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Preparation and structural features of new dialkylamino-substituted cyclopropenylidenepentacarbonylchromium complexes

Armin de Meijere [a,*], Stephan Müller [a], Thomas Labahn [b]

[a] *Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany*
[b] *Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany*

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Abstract

The (2-ethoxy-3-dimethylaminocyclopropenylidene)pentacarbonylchromium complex **2** was prepared from dimethylaminoacetylene in 78% yield. It reacted with dimethylamine and diethylamine at room temperature to give quantitative yields of the bis(dialkylamino)cyclopropenylidene complexes **3a**,**b**. The structural data and ^{13}C-NMR chemical shifts of **2** and **3b** show interesting differences relating to the different donor abilities of alkoxy and dialkylamino groups.

Among the α,β-unsaturated Fischer carbene-chromium complexes, the β-dialkylamino-substituted ones have gained particular importance for organic synthesis since we discovered that they provide ready and general access to highly functionalized five-membered rings under appropriate conditions [1]. These reaction modes were found to rely on the β-dialkylamino substitution. Since such complexes are most readily prepared by Michael-type addition of a secondary amine to an alkynyl-substituted Fischer carbene complex [2,3], we attempted to prepare a 1-alkoxy-3,3-bis(dialkylamino)propenylidenepentacarbonylchromium complex along the usual route via the corresponding dialkylaminopropynylidene complex. At that point we were unaware of a report by Hegedus et al. that lithium ethoxyacetylide reacted with hexacarbonylchromium to yield an ethoxycyclopropenylidene complex, and lithium (methylphenylamino)acetylide reacted in the same way to give the corresponding amino-substituted cyclopropenylidene complex, albeit in very poor yield [4].

In fact, when hexacarbonylchromium was added to a solution of lithium (dimethylamino)acetylide, generated by treatment of dimethylaminoacetylene [5] in THF with *n*-butyllithium, and the resulting mixture treated with triethyloxonium tetrafluoroborate, the (ethoxydimethylaminocyclopropenylidene)pentacarbonylchromium complex **2** could be isolated in 79% yield. Its structure was established by an X-ray crystal analysis (Fig. 1A).

While the previously reported diethoxycyclopropenylidene complex **4** upon treatment with *N*-methylaniline only yielded a monoaminomonoethoxy-substituted complex of type **2** [4], treatment of **2** with dimethylamine in diethyl ether or neat diethylamine at ambient temperature gave the 1,2-bis(dialkylamino)cyclopropenylidene complexes **3a**,**b** within 5 to 10 min in quantitative yields [6] (Scheme 1). No reaction was observed even in neat diisopropylamine at room temperature after 1 h [7]. The complex **3b** was also characterized by an X-ray crystal structure analysis (Fig. 1B).

It is interesting to compare the structural features of complexes **2** and **3b** with each other and with those of the diethoxycyclopropenylidene complex **4** reported by Hegedus et al. [4] (Table 1). There is a significant steady increase in the Cr=C1 bond length, the C2,C1,C3 bond

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* Corresponding author.

E-mail address: armin.demeijere@chemie-uni-goettingen.de (A. de Meijere).

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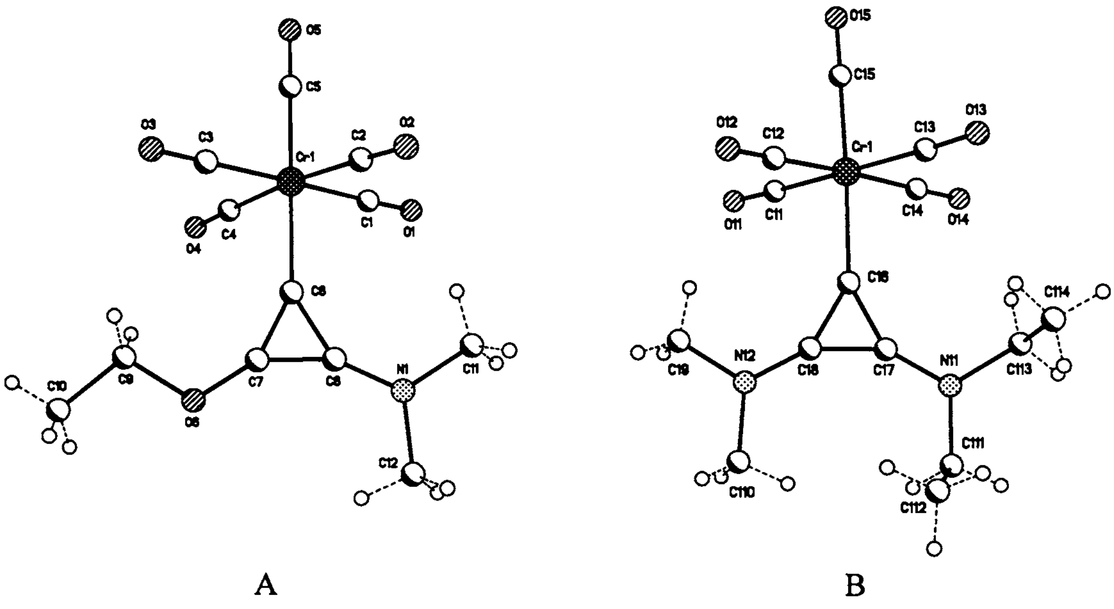


Fig. 1. Structures of (ethoxydimethylaminocyclopropenylidene)pentacarbonylchromium **2** (A) and (diethylaminodimethylaminocyclopropenylidene)pentacarbonylchromium **3b** (B) in the crystal. The numbering of the atoms in these drawings does not comply with the numbering according to IUPAC rules as used in Table 1.

angle, and the C2,C3 double bond length upon going from the diethoxy- **4** via the dialkylaminoethoxy- **2** to the bis(dialkylamino)cyclopropenylidene complex **3b**, i.e. with increasing electron-donating power of the substituents on the three-membered ring. This goes along with a shift of all three ^{13}C-NMR signals of the carbon atoms in the three-membered ring to higher fields. This corresponds to an increased shielding, due to the additional electron-donating ability of the dialkylamino substituents, which is tapped according to the cyclopropenylium cation type resonance structure **4** of these complexes [8].

The chemistry of these interesting complexes still needs and deserves to be further explored, although they have been found to be remarkably unreactive towards some of the substrates that would typically react with carbon–metal double bonds [4].

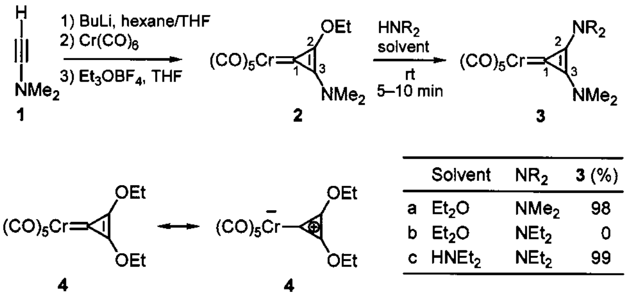
1. Experimental

1.1. General

Melting points: Melting point apparatus by Büchi; melting points are uncorrected. IR: Bruker IFS 66 (FT-IR). ^{1}H-NMR: Bruker AMX 250 (250 MHz); δ(ppm) = 0 for tetramethylsilane, 7.15 for [D$_5$]benzene, 7.26 for deuterochloroform. ^{13}C-NMR: Bruker AM 250 (62.9 MHz); δ(ppm) = 77.0 for deuterochloroform, 128.0 for [D$_6$]benzene. MS: Varian MAT 731, MAT 311A (high resolution; correct HRMS preselected ion peak matches at R $\gg$ 10 000 with an error range of ± 2 ppm with the exact mass. All experiments were carried out in an inert atmosphere.

1.2. (2-Ethoxy-3-dimethylaminocyclopropen-1-yliden)-pentacarbonylchromium (2)

To a solution of 2.36 g (44% solution in diethyl ether–hexane, 15.0 mmol) of dimethylaminoethyne kept at −78°C, was added 9.75 ml (15.0 mmol) of a 1.54 m solution of *n*-butyllithium in hexane. The mixture was stirred at −78°C for 30 min, then 3.30 g (15.0 mmol) of hexacarbonylchromium was added. This mixture was warmed up to room temperature and stirred for an additional 1 h. After cooling to 0°C, 3.04 g (16.0 mmol) of triethyloxonium tetrafluoroborate was added with stirring. After 5 min of further stirring at room temperature, 50 ml of diethyl ether was added, the solution cooled to −78°C, filtered through Celite (30 g), and concentrated under reduced pressure. The



	Solvent	NR$_2$	3 (%)
a	Et$_2$O	NMe$_2$	98
b	Et$_2$O	NEt$_2$	0
c	HNEt$_2$	NEt$_2$	99

Scheme 1.

Table 1
Relevant structural and NMR spectroscopic data of alkoxy- and dialkylamino-substituted cyclopropenylidenechromium complexes **2**–**4**

	4 [a]	**2**	**3b**
Bond lengths (Å)			
Cr,C1	2.010(7)	2.068(2)	2.086(1)
C1,C2	1.410(8)	1.360(3)	1.393(2)
C1,C3	1.410(8)	1.424(2)	1.393(2)
C2,C3	1.337(7)	1.350(3)	1.367(2)
C2,X (N,O)	1.300(5)	1.313(2)	1.326(2)
C3,X (N,O)	1.300(5)	1.319(2)	1.323(2)
Bond angles (°)			
Cr,C1,C2	151.7(2)		
Cr,C1,C3	151.7(2)		
C2,C1,C3	56.6(4)	58.0(1)	58.8(1)
X,C2,C3	149.2(2)	146.7(2)	150.6(1)
X,C3,C2	149.1(4)	153.9(2)	151.5(1)
^{13}C chemical shifts (δ_{TMS})			
C1	191.7	168.3	157.5
C2	170.7	160.1	155.7
C3	170.7	166.2	152.9

[a] According to Ref. [4].

residue was subjected to column chromatography on silica gel (120 g, 4 × 15 cm, pentane–Et_2O 1:1) to give 3.75 g (79%) of **2** ($R_f = 0.40$, pentane–Et_2O 3:1) as weakly yellow crystals (mp 38°C). IR (KBr): $\tilde{\nu} = 2056$ cm^{-1} (C=O), 1917 (C=O), 1519 (C=C), 1414, 1341, 1219, 1019, 675, 664, 647. ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 1.52$ (t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 3.06, 3.33 [2 × s, 6H, $N(CH_3)_2$], 4.62 (q, $^3J = 7.0$ Hz, 2H, OCH_2CH_3). ^{13}C-NMR (62.9 MHz, C_6D_6, additionally DEPT): $\delta = 15.11$ (+, OCH_2CH_3), 38.56, 42.71 [+, $N(CH_3)_2$], 70.31 (−, OCH_2CH_3), 160.61 (C_{quat}, C-2), 166.15 (C_{quat}, C-3), 168.31 (C_{quat}, C-1), 218.65, 222.94 (C_{quat}, CO). MS (70 eV), m/z (%): 317 (17) [M^+], 289 (2) [$M^+ - CO$], 261 (3) [$M^+ - 2CO$], 233 (5) [$M^+ - 3CO$], 205 (14) [$M^+ - 4CO$], 177 (100) [$M^+ - 5CO$], 120 (14), 52 (3) [Cr^+]. Anal. Calc. for $C_{12}H_{11}CrNO_6$ (317.2): C, 45.44; H, 3.50. Found: C, 46.20; H, 3.56%.

*1.3. [2,3-Bis(dimethylamino)cyclopropen-1-ylidene]-pentacarbonylchromium (**3a**)*

Into a solution of 1.00 g (3.15 mmol) of **2** in 15 ml of diethyl ether was introduced at room temperature gaseous dimethylamine, until no starting material could be detected by TLC. During the introduction of dimethylamine, a yellow precipitate formed. Column chromatography of this precipitate on silica gel (40 g, 1.5 × 15 cm, Et_2O) gave 980 mg (98%) of **3a** ($R_f = 0.50$ Et_2O) as weakly yellow crystals (decomp. at 128°C). IR (KBr): $\tilde{\nu} = 2051$ cm^{-1} (C=O), 1913 (C=O), 1539 (C=C), 1409, 1355, 1220, 1000, 789, 674. ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 3.14$, 3.23 [2 × s, 12H, $N(CH_3)_2$]. ^{13}C-NMR (62.9 MHz, C_6D_6, additionally DEPT): $\delta = 39.05$, 42.49 [+, $N(CH_3)_2$], 153.11 (C_{quat}, C-1), 157.16 (2 × C_{quat}, C-2, C-3), 219.34, 223.82 (C_{quat}, CO). MS (70 eV), m/z (%): 316 (18) [M^+], 288 (2) [$M^+ - CO$], 260 (5) [$M^+ - 2CO$], 232 (4) [$M^+ - 3CO$], 204 (16) [$M^+ - 4CO$], 176 (100) [$M^+ - 5CO$], 133 (11), 120 (21), 105 (11), 52 (19) [Cr^+] Anal. Calc. for $C_{12}H_{12}CrN_2O_5$ (316.2): C, 45.58; H, 3.82. Found: C, 45.86; H, 3.93%.

Table 2
(2-Ethoxy-3-dimethylaminocyclopropen-1-yliden)pentacarbonylchromium (**2**) and (2-diethylamino-3-dimethylaminocyclopropen-1-ylidene)-pentacarbonylchromium (**3b**)

	2	**3b**
Structural characteristic	t	t
Molecular formula	$C_{12}H_{11}CrNO_6$	$C_{14}H_{16}CrN_2O_5$
Molecular mass	317.22	344.29
Temperature (K)	133(2)	133(2)
Wavelength (pm)	71.073	71.073
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions		
a (pm)	1237.84(2)	924.04(18)
b (pm)	1441.50(2)	935.0(3)
c (pm)	1670.59(3)	986.5(2)
α (°)	90	83.900(17)
β (°)	98.4430(10)	78.920(17)
γ (°)	90	75.507(12)
Cell volume (nm^3)	2.94860(8)	0.8082(3)
Formula units per cell Z	8	2
Calculated density (Mg m^{-3})	1.429	1.415
Absorption coefficient (mm^{-1})	0.798	0.731
$F(000)$	1296	356
Crystal size (mm)	0.70 × 0.70 × 0.60	0.50 × 0.50 × 0.50
Measured θ range (°)	2.38–25.03	2.25–28.28
Index ranges	$-11 \leq h \leq 14$ $-17 \leq k \leq 17$ $-19 \leq l \leq 19$	$-12 \leq h \leq 12$ $-12 \leq k \leq 12$ $-13 \leq l \leq 9$
Number of recorded reflections	17847	12780
Independent reflections	2602 ($R_{int} = 0.0326$)	3979 ($R_{int} = 0.0243$)
Max. and min. transmission	0.6462 and 0.6052	0.7114 and 0.7114
Structural refinement	Full matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/paramenters	2602/6/184	3979/0/203
Goodness-of-fit on F^2	1.084	1.050
Final R values [$I > 2\sigma(I)$]	$R_1 = 0.0286$, $wR_2 = 0.0734$	$R_1 = 0.0286$, $wR_2 = 0.0708$
R values (all data)	$R_1 = 0.0340$, $wR_2 = 0.0770$	$R_1 = 0.0363$, $wR_2 = 0.0740$
Largest 5 maximum and minimum (e nm^{-3})	248 and −267	305 and −346

*1.4. (2-Diethylamino-3-dimethylaminocyclopropen-1-ylidene)pentacarbonylchromium (**3b**)*

To 100 mg (0.315 mmol) of **2** was added 4 ml of diethylamine, and the mixture was stirred at room temperature for 3 h. After column chromatography on silica gel (40 g, 5 × 15 cm, $\mathrm{Et_2O}$) 107 mg (99%) of **3b** ($R_f = 0.58$, $\mathrm{Et_2O}$) was obtained as weakly yellow crystals (m.p. 85°C). IR (KBr): $\tilde{\nu} = 2940\ \mathrm{cm}^{-1}$ (C–H), 2051 (C=O), 1909 (C=O), 1522 (C=C), 1450, 1420, 1357, 1250, 1200, 692, 680, 660, 644. ^{1}H-NMR (250 MHz, $\mathrm{C_6D_6}$): $\delta = 1.25$ [$\mathrm{m_c}$, 6H, $\mathrm{N(CH_2C\mathit{H}_3)_2}$], 3.29–3.90 [m, 10H, $\mathrm{N(C\mathit{H}_2CH_3)_2}$, $\mathrm{N(CH_3)_2}$]. ^{13}C-NMR (62.9 MHz, $\mathrm{C_6D_6}$, additionally DEPT): $\delta = 14.00$ [+, $\mathrm{N(CH_2\mathit{C}H_3)_2}$], 25.14, 30.01 [−, $\mathrm{N(\mathit{C}H_2CH_3)_2}$], 41.22, 44.35 [+, $\mathrm{N(CH_3)_2}$], 152.87 ($\mathrm{C_{quat}}$, C-1*), 155.69 ($\mathrm{C_{quat}}$, C-2*), 157.52 ($\mathrm{C_{quat}}$, C-3*), 219.30, 223.60 ($\mathrm{C_{quat}}$, CO). MS (70 eV), m/z (%): 344 (18) [$\mathrm{M^+}$], 316 (1) [$\mathrm{M^+ - CO}$], 288 (4) [$\mathrm{M^+ - 2CO}$], 260 (4) [$\mathrm{M^+ - 3CO}$], 232 (15) [$\mathrm{M^+ - 4CO}$], 204 (100) [$\mathrm{M^+ - 5CO}$], 120 (9), 86 (31), 84 (33), 52 (3) [$\mathrm{Cr^+}$]. Anal. Calc. for $\mathrm{C_{14}H_{16}CrN_2O_5}$ (344.3): C, 48.84; H, 4.68. Found: C, 51.90; H, 5.31%.

For crystal structure data, see Table 2.

2. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146919 for compound **2**, and CCDC no. 146920 for compound **3b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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