

Aminocarbene complexes of chromium. VII. Modification of the reactivity of nitrogen–ylide complexes derived therefrom upon removal of the metal

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Abstract

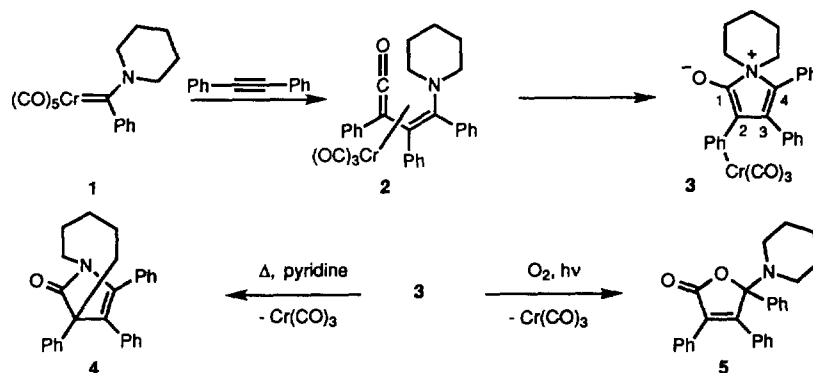
The nitrogen–ylide complex **3** reacted with HBF₄ to give in high yield the fluoroborate complex **6** which upon UV irradiation in the presence of O₂ led to the metal-free fluoroborates **7** and **8** fully characterized by X-ray crystallography; deprotonation of **7** in the presence of trace amount of water led instantaneously, upon hydrolysis, to the lactone **11**, whereas deprotonation of **8** in the presence of ethanol gave the aminoester **12**. © 1997 Elsevier Science S.A.

1. Introduction

Five years ago [1] we reported on the synthesis, structure, and reactivity of the first stable zwitterionic complexes resulting from the insertion of alkynes into aminocarbene complexes of chromium (Scheme 1).

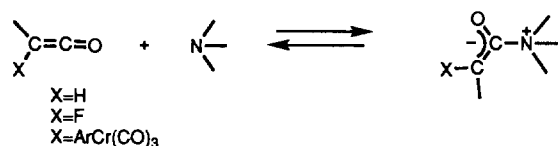
The key step in these transformations was the interaction of a tertiary amine with the central carbon atom of a ketene, a reaction which is also known in classical organic chemistry, but which leads in that case to short-lived intermediates [2,3] (Scheme 2, X = H, X = F).

Of special interest was the transformation of complex **1** into the moisture-stable complex **3**, the thermolysis of which gave the bridgehead lactam **4** [4,5].



Scheme 1.

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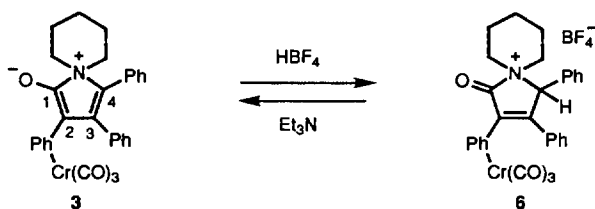


Scheme 2.

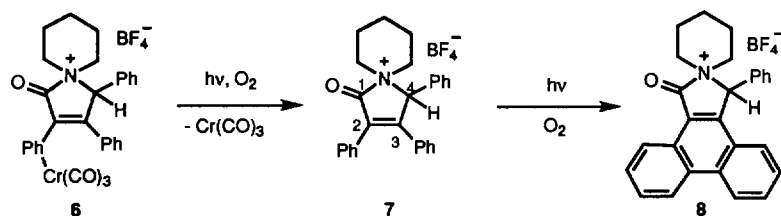
In order to determine the role, if any, of the metal in the stabilization and thus in the rearrangement of the ylide complexes such as **3**, attempts were made to remove it so as to study the evolution of the metal-free N-ylide. However, demetallation by classical methods (O_2 , UV irradiation) failed since easy oxidation of the ylide complexes to aminolactone complexes and aminolactones (e.g. **3** \rightarrow **5**) occurred [6]. Thus, less direct access to the metal-free ylides had to be found. For that purpose, the following sequence: protonation of the N-ylide complex, decooordination of the metal, followed by deprotonation, was devised and successfully used.

2. Results

Protonation [4] of complex **3** with fluoroboric acid gave complex **6** as a deep red solid: this reaction is reversible since deprotonation of **6** with triethylamine in dichloromethane led back, as demonstrated by ^1H NMR to the starting complex **3**.



When a solution of complex **6** was irradiated under a steady flow of oxygen, a progressive disappearance of the red colour of the starting complex was observed, leading after 2 h to a greenish precipitate, insoluble in organic solvents, and a yellow solution. According to the IR and ^{13}C NMR spectra, no more metallic COs were present in the very polar product **7** obtained in 70% yield from the solution after removal of the precipitate. Its ^1H NMR spectrum displayed, among others, four multiplets for the two NCH_2 groups and a singlet at δ 6.61 ppm for the benzylic proton, whereas a signal for a carbonyl group at δ 175.2 appeared in the ^{13}C NMR spectrum.



Crystals of the new compound **7** suitable for an X-ray analysis could be grown from dichloromethane/pentane. Its structure appears in Fig. 1 whereas the crystallographic data, the most important bond distances and bond angles can be found in Tables 1 and 2. It confirms that, fortunately enough, no reaction but removal of the metal through its oxidation took place. When, however, the irradiation was carried out under the same conditions but for a longer period of time, a new pale yellow crystalline product **8** was obtained in 88% yield. The most striking differences with compound **1** appeared in the ^1H NMR spectrum: signals down to 8.85 ppm, typical for those of phenanthrenes, were observed together with a singlet at δ 7.32 ppm; moreover, a signal for a carbonyl group, at δ 173.4, was still observed in the ^{13}C NMR spectrum.

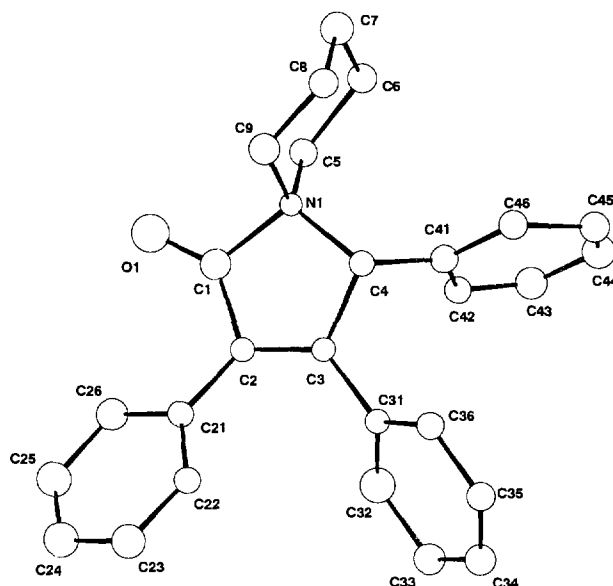


Fig. 1. X-ray structure of **7**. Selected distances (Å) and angles (°): O(1)–C(1) 1.15(2), N(1)–C(1) 1.54(2), N(1)–C(4) 1.53(2), N(1)–C(5) 1.56(2), N(1)–C(9) 1.51(2); C(1)–N(1)–C(4) 107.1(12), C(1)–N(1)–C(5) 107.2(13), C(4)–N(1)–C(5) 116.8(10), C(1)–N(1)–C(9) 106.1(14).

That the new product **8** originated directly from **7** could be easily demonstrated: irradiation of a solution of **7** in dichloromethane, in an NMR tube, for 3 h in the presence of oxygen led quantitatively to **8**. Moreover, according to its mass spectrum, **8** is the result of the dehydrogenation of **7**. The structure of this new product could also be assessed by an X-ray study. The ORTEP view, shown in Fig. 2, confirms that a photocyclisation with dehydrogenation akin to that

Table 1
Crystal data for **7**, **8**, and **11**

Fw	467.3
a (Å)	10.373(5)
b (Å)	12.879(5)
c (Å)	17.635(3)
α (°)	90.
β (°)	90.
γ (°)	90.
V (Å ³)	2356
Z	4
Crystal system	Orthorhombic
Space group	P c 2 ₁ n
Linear absorption coefficient μ (cm ⁻¹)	0.95
Density ρ (g.cm ⁻³)	1.32
Diffractometer	PHILIPS PW1100
Radiation	MoK α ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	1.20 + 0.345 tg θ
θ Limits (°)	2 - 20
Temperature of measurement	room temperature
Octants collected	0, 9; 0, 12; 0, 16
Nb of data collected	1299
Nb of unique data collected	1153
Nb of unique data used for refinement	650 (Fo) ² > 3 σ (Fo) ²
R (int)	no
R = $\sum Fo - Fc / \sum Fo $	0.0819
Rw = $[\sum w(Fo - Fc)^2 / \sum wFo^2]^{1/2}$	0.0803 w = 1.0
Absorption correction	no
Extinction parameter (x 10 ⁻⁶)	no
Nb of variables	137
$\Delta\rho_{min}$ (e.Å ⁻³)	-0.29
$\Delta\rho_{max}$ (e.Å ⁻³)	0.48

Table 1 (continued)

Fw	397.5
a (Å)	22.393(4)
b (Å)	13.655(4)
c (Å)	18.109(6)
α (°)	90.
β (°)	126.57(3)
γ (°)	90.
V (Å ³)	4447(92)
Z	8
Crystal system	Monoclinic
Space group	C 2/c
Linear absorption coefficient μ (cm ⁻¹)	0.69
Density ρ (g.cm ⁻³)	1.19
Diffractometer	CAD4 - Enraf-Nonius
Radiation	MoKα (λ = 0.71069 Å)
Scan type	ω/2θ
Scan range (°)	0.80 + 0.345 tgθ
θ Limits (°)	1 - 23
Temperature of measurement	Room temperature
Octants collected	-24, 19 ; 0, 14 ; 0, 19
Nb of data collected	3368
Nb of unique data collected	3097
Nb of unique data used for refinement	862 (Fo) ² > 3σ(Fo) ²
R (int)	0.050
R = Σ Fo - Fc / Σ Fo	0.071
Rw = [Σw(Fo - Fc) ² / ΣwFo ²] ^{1/2}	0.070 w = 1.0
Absorption correction	DIFABS (min = 0.83, max = 1.10)
Extinction parameter (x 10 ⁻⁶)	no
Nb of variables	127
Δρmin (e.Å ⁻³)	-0.25
Δρmax (e.Å ⁻³)	0.25

known for simple stilbenes took place [7]. The most important bond distances and bond angles of **8** can be found in Table 3.

In order to study the reactivity of these two compounds and especially of their deprotonation products, three separate experiments were carried out.

In the first one, the interaction of **7** with one equivalent of triethylamine was followed by ¹H NMR: as for complex **6**, deprotonation to the ylide took place instantaneously as indicated by the disappearance of the signal at δ 6.45 ppm,

Table 2
Selected bond distances (Å) and bond angles (°) for **7**

O(1) - C(1)	1.21(2)	N(1) - C(1)	1.57(2)
N(1) - C(4)	1.55(2)	N(1) - C(5)	1.45(2)
N(1) - C(9)	1.53(3)	C(1) - C(2)	1.47(3)
C(2) - C(3)	1.34(2)	C(2) - C(21)	1.44(3)
C(3) - C(4)	1.51(2)	C(3) - C(31)	1.46(3)
C(4) - C(41)	1.53(3)	C(5) - C(6)	1.54(3)
C(6) - C(7)	1.47(3)	C(7) - C(8)	1.51(3)
C(8) - C(9)	1.46(3)		
C(1) - N(1) - C(4)	104.5(15)	C(1) - N(1) - C(5)	108.7(16)
C(4) - N(1) - C(5)	120.0(15)	C(1) - N(1) - C(9)	105.5(16)
C(4) - N(1) - C(9)	108.1(15)	C(5) - N(1) - C(9)	109.0(16)
O(1) - C(1) - N(1)	118.2(20)	O(1) - C(1) - C(2)	134.0(23)
N(1) - C(1) - C(2)	107.8(19)	C(1) - C(2) - C(3)	108.9(19)
C(1) - C(2) - C(21)	118.2(19)	C(3) - C(2) - C(21)	132.5(19)
C(2) - C(3) - C(4)	115.1(18)	C(2) - C(3) - C(31)	126.8(19)
C(4) - C(3) - C(31)	118.1(17)	N(1) - C(4) - C(3)	103.3(15)
N(1) - C(4) - C(41)	115.9(15)	C(3) - C(4) - C(41)	111.2(17)
N(1) - C(5) - C(6)	115.7(17)	C(5) - C(6) - C(7)	110.8(20)
C(6) - C(7) - C(8)	111.5(20)	C(7) - C(8) - C(9)	113.2(19)
N(1) - C(9) - C(8)	111.2(18)		

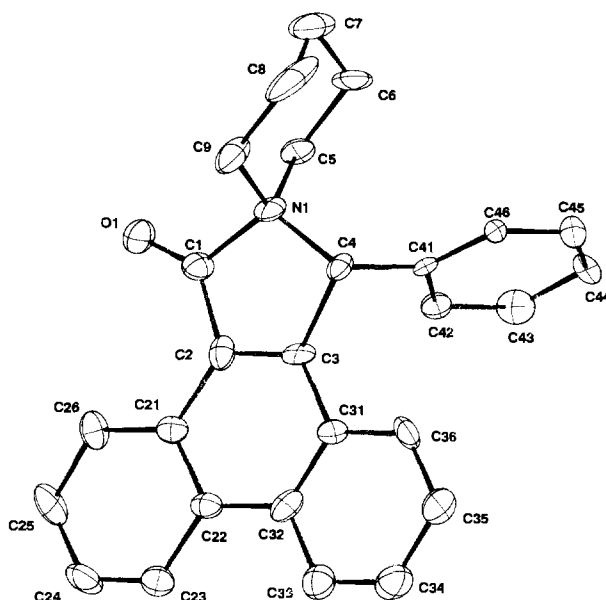
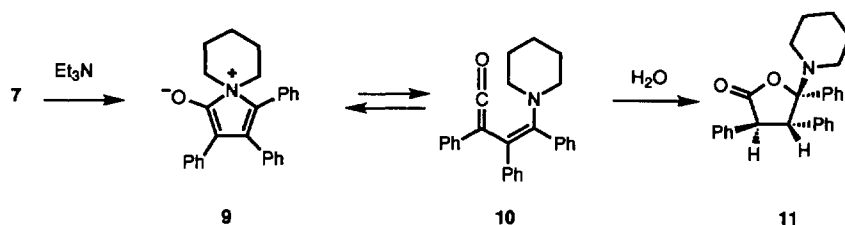


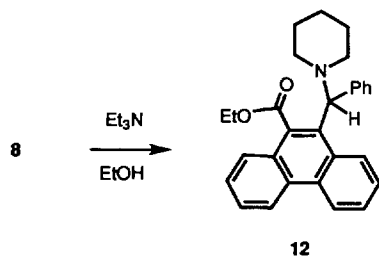
Fig. 2. X-ray structure of **8**. Selected bond distances (Å) and angles (°): O(1)–C(1) 1.21(2), N(1)–C(1) 1.57(2), N(1)–C(4) 1.55(2), N(1)–C(5) 1.45(2), N(1)–C(9) 1.53(3); C(1)–N(1)–C(4) 104.5(15), C(1)–N(1)–C(5) 108.7(16), C(4)–N(1)–C(5) 120.0(15), C(1)–N(1)–C(9) 105.5(16).

but unexpectedly signals due to the aminolactone **11**, the hydrolysis product of the elusive zwitterion **9** (or aminoketene **10**) appeared.



In the second experiment, a slight excess of triethylamine was added to compound **7** in a 1:1 mixture of dichloromethane and toluene. After 12 h of reflux, the same aminolactone **11** could be isolated in 62% yield and its structure, which appears in Fig. 3, established by X-ray crystallography: no rearrangement product **4** of the metal-free zwitterion **9** could be detected.

Finally, addition of Et_3N to the fluoroborate **8**, in the presence of ethanol, led instantaneously to the aminoester **12** in 40% yield.



3. Discussion

The most striking feature of these experiments is the ease by which the deprotonation products of **7** and **8** undergo the hydrolysis and ethanolysis reactions: this result clearly reflects the weakening of the nitrogen-to-carbon (1) bond upon removal of the $\text{Cr}(\text{CO})_3$ group. Although slow hydrolysis has been observed for the less hindered complexed zwitterions of the type **3**, acid catalysis (by silica gel) was necessary [4]. The role of the metal could thus be two-fold.

– It is known that the chromium tricarbonyl group activates aromatic systems towards nucleophilic attack, by electron density removal [8]; for the same reasons, once coordinated to the aromatic ring of an aryl ketene (e.g. **2**), it can increase the electrophilicity of the central carbon atom of the ketene function and promote the formation of zwitterionic species. The driving force for the formation of the zwitterion from the aminoketene intermediate **2** is thus linked to the complexation of $\text{Cr}(\text{CO})_3$ to an aryl group linked to the ketene function or, in the absence of an aryl group, to the carbon–carbon double bond of the ketene.

– Chromium tricarbonyl also stabilizes benzylic carbanions [8]; thus, once formed, the zwitterion **3** with its negative charge partially localized α to the aromatic ring bearing the $\text{Cr}(\text{CO})_3$ group is stabilized. The bond between carbon (1) and nitrogen should thus be stronger than in the metal-free zwitterion. The $\text{Cr}(\text{CO})_3$ group in complex **3** can thus be compared to that of fluorine in a fluoroketene (Scheme 2, $\text{X} = \text{F}$, $\text{X} = \text{ArCr}(\text{CO})_3$): in contrast to alkyl- or aryl-substituted ketenes for which the ketene is the stable form in the presence of a tertiary amine, the zwitterion and not the ketene is the stable form in the case of a fluoroketene due to the electronegativity of fluorine [9,10]. Removal of the metal in **3** will destabilize the zwitterionic form **9** either by weakening of the carbon (1)–nitrogen bond or even by reverting it to the enaminketene form **10**: trace amounts of water could then lead to one of its hydrolysis products, the aminolactone **11** and, as a consequence, prevent the formation of the expected rearrangement product **4**.

4. Conclusion

It appears thus that the role of the metal is not restricted to the promotion of the alkyne and CO insertions in the starting aminocarbene complexes: it induces also the formation of the nitrogen ylide complexes and considerably strengthens, by coordination, the bond between nitrogen and the central carbon atom of the intermediate ketene. Taken as a whole, the results described herein reflect a stabilizing effect of the metal on the natural intermolecular and attractive interaction between the nucleophilic and electrophilic centres of the intermediate aminoketenes. As a consequence, its presence enables the rearrangement of the ylides to lactams to occur and prevents the classical hydrolysis to aminoacids.

5. Experimental section

5.1. General methods

^1H and ^{13}C NMR spectra were recorded on Bruker AC 200 or ARX 400 spectrometers. IR spectra were recorded on a Perkin–Elmer 1420 spectrometer. Mass spectra were recorded on a ZAB HSQ (Fisons) instrument. Column chromatography was performed with Merck silica gel (70–230 mesh) using various ratios of ethyl acetate/light petroleum ether or dichloromethane/light petroleum ether as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under an argon atmosphere in carefully dried glassware. Benzene, tetrahydrofuran (THF), and diethyl ether were distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) was distilled from phosphorus pentoxide under a nitrogen atmosphere.

5.2. X-ray structure determinations

Data were collected on an Enraf–Nonius CAD4 diffractometer. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centred reflections. No significant variations were observed in the intensities of two checked reflections during data collections. Complete crystallographic data and collection parameters are listed in Table 1. The data were collected for Lorentz and polarization effects. Computations were performed using the PC version of CRYSTALS [11]. Scattering factors and corrections for anomalous absorption were taken from Ref. [12]. The structures were solved by using SHELXS [13] and refined by full-matrix least-squares with isotropic thermal parameters for **7** and **11** and anisotropic thermal parameters for **8**. For **7** and **8**, hydrogen atoms were introduced in calculated positions in the last refinement. For compound **11**, hydrogen atoms were located on a difference map and introduced in the last refinement with only an overall isotropic thermal parameter.

5.3. Tetrafluoroborate complex 6

Obtained from the ylide complex **3** (0.51 g, 1 mmol) in dichloromethane (60 ml) upon addition of one equivalent of a 54 wt.% solution of tetrafluoroboric acid in diethyl ether (0.144 ml) at room temperature. The yellow solution rapidly turned deep red. After addition of diethyl ether (60 ml), the solution was kept at -20°C for three days. Precipitation of complex **6** as a red powder was observed (0.55 g, 91%), m.p. 160°C . Spectral data of **6**: IR (CHCl_3) 1990, 1800, 1600 cm^{-1} ; $^1\text{H NMR}$ (CD_2Cl_2) δ 7.94–7.17 (m, 10H, Ar), 6.45 (s, 1H, CHPh), 5.81–5.35 (m, 5H, Ar–Cr), 4.07 (m, 1H, NCH), 3.74 (m, 1H, NCH), 3.56 (m, 1H, NCH), 3.14 (m, 1H, NCH), 2.36–1.26 (m, 6H, 3CH_2); $^{13}\text{C NMR}$ (CD_2Cl_2) δ 235.5 (CO), 173.76 (CO), 134.06–128.18 (Ar, C=C), 98.06–76.28 (ArCr), 65.95 (NCHPh), 54.89 (NCH₂), 52.73 (NCH₂), 22.31, 20.61 (CH₂). HRMS calc. for $\text{C}_{30}\text{H}_{25}\text{NO}_4\text{Cr}$ ($\text{M}^+ - \text{HBF}_4$) 515.1188, measd. 515.1185.

5.4. Tetrafluoroborate 7

Obtained upon UV/visible irradiation (Philips 400 W lamp) of a solution of complex **6** (1 g, 1.6 mmol) in dichloromethane (60 ml) in a water-cooled glassware photoreactor while oxygen was bubbled through the solution for 2 h. The solution turned from red to yellow. After filtration through Celite and evaporation of the solvent, the solid residue was recrystallized from pentane/dichloromethane solutions to give yellow crystals (0.61 g, 70%), m.p. 190°C . Spectral data of **7**: IR (CHCl_3) 1780 cm^{-1} ; $^1\text{H NMR}$ (CD_2Cl_2) δ 7.98 (d, 1H), 7.55–7.09 (m, 14H, Ar), 6.61 (s, 1H, CHPh), 4.11 (m, 1H, NCH), 3.71 (m, 1H, NCH), 3.55 (m, 1H, NCH), 3.13 (m, 1H, NCH), 2.45 (m, 1H), 2.25 (m, 1H), 1.86–1.50 (m, 4H); $^{13}\text{C NMR}$ (CDCl_2) δ 175.21 (CO), 167.90, 134.10–124.43 (13 peaks), 124.43 (C=C, Ar), 76.50 (HCPH), 64.03 (NC), 54.41 (NC), 21.78, 20.65, 20.45 (3CH_2). HRMS calc. for $\text{C}_{27}\text{H}_{25}\text{ON}$ ($\text{M} - \text{HBF}_4$) 379.1936, measd. 379.1937.

5.5. Tetrafluoroborate 8

Obtained upon UV irradiation of a solution of complex **6** in dichloromethane (100 ml), obtained from complex **3** (1.0 g, 1.9 mmol) and HBF_4 in diethyl ether (0.3 ml), in the presence of oxygen as above, for 6 h. After work-up as above, a yellow solid was obtained (0.796 g, 88%), m.p. 220°C . Spectral data of **8**: IR (CHCl_3) 1790 cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ 8.85 (d, 1H), 8.71 (d, 1H), 8.64 (d, 1H), 8.44 (d, 1H), 8.04 (d, 1H), 7.82 (m, 3H), 7.61 (m, 2H), 7.36 (t, 1H), 7.32 (s, 1H, CHPh), 7.07 (t, 1H), 6.40 (d, 1H), 3.98 (m, 1H, NCH), 3.62 (t, 1H, NCH), 3.50 (t, 1H, NCH), 3.12 (m, 1H, NCH), 2.57 (m, 1H), 2.12 (m, 1H), 1.92 (m, 2H), 1.73 (m, 1H), 1.57 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3) δ 173.47 (CO), 133.12, 133.70–123.65 (C=C, Ar), 74.22 (NCPH), 64.29 (NCH₂), 53.37 (NCH₂), 22.06, 20.74, 20.52 (3CH_2). HRMS calc. for $\text{C}_{27}\text{H}_{23}\text{NO}$ ($\text{M}^+ - \text{HBF}_4$) 377.1779, measd. 377.1779.

Table 4
Selected bond distances (Å) and bond angles ($^{\circ}$) for **11**

O(1) - C(1)	1.21(1)	O(2) - C(1)	1.33(1)
O(2) - C(4)	1.50(1)	N(1) - C(4)	1.41(1)
N(1) - C(5)	1.49(1)	N(1) - C(9)	1.49(1)
C(1) - C(2)	1.52(1)	C(2) - C(3)	1.49(1)
C(2) - C(21)	1.53(1)	C(3) - C(4)	1.57(1)
C(3) - C(31)	1.51(1)	C(4) - C(41)	1.51(1)
C(5) - C(6)	1.48(2)	C(6) - C(7)	1.52(2)
C(7) - C(8)	1.51(2)	C(8) - C(9)	1.50(2)
C(1) - O(2) - C(4)	111.9(9)	C(4) - N(1) - C(5)	115.2(8)
C(4) - N(1) - C(9)	120.4(9)	C(5) - N(1) - C(9)	107.7(9)
O(1) - C(1) - O(2)	121.9(12)	O(1) - C(1) - C(2)	128.0(12)
O(2) - C(1) - C(2)	110.1(11)	C(1) - C(2) - C(3)	103.7(9)
C(1) - C(2) - C(21)	111.4(10)	C(3) - C(2) - C(21)	114.9(10)
C(2) - C(3) - C(4)	104.6(8)	C(2) - C(3) - C(31)	117.1(9)
C(4) - C(3) - C(31)	114.1(9)	O(2) - C(4) - N(1)	110.4(8)
O(2) - C(4) - C(3)	101.3(8)	N(1) - C(4) - C(3)	113.7(8)
O(2) - C(4) - C(41)	109.0(8)	N(1) - C(4) - C(41)	111.9(9)
C(3) - C(4) - C(41)	110.0(9)	N(1) - C(5) - C(6)	110.1(10)
C(5) - C(6) - C(7)	112.7(11)	C(6) - C(7) - C(8)	110.5(11)
C(7) - C(8) - C(9)	113.2(12)	N(1) - C(9) - C(8)	110.0(11)

Table 5
Fractional parameters for **7**

Atom	x/a	y/b	z/c	U(iso)
O(1)	-0.066(2)	0.396(1)	0.817(1)	0.093(6)
N(1)	0.160(1)	0.428(1)	0.8249(8)	0.033(4)
C(1)	0.024(2)	0.439(2)	0.787(1)	0.061(7)
C(2)	0.039(2)	0.501(2)	0.718(1)	0.038(5)
C(3)	0.162(2)	0.534(2)	0.713(1)	0.036(5)
C(4)	0.252(2)	0.489(2)	0.772(1)	0.042(5)
C(5)	0.150(2)	0.456(2)	0.904(1)	0.049(6)
C(6)	0.266(2)	0.428(2)	0.954(1)	0.055(6)
C(7)	0.300(2)	0.318(2)	0.945(1)	0.070(8)
C(8)	0.311(2)	0.289(2)	0.862(1)	0.055(6)
C(9)	0.195(2)	0.313(2)	0.819(1)	0.063(7)
C(21)	-0.068(2)	0.508(2)	0.667(1)	0.043(6)
C(22)	-0.049(2)	0.518(2)	0.590(1)	0.045(6)
C(23)	-0.150(2)	0.522(2)	0.539(1)	0.074(8)
C(24)	-0.273(3)	0.522(2)	0.565(1)	0.078(8)
C(25)	-0.296(2)	0.520(2)	0.640(1)	0.078(8)
C(26)	-0.196(2)	0.510(2)	0.692(1)	0.065(7)
C(31)	0.216(2)	0.605(2)	0.657(1)	0.040(6)
C(32)	0.153(3)	0.700(2)	0.645(1)	0.081(9)
C(33)	0.201(2)	0.773(2)	0.590(1)	0.063(7)
C(34)	0.315(2)	0.749(2)	0.553(1)	0.062(7)
C(35)	0.377(2)	0.659(2)	0.566(1)	0.052(6)
C(36)	0.330(2)	0.585(2)	0.619(1)	0.049(6)
C(41)	0.332(2)	0.574(2)	0.810(1)	0.049(7)
C(42)	0.285(2)	0.670(2)	0.835(1)	0.046(6)
C(43)	0.363(2)	0.738(2)	0.867(1)	0.066(7)
C(44)	0.491(2)	0.725(2)	0.872(1)	0.071(8)
C(45)	0.546(2)	0.643(2)	0.844(1)	0.058(7)
C(46)	0.467(2)	0.557(2)	0.814(1)	0.053(7)
B(1)	-0.577(4)	0.271(3)	0.638(2)	0.11(1)
F(1)	-0.576(3)	0.172(3)	0.626(2)	0.23(1)
F(2)	-0.523(2)	0.318(1)	0.6971(9)	0.120(6)
F(3)	-0.526(2)	0.321(1)	0.574(1)	0.134(6)
F(4)	-0.707(1)	0.305(1)	0.6383(8)	0.088(5)

5.6. Aminolactone **11**

Obtained upon treatment of **7** (0.134 g, 0.28 mmol) in dichloromethane (6 ml) and toluene (6 ml) with triethylamine (1.1 equiv., 44 μ l) at room temperature. The pale yellow solution turned to orange. After heating under reflux for 24 h,

Table 6
Fractional parameters for **8**

Atom	x/a	y/b	z/c	U(eq)
O(1)	0.104(2)	0.510(1)	0.6238(8)	0.0741
N(1)	-0.117(2)	0.292(1)	0.6394(9)	0.0493
C(1)	0.030(2)	0.424(2)	0.674(1)	0.0537
C(2)	0.042(2)	0.403(2)	0.769(1)	0.0514
C(3)	-0.076(2)	0.276(2)	0.797(1)	0.0330
C(4)	-0.193(2)	0.203(2)	0.722(1)	0.0437
C(5)	-0.222(2)	0.363(2)	0.584(1)	0.0581
C(6)	-0.347(3)	0.250(3)	0.530(1)	0.0813
C(7)	-0.284(5)	0.160(5)	0.469(2)	0.1030
C(8)	-0.193(5)	0.079(3)	0.522(2)	0.0975
C(9)	-0.055(3)	0.193(2)	0.579(1)	0.0759
C(21)	0.164(2)	0.496(2)	0.830(1)	0.0476
C(22)	0.158(2)	0.449(2)	0.920(1)	0.0497
C(23)	0.281(2)	0.537(2)	0.981(1)	0.0615
C(24)	0.393(2)	0.661(3)	0.953(1)	0.0729
C(25)	0.400(2)	0.703(2)	0.866(2)	0.0658
C(26)	0.286(2)	0.625(2)	0.805(1)	0.0589
C(31)	-0.081(2)	0.224(2)	0.887(1)	0.0521
C(32)	0.035(2)	0.310(2)	0.947(1)	0.0521
C(33)	0.033(2)	0.266(2)	1.037(1)	0.0708
C(34)	-0.084(3)	0.141(3)	1.062(1)	0.0833
C(35)	-0.199(3)	0.050(2)	1.000(1)	0.0680
C(36)	-0.193(2)	0.092(2)	0.914(1)	0.0561
C(41)	-0.358(2)	0.201(2)	0.7426(9)	0.0377
C(42)	-0.384(2)	0.329(2)	0.779(1)	0.0516
C(43)	-0.535(3)	0.321(2)	0.802(1)	0.0565
C(44)	-0.666(2)	0.186(3)	0.787(1)	0.0197
C(45)	-0.634(2)	0.058(2)	0.752(1)	0.0584
C(46)	-0.487(2)	0.067(2)	0.731(1)	0.0402
B(1)	0.140(4)	0.227(4)	0.302(2)	0.0845
F(1)	0.278(2)	0.191(2)	0.288(1)	0.1595
F(2)	0.132(2)	0.329(2)	0.251(1)	0.1509
F(3)	0.035(2)	0.085(2)	0.285(1)	0.1591
F(4)	0.146(2)	0.258(2)	0.389(1)	0.1635

Table 7
Fractional parameters for **11**

Atom	x/a	y/b	z/c	U(1 σ)	U(eq)
O(1)	0.5401(4)	0.0651(6)	0.1396(6)		0.0681
O(2)	0.4917(4)	0.2127(5)	0.0835(5)	0.042(2)	
N(1)	0.4055(5)	0.3452(7)	0.0287(6)	0.044(3)	
C(1)	0.4868(7)	0.1154(9)	0.0848(9)	0.054(4)	
C(2)	0.4088(6)	0.0817(8)	0.0063(8)	0.042(3)	
C(3)	0.3640(5)	0.1736(7)	-0.0240(7)	0.034(3)	
C(4)	0.4213(5)	0.2573(7)	0.0027(7)	0.031(3)	
C(5)	0.4592(6)	0.4265(9)	0.0551(8)	0.052(3)	
C(6)	0.4239(7)	0.5217(9)	0.0460(9)	0.067(4)	
C(7)	0.3963(8)	0.5280(9)	0.105(1)	0.075(4)	
C(8)	0.3508(7)	0.438(1)	0.0908(8)	0.070(4)	
C(9)	0.3877(7)	0.3440(9)	0.0961(9)	0.066(4)	
C(21)	0.3815(7)	-0.0003(9)	0.0371(8)	0.054(4)	
C(22)	0.3449(8)	-0.079(1)	-0.0221(9)	0.081(5)	
C(23)	0.3150(9)	-0.151(1)	0.007(1)	0.111(6)	
C(24)	0.3217(9)	-0.137(1)	0.084(1)	0.104(6)	
C(25)	0.3569(9)	-0.061(1)	0.142(1)	0.096(5)	
C(26)	0.3883(7)	0.010(1)	0.1176(9)	0.069(4)	
C(31)	0.2952(6)	0.1777(8)	-0.1226(7)	0.046(3)	
C(32)	0.2395(7)	0.2437(9)	-0.1484(8)	0.058(4)	
C(33)	0.1766(7)	0.254(1)	-0.239(1)	0.078(4)	
C(34)	0.1677(8)	0.193(1)	-0.302(1)	0.088(5)	
C(35)	0.2208(8)	0.125(1)	-0.283(1)	0.090(5)	
C(36)	0.2855(7)	0.1170(9)	-0.1907(9)	0.065(4)	
C(41)	0.4291(6)	0.2732(8)	-0.0736(7)	0.040(3)	
C(42)	0.4779(6)	0.2169(8)	-0.0786(7)	0.050(3)	
C(43)	0.4795(7)	0.227(1)	-0.1552(9)	0.063(4)	
C(44)	0.4316(7)	0.2895(9)	-0.2243(8)	0.062(4)	
C(45)	0.3829(6)	0.3462(9)	-0.2207(8)	0.056(4)	
C(46)	0.3802(6)	0.3374(8)	-0.1449(7)	0.046(3)	

filtration of the precipitate, and evaporation of the solvents, the residue was purified by silica gel chromatography. Elution with petroleum ether/dichloromethane (50/50) gave **11** as a white solid (0.072 g, 62%) which was recrystallized from methanol/dichloromethane, m.p. 178 °C. Spectral data of **11**: IR (CHCl₃) 1750 cm⁻¹; ¹H NMR (CDCl₃) δ 7.26–6.71 (m, 15H, Ar), 4.74 (d, *J* = 13.1 Hz, 1H, CHCO), 4.05 (d, *J* = 13.1 Hz, 1H, CH), 3.18 (m, 2H, NCH₂), 2.79 (m, 2H, NCH₂), 1.58 (m, 6H, 3CH₂); ¹³C NMR (CDCl₃) and 176.03 (CO), 137.34–121.27 (Ar), 107.7 (OCN), 52.86 (CHPh), 50.08 (CHPh), 48.10 (NCH₂), 26.44, 24.96 (CH₂). Anal. Found: C, 81.57; H, 6.90; N, 3.43. C₂₇H₂₅NO₂ Calc.: C, 81.68; H, 6.80; N, 3.52%.

5.7. Aminoester **13**

Obtained from **8** (0.225 g, 0.48 mmol) in dichloromethane (4 ml) upon addition of absolute ethanol (1 ml), then triethylamine (1 ml) at room temperature. The solution turned from pale yellow to orange. Evaporation of the solvents followed by silica gel chromatography of the residue gave, with petroleum ether/dichloromethane as the eluents, a white solid (0.081 g, 40%), m.p. 168 °C. Spectral data for **13**: IR (CHCl₃) 1710 cm⁻¹; ¹H NMR (CDCl₃) δ 8.93 (d, 1H), 8.56 (m, 2H), 7.77–6.99 (m, 10H, Ar), 4.90 (s, 1H, CHN), 4.66 (dq, 2H, OCH₂), 2.58 (m, 2H, NCH₂), 2.37 (m, 2H, NCH₂), 1.52 (m, 6H, CH₂), 1.61–1.47 (t, 3H, CH₃ and m, 6H, 3CH₂); ¹³C NMR (CDCl₃) δ 171.16 (CO), 141.13–122.96 (Ar), 74.09 (NCPH), 61.88 (OCH₂), 54.34 (NCH₂), 26.54, 25.06 (CH₂), 14.88 (CH₃). HRMS calc. for C₂₉H₂₉NO₂ (M⁺) 423.2198, measd. 423.2198. Tables 4–7

6. Supporting material available

Tables 8 to 15 give complete sets of bond lengths and bond angles, anisotropic thermal parameters, and structure factors (16 pages) for **7**, **8**, and **11**.

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