2.38 s	7.38 d; 7.69 d (15 Hz)	5.20 d; 5.27 t; 5.56 t; 5.88 d (all 7 Hz)	7.44–7.65 m; 8.02 d (7 Hz)
2	3.86 s	7.40 d; 7.81 d (16 Hz)	5.01 t; 5.15 d; 5.71 t; 6.03 d (all 7 Hz)	7.46–7.66 m; 8.00 d (7 Hz)
3	1.48 t (7.2 Hz); 4.04 m (7.3 Hz, 1.2 Hz)	7.44 d; 7.78 d (16 Hz)	4.98 t; 5.10 d; 5.68 t; 6.00 d (all 7 Hz)	7.45–7.62 m; 7.99 d (7 Hz)
4	2.79 s	7.28 d; 7.74 d (15 Hz)	5.03 t; 5.07 d; 5.65 t; 5.93 d (all 7 Hz)	7.45–7.64 m; 8.00 d (7 Hz)
6	2.28 s	7.33 pseudo s [2 H]	5.32 m [1 H]; 5.48 m [3 H]	7.52 t; 7.62 t [3 H]; 8.00 d (7 Hz)
7	3.80 s	7.26 d; 7.36 d (16 Hz)	5.18 d; 5.23 dd'; 5.38 d'; 5.62 t (6 Hz and 2 Hz[(')])	7.48 t; 7.57 t [3 H] (7 Hz); 7.94 d (7 Hz)
8	2.95 s	7.23 d; 7.38 d (15 Hz)	4.86 d; 4.96 s; 5.14 d; 5.66 t (all 7 Hz)	7.44–7.66 m; 7.97 d (7 Hz)

Comp.	CH_3[a]	CO_2CH_3	ArCH-	$CH(CO_2CH_3)_2$	CH_2CO	$C_6H_4-Cr(CO)_3$	C_6H_5
1M	2.46 s	3.59 s[b]/3.65 s[b]	4.27 td (6 Hz, 6 Hz)	3.86 d (6 Hz)	3.52 dd; 3.81 dd (19 Hz, 6 Hz; 19 Hz, 6 Hz)	5.02 d; 5.08 t; 5.48 t; 5.71 d (all 7 Hz)	7.40–7.60 m; 8.02 d (7 Hz)
2M	3.75 s	3.63 s[b]/3.64 s[b]	4.40 m	4.08 d (6 Hz)	3.44 dd; 3.92 dd (18 Hz, 4 Hz; 18 Hz, 8 Hz)	4.84 t; 4.96 d; 5.52 t; 5.92 d (all 7 Hz)	7.42–7.59 m; 8.01 d (8 Hz)
3M	1.46 pt 3.91 q[b]/3.98 q[b]	3.62 s	4.42 m	3.44 m	3.77–4.24 m	4.83 t; 4.94 d; 5.53 t; 5.91 d (~ 7 Hz)	7.40–7.61 m; 8.00 d (7 Hz)
4M	2.86 s	3.59 s	4.47 m	3.52 m	3.94–4.18 m (?)	5.03 t; 5.34 d; 5.45 t; 5.67 d (~ 7 Hz)	7.41–7.62 m; 8.02 d (7 Hz)
6M	2.16 s[c] 2.19 s[c]	3.62 s[b]/3.73 s[b]	——— 3.76–3.95 m [3 H] ———		3.48 dd (19 Hz, 6 Hz)	5.14–5.51 m [4 H]	7.40–7.63 m; 7.98 d (7 Hz)
7M	3.60 s[c] 3.62 s[c]	3.70 s[b]/3.72 s[b]	——— 3.68–4.07 m ———	4.07 d (7 Hz)	3.50 dd (18 Hz, 2 Hz)	4.97 d_1; 5.07 d_2; 5.16 t_1; 5.31 s_2 5.46 s_1; 5.49 t_2; two additional d between 5.42–5.52 (all ~ 7 Hz)	7.42–7.62 m; 7.97 d; 8.00 d (~ 6 Hz)
8M	2.86 s[c] 2.88 s[c]	3.70 s[b]/3.62 s[b] 3.70 s[b]/3.69 s[b]	——— 3.42–3.5 m and 3.80–4.05 m ———			4.72 d_2; 4.78 d_1; 4.88 d_1; 4.97 s_2; 5.06 d_2; 5.15 s_1; 5.48 t_2; 5.54 t_1 (7 Hz)	7.42–7.62 m; 7.98 d (~ 7 Hz)

[a] C_2H_5 for **3** and **3M**.
[b] Peak splitting due to diastereotopicity.
[c] Signals probably due to diastereoisomers (see text).

η^6-Tricarbonylchromium complexes of o- and m-dimethylaminobenzaldehyde

To a stirred solution of 0.5 g (2 mmol) (N,N-dimethylaniline)$Cr(CO)_3$ in 50 ml of dry *THF*, 0.23 g (2 mmol) N,N,N',N'-tetramethylethylenediamine was added. The reaction mixture was cooled to − 60 °C, and 4 ml of a *Bu*Li-solution (1.6 molar in hexane, 6 mmol) was added during 30 min. After stirring an additional hour at the same temperature, dry *DMF* (15 ml) was added dropwise during 30–40 min. The reaction mixture was then again stirred for 3 h at − 60 °C, allowed to warm up to 0 °C, and finally poured on crushed ice. A color change from yellow to red was observed immediately. The organic material was extracted into ether, and the extracts were washed with saturated $NaHCO_3$ solution and water subsequently. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on SiO_2 (column 2.5 × 30 cm) in benzene. From the first yellow band 0.13 g (22.8%) of starting material could be recovered. Elution of the second red-orange band afforded 0.14 g (24.6%) (*m*-N,N-dimethylaminobenzaldehyde)$Cr(CO)_3$, m.p. 95–97 °C (from benzene/hexane, 2 : 8). For $C_{12}H_{11}CrNO_4$ (285.2). Calc. C 50.33, H 3.88, N 4.90%. Found C 50.83, H 3.75, N 4.80%. ^{1}H NMR: 2.92 (s, 6 H, N*Me*$_2$), 5.06 (d, 1 H, H 6), 5.13 (s, 1 H, H 2), 5.35 (d, 1 H, H 4), 5.60 (t, 1 H, H 5), 9.60 (s, 1 H, CHO). From the third band 0.13 g (22.8%) of (*o*-N,N-dimethylaminobenzaldehyde)$Cr(CO)_3$, m.p. 94.5–95.5 °C (from benzene/hexane, 2 : 8). For $C_{12}H_{11}CrNO_4$ (285.2). Calc. C 50.33, H 3.88, N 4.90%. Found C 50.47, H 3.76, N 4.92%. ^{1}H NMR: 2.92 (s, 6 H, N*Me*$_2$), 4.70 (d, 1 H, H 6), 4.98 (t, 1 H, H 5), 5.83 (t, 1 H, H 4), 6.25 (d, 1 H, H 3), 9.71 (s, 1 H, CHO).

Two additional compounds were also detected but not isolated. One of them was (*p*-dimethylaminobenzaldehyde)$Cr(CO)_3$. This was converted to the corresponding chalcon by condensation with acetophenone and compared with an authentical sample by TLC (see below).

3-(p-Dimethylaminophenyl)$Cr(CO)_3$*-1-phenyl-2-propenone*

A solution of 500 mg 1-*p*-dimethylaminophenyl-3-phenyl-2-propenone (2 mmol) and 10 g $Cr(CO)_6$ (40 mmol) in 50 ml of dry 1,4-dioxane was refluxed for 72 h. After evaporation of the solvent unreacted $Cr(CO)_6$ was removed by sublimation (8.7 g). The residue was dissolved in benzene and chromatographed on SiO_2. Elution with benzene : ethylacetate afforded 0.1 g of unidentified material followed by 0.35 g of product, isolated as red crystalls (45%), m.p.: 280 °C (dec.). For $C_{20}H_{17}CrNO_4$ (387.3). Calc. C 62.0, H 4.42, N 3.60%. Found C 61.67, H 4.48, N 3.50%.

3-(m-Dimethylaminophenyl)$Cr(CO)_3$*-1-phenyl-2-propenone* (**8**)

A solution of 100 mg (*m*-dimethylaminobenzaldehyde)tricarbonylchromium (0.35 mmol) in 5–7 ml ethanol (dried and degassed) was warmed up to 40 °C and 40 mg freshly distilled acetophenone (0.33 mmol) and 1 ml of an aqueous NaOH solution (15%) were added subsequently. After completion of the reaction the mixture was poured into water and the organic material was extracted into ether. The combined extracts were washed with water and finally dried over anhydrous Na_2SO_4. After evaporation of the solvent the residual oil was purified by crystallisation from benzene : *n*-hexane (1 : 9) to give the desired product in 75% yield, dark red crystalls, m.p.: 144.5–145.5 °C. For $C_{20}H_{17}CrNO_4$ (387.3). Calc. C 62.0, H 4.42, N 3.60%. Found C 61.9, H 4.38, N 3.44%. ^{1}H NMR: see Table 3.

3-(o-Dimethylaminophenyl)$Cr(CO)_3$*-1-phenyl-2-propenone* (**4**)

The preparation was similar as given for **8** with slight modifications: After 2 h of additional stirring, 0.3 ml of an aqueous NaOH-solution (15%) and 3 drops of acetophenone were added and stirring was continued for 3 h more, followed by the usual workup (see above). Purification was done by column chromatography on SiO_2 in benzene-ethylacetate (95 : 5) to afford **4** in 75% yield as deep-red crystalls. m.p.: 119.5–120.5 °C (benzene − *n*-hexane, 2 : 8). For $C_{20}H_{17}CrNO_4$ (387.3). Calc. C 62.0, H 4.42, N 3.60%. Found C 61.2, H 4.39, N 3.10%. ^{1}H-NMR: see Table 3.

The Michael additions were conducted at room temperature using **1–4** and **6–8** (racemic and/or optically active) following the procedure given in [12]. The conversion was complete within 1 hour (TLC). Especially the *ortho*-compounds tend to produce little orange colored by-products. These were separated by TLC. The characterisation was done by ^{1}H-NMR (see Table 3) and MS.

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