DOI: 10.1002/ejoc.200700192

N-Heterocyclic Carbenes of 5-Haloindazoles Generated by Decarboxylation of 5-Haloindazolium-3-carboxylates

Andreas Schmidt,*[a] Bohdan Snovydovych,[a] Tobias Habeck,[a] Petra Dröttboom,[b] Mimoza Gjikaj,[c] and Arnold Adam[c]

Keywords: Thermogravimetric analysis / Betaines / Carbenes / Differential scanning calorimetry

Syntheses and properties of 5-fluoro-, chloro- bromo-, and iodo-substituted 1,2-dimethylindazolium-3-carboxylates as new representatives of pseudo-cross-conjugated heterocyclic mesomeric betaines are described, and results of an X-ray single crystal analysis of the nonhalogenated parent compound are presented. These betaines decarboxylate on heating to yield 5-halo-1,2-dimethylindazol-3-ylidenes, which can be trapped by protons, sulfur, and 2,4-dichlorophenyl isocyanate, respectively. The decarboxylation is studied by electrospray-ionization mass spectrometry, NMR spectroscopy, thermogravimetric analysis, and differential scanning calorimetry.

Introduction

After first examinations of N-heterocyclic carbenes (NHC) by Wanzlick,[1] Arduengo published the synthesis, isolation, and X-ray analysis of a stable imidazol-2-ylidene[2] and derivatives[3] in 1991 and 1992, respectively. Meanwhile 1,2,4-triazol-5-ylidenes,[4] thiazol-2-ylidenes,[5] saturated systems such as imidazolin-2-ylidene,[6] and acyclic carbenes such as diaminocarbenes[7] and aminooxy- as well as aminothiocarbenes[8] and aminoarylcarbenes were developed.[9] N-Heterocyclic carbenes serve are versatile ligands in numerous transition-metal-catalyzed reactions. Thus, Suzuki couplings,[10] ring enlargements,[11] reductive cyclizations,[12] living polymerizations,[13] intramolecular insertions,[14] formations of 1,4-diketones, and α-aminoketones[15] are widely applied reactions. Recently, polymeric carbene–metal complexes,[16] oxidative esterifications,[17] cyanosilylations,[18] and the formation of spiro-γ-butyrolactones[19] under NHC catalysis were described. Some review articles appeared.[20]

The synthesis of known nucleophilic carbenes starts either from the corresponding salts, which can be deprotonated with potassium *tert*-butoxide,[21] sodium, or potassium hydride in the presence of catalytic amounts of either *t*BuOK or the dimethyl sulfoxide anion,[2] or from imidazole–thiones with potassium in boiling THF.[22] 1,2,4-Triazol-5-ylidenes were obtained by the thermal elimination of 5-methoxytriazoles in vacuo.[4] The thermal extrusion of leaving groups from heterocyclic mesomeric betaines is usually observed for an architecture that is depicted in Figure 1. A dipole partial structure of type **I**, in which the charges are delocalized within a common π-electron system, undergoes cleavage of the union bond ("*u*") to form a heterocumulene and nucleophilic carbene **II**. Mesomeric betaines that possess masked dipole **I** are referred to as pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB). They form one of the four distinct categories of this class of compounds, which display profound differences in their chemistry.[23,24]

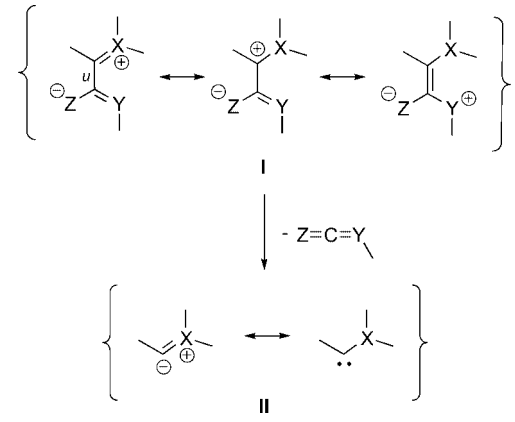


Figure 1. Architecture of pseudo-cross-conjugated systems and their conversion into N-heterocyclic carbenes.

Known pseudo-cross-conjugated heterocyclic mesomeric betaines, which form N-heterocyclic carbenes by in situ de-

[a] Clausthal University of Technology, Institute of Organic Chemistry,
Leibnizstrasse 6, 38678 Clausthal-Zellerfeld, Germany
Fax: +49-5323-722858
E-mail: schmidt@ioc.tu-clausthal.de
[b] Clausthal University of Technology, Institute of Polymer Materials and Plastics Engineering,
Agricolastrasse 6, 38678 Clausthal-Zellerfeld, Germany
[c] Clausthal University of Technology, Institute of Inorganic Chemistry,
Paul-Ernst-Strasse 4, 38678 Clausthal-Zellerfeld, Germany
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

carboxylation, are presented in Figure 2. The alkaloid Homarine (**III**, $R^1 = R^2 = R^3 = H$),[25] and quinolinium (**III**, $R^1 = H$, R^2–R^3 = –CH=CH–CH=CH–), as well as isochinolinium derivatives (**III**, R^1–R^2 = –CH=CH–CH=CH–, $R^3 = H$),[26] imidazolium-2-carboxylates **IV**,[27] pyrazolium-3-carboxylates **V**,[28] as well as indazolium-3-carboxylates **V** (R^1–R^2 = –CH=CH–CH=CH–)[29] were found to undergo thermal fragmentation to CO_2 and the corresponding hetarene ylidenes. Extrusions of isocyanates and isothiocyanates have been reported as well.[29] The reverse process, namely, the formation of PCCMB by the reaction of NHC with heterocumulenes, has also been described.[30]

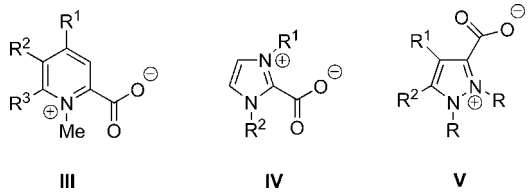


Figure 2. PCCMB which form NHC on decarboxylation.

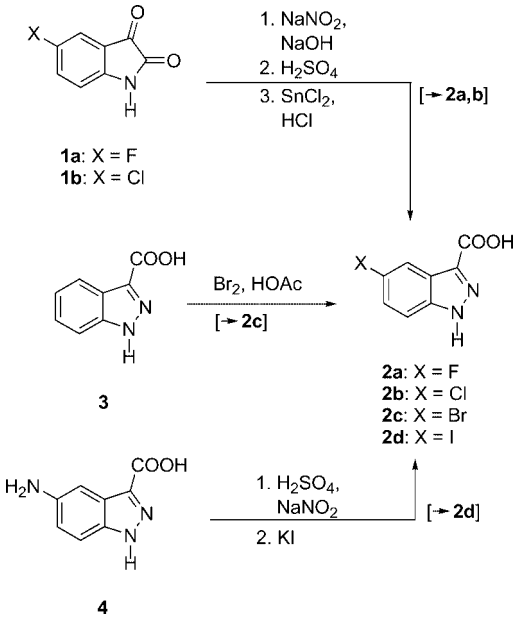
In continuation of our interest in heterocyclic mesomeric betaines[31] and their relationship to N-heterocyclic carbenes,[29] we describe here the syntheses of 5-fluoro-, chloro-, bromo-, and iodo-substituted 1,2-indazolium-3-carboxylates, their decarboxylations to NHC, and some trapping experiments. In addition, we present results of thermogravimetric analyses and differential scanning calorimetry.

Results and Discussion

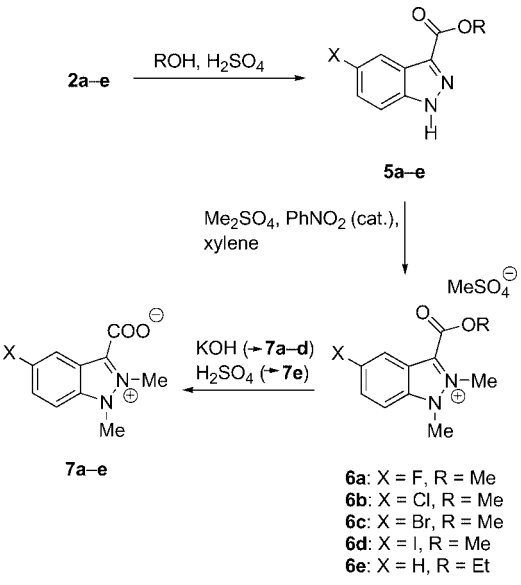
Syntheses and Characterizations

5-Fluoro- and 5-chloroindazole-3-carboxylic acids (**2a**,**b**) were synthesized starting from 1*H*-indole-2,3-diones **1a**,**b** by diazonium salts that were reduced in situ by tin(II)chloride to the target indazoles[32] (Scheme 1). 5-Bromoindazol-3-carboxylic acid **2c** was prepared by bromination of indazole-3-carboxylic acid **3**. In contrast to the information given in the literature,[33] aqueous acetic acid as a solvent was essential for the success of this reaction. 5-Iodo derivative **2d** was obtained on diazotization of 5-aminoindazole-3-carboxylic acid and subsequent substitution by iodide.

The 5-halogen substituted indazol-2,3-carboxylic acids were first subjected to esterification with methanol to give **5a**–**d** (Scheme 2). Methylation of **5a**–**d** to form **6a**–**d** was accomplished with dimethyl sulfate in xylene in the presence of catalytic amounts of nitrobenzene. Final saponification yielded pseudo-cross-conjugated mesomeric betaines **7a**–**d** in one step from **5a**–**d**. The ester cleavage of **7e** was performed with diluted sulfuric acid, which is an alternative approach.[29]



Scheme 1. Synthesis of 5-haloindazolecarboxylic acids.



Scheme 2. Formation of 1,2-dimethylindazolium-3-carboxylates as new representatives of PCCMB.

X-ray Single Crystal Analysis of 1,2-Dimethylindazolium-3-carboxylate (7e)

Single crystals of the pseudo-cross-conjugated mesomeric betaine 7**e** were obtained by the slow evaporation of a concentrated solution in *n*-propanol. The molecular drawing is presented in Figure 3.[34] In the elemental cell, this betaine is essentially planar ($\tau_{min} = 0.7°$, $\tau_{max} = 1.8°$) except for the carboxylate group which adopts an angle of τ(O11–C10–C3–N2) = 21.5° with respect to the indazole ring. The bond length of the union bond *u* depicted in Figure 1 was determined to be 151.96 pm (C3–C10), which is considerably longer than a C(sp^2)–C(sp^2) single bond (147 pm). In the single crystal, the betaine binds three equivalents of water of crystallization. The 1,2-dimethylindazolium-3-carboxylate units form layers, which alternate with layers of

water molecules. They are linked by hydrogen bonds, with O(w)···O(carboxylate) bond lengths from 278.0 to 290.7 pm and O(w)···O(w) bond lengths from 276.1 to 282.2 pm.

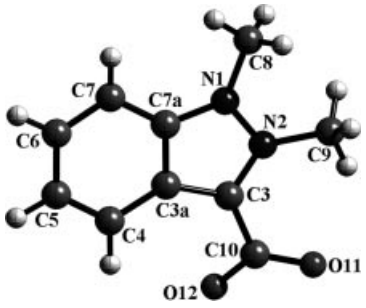


Figure 3. Molecular drawing of **7e**.

In view of these results, a charge-separation between the positive and the negative partial structure of the mesomeric betaine is therefore maintained by a diminished conjugation as a consequence of torsion angle as well as bond length. In accordance with the definition of pseudo-cross-conjugated mesomeric betaines, the negative partial structure is joined to the positive through an unstarred position of the isoconjugated equivalent, the propenyl anion (**VI**, Figure 4). This position is an inactive position of the HOMO of the molecule (**VII**, Figure 4). This nodal position thus serves as an "isolator" between the charge-separated partial structures of the mesomeric betaine.

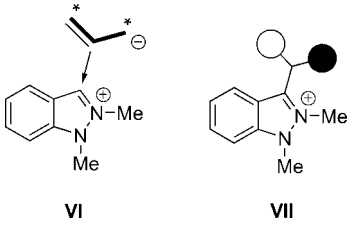


Figure 4. Characteristic features of pseudo-cross-conjugation.

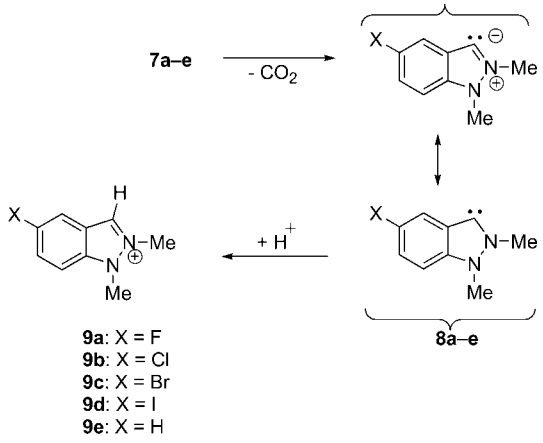
Properties

The UV absorption maxima of **7a**–**e** are dependent on the substitution pattern. Each betaine displays three intense peaks between λ_{max} = 224 and 328 nm which shift bathochromically on changing the halogen from fluorine to iodine (Table 1).

Table 1. UV absorption maxima of the betaines in MeOH [nm].

Betaine	Peak 1	Peak 2	Peak 3
7a	228	264	310
7b	230	268	314
7c	230	270	322
7d	238	270	328
7e	224	270	310

On heating, the color of the betaines changes to red while carbon dioxide is extruded and indazol-3-ylidenes **8a**–**e** are formed (Scheme 3). Carbenes **8a**–**e** decompose under these conditions. They can be detected, however, in high resolution electrospray ionization mass spectrometry (HRESIMS) as sodium adducts under very mild conditions (Table 2). In addition, spraying samples of **7a**–**e** dissolved in methanol from the same solvent at zero volt fragmentor voltage gave prominent peaks of the proton-trapped carbenes, namely, indazolium salts **9a**–**e**.



Scheme 3. Conversion of PCCMB into NHC.

Table 2. High resolution electrospray ionization mass spectroscopic detection of N-heterocyclic carbenes **8a**–**e** as Na^+ adducts and of indazolium cations **9a**–**e**.

Carbene/Cation	Calcd.	Found	Formula
8a	187.0647	187.0646	$C_9H_9FN_2Na$
8b	203.0352	203.0353	$C_9H_9ClN_2Na$
8c	246.9847	246.9847	$C_9H_9BrN_2Na$
8d	294.9709	294.9708	$C_9H_9IN_2Na$
8e	169.0742	169.0738	$C_9H_{10}N_2Na$
9a	165.0823	165.0753	$C_9H_{10}FN_2$
9b	181.0527	181.0550	$C_9H_{10}ClN_2$
9c	225.0022	225.0024	$C_9H_{10}BrN_2$
9d	272.9883	272.9875	$C_9H_{10}IN_2$
9e	147.0917	147.0912	$C_9H_{11}N_2$

A similar behavior was observed in [D_6]DMSO solution. Indazolium-3-carboxylates **7a**–**e** decarboxylate on warming to give N-heterocyclic carbenes, which are in turn intercepted by protons. A series of VTNMR experiments revealed that the ratio of betaines to salts in [D_6]DMSO is dependent on several competing and interplaying parameters such as the concentration of the solution, the halogen atom attached to C-5, the amount of water of crystallization, temperature, and time. Thus, a solution of **7a** contained 35% of indazolium salt **9a** after 10.0 min at 25 °C. Under analogous conditions, **7b** contained 25% of **9b** and **7c** contained 17% of **9c**. After 60.0 min at 80 °C, however, 5-chloroindazolium-3-carboxylate **7b** was completely converted into the 5-chloroindazolium salt **9b**, whereas the 5-fluoroindazolium and the 5-bromoindazolium salts were present in 78 and 58%, respectively. In either case, yet unidentified decomposition products were seen in the spectra.

To determine the amount of absorbed water of crystallization and the decarboxylation temperature in the solid state we performed thermogravimetric analyses (TGA) and

differential scanning calorimetry (DSC). The former mentioned type of testing enables the determination of changes in weight in relation to change in temperature. Figure 5 displays the TGA thermograms, the weight loss as a function of temperature, of 5-halogen-substituted indazolium-3-carboxylates **7a**–**d**. The species evolved at temperatures up to 100 °C is the water of crystallization that is present in **7c** and **7e** (cf. Figure 6) even after a 5 h period of drying in vacuo. In either case one equivalent of water of crystallization is evolved. During the thermogravimetric analyses, the decarboxylation of **7a**–**e** can be detected between 71 and 191 °C, depending on the substitution pattern. Details are presented in Table 3. The lowest temperatures for the decarboxylation were determined for the chlorine and bromine derivatives **7b** and **7c**, respectively. By contrast, substitution of the 5-position by iodine in **7d** requires up to 191 °C for the thermal elimination of CO_2 from the solid sample.

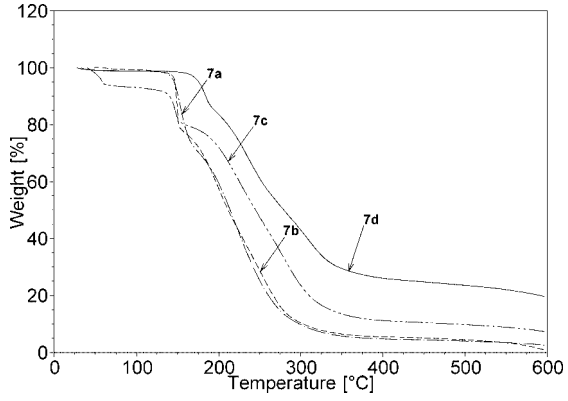


Figure 5. Thermogravimetric analyses of **7a**–**d**.

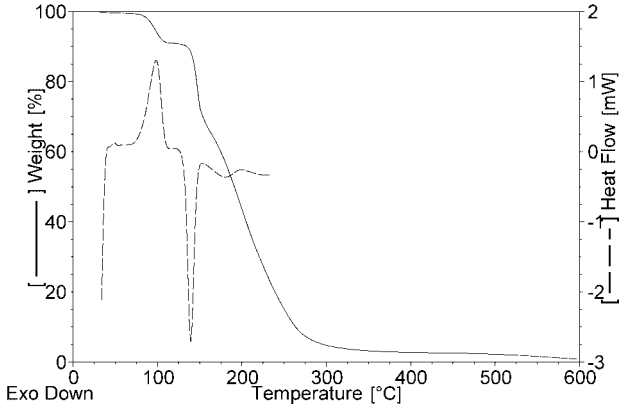


Figure 6. Combined TGA (–) and DSC (---) thermograph of **7e**.

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The DSC thermogram of unsubstituted betaine **7e** is presented in Figure 6, in combination with the TGA thermograph as a comparison. The endothermic process, detected as the maximum of the curve at 98.6 °C, displays the loss of water of crystallization and corresponds well to the TGA curve.

Table 3. Thermogravimetric data of betaines **7a**–**e**.

	Temp. range [°C]	Weight loss [%]	Species evolved	Calcd. weight loss [%]
7a	40–80	1.0	H_2O	0
	100–170	26.1	CO_2	21.1
7b	48–94	0.6	H_2O	0
	94–153	20.5	CO_2	19.6
7c	40–92	6.7	H_2O	6.3[a]
	92–154	12.3	CO_2	16.4
7d	33–71	1.0	H_2O	0
	71–191	12.7	CO_2	13.9
7e	33–116	8.9	H_2O	8.7[a]
	116–152	19.6	CO_2	23.1

[a] calcd. for 1 equiv. of water of crystallization.

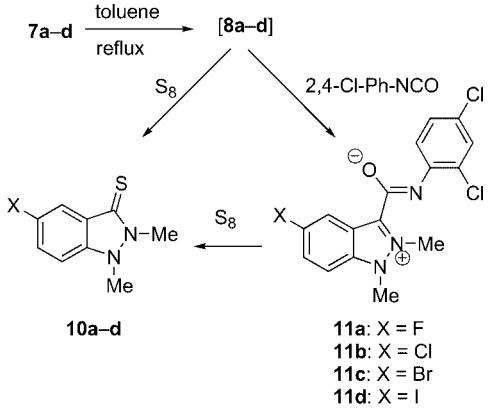
The decarboxylation can be observed at 139.5 °C by a strongly exothermic process. This value is in accord with the weight loss in the TGA. Analogous curves were obtained on examination of derivatives **7a**–**d**, respectively (see Supporting Information). Details, including the measured enthalpies of transition, are given in Table 4.

Table 4. Differential Scanning Calorimetric data of **7a**–**e**.

	Heat flow [°C]	Enthalpy of transition [J g^{-1}]
7a	147.1	121.7
7b	138.4	329.8
7c	90.9	–132.6
	138.9	119.6
7d	167.3	71.3
7e	98.6	–196.6
	139.5	201.0

Chemical Properties

The decarboxylation temperature in the solid state differs from the temperature in solution. Thus, N-heterocyclic carbenes **8a**–**d**, generated in situ from **7a**–**d** in toluene at reflux temperature, can be trapped by sulfur, which form thiones **10a**–**d** in very high yields (Scheme 4). 2,4-Dichlorophenyl isocyanate as a trapping reagent results in the formation of indazolium-3-amidates **11a**–**d** from **8a**–**d**, which



Scheme 4. Trapping experiments with in situ generated N-heterocyclic carbene.

are new representatives of the class of pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB). The extrusion of heterocumulenes from PCCMB with the formation of NHC is not restricted to carbon dioxide. Thus, amidates **11a**–**d** react with sulfur to give thiones **10a**–**d**, obviously via carbenes **8a**–**d**, formed by extrusion of 2,4-dichlorophenyl isocyanate (Scheme 4). This observation is in agreement with the aforementioned architecture of pseudo-cross-conjugated mesomeric betaines (cf. Figure 1).

Conclusions

We present 5-halogen-substituted indazolium-3-carboxylates, which decarboxylate to indazole-3-ylidenes. These undergo typical trapping reactions. The decarboxylation in the solid state can be observed by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC). In solution, additional parameters such as concentration, water of crystallization, and others also influence the formation of N-heterocyclic carbenes.

Experimental Section

5-Fluoro-,[32] 5-chloro-,[35] and 5-bromoindazole-3-carboxylic acid[32] were prepared according to literature procedures. The ^{1}H and ^{13}C NMR spectra were recorded with Bruker ARX-400 and DPX-200 spectrometers and were taken in [D$_6$]DMSO, D$_2$O, or $CDCl_3$ at 200 and 400 MHz. The chemical shifts are reported in ppm relative to internal tetramethylsilane (δ = 0.00 ppm) or HDO (δ = 4.65 ppm). Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br. = broad. Peak assignments were accomplished by results of HMBC-, HSQC-NMR, and HH-NOESY measurements. Spectroscopic data are presented here unless they are described in the literature. FTIR spectra were obtained with a Bruker Vektor 22 in the range of 400 to 4000 cm^{-1} (2.5% pellets in KBr). The GC–MS spectra (EI) were recorded either with a GC Hewlett–Packard 5980, Serie II/MS Hewlett Packard 5989 B, or a Varian GC3900 with SAT2100T mass spectrometer. Under EI conditions, the betaines decarboxylate so that the corresponding indazolium salts gave the base peaks. The ESI mass spectra were measured with an Agilent LCMSD Series HP1100 with APIES. Samples were sprayed from methanol at a fragmentor voltage of 0 V, unless otherwise noted. HRSEIMS data refer to ^{35}Cl and ^{79}Br peaks. All samples were dried for 5 h in vacuo at room temp. prior to thermogravimetric analyses and differential scanning calorimetry. The TGA were performed with a TGA 2950 and DSC examinations on DSC 2920 TA Instruments. The DSC scan rate was 5 K min^{-1}. Nitrogen purge gas was used at a flow rate of 24 mL min^{-1}. Melting points were determined with a Boëtius melting apparatus and are not corrected.

5-Fluoroindazole-3-carboxylic Acid (2a): ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 13.94 (s, 1 H), 13.07 (s, 1 H), 7.70 (m, 2 H), 7.35 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.4, 158.3 (d, J = 235 Hz), 139.1, 138.0 (d, J = 2 Hz), 122.5 (d, J = 10.7 Hz), 116.0 (d, J = 27.6 Hz), 112.9, 104.9 (d, J = 24.3 Hz) ppm.

5-Bromoindazole-3-carboxylic Acid (2c): ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 13.36 (br. s, 2 H), 8.23 (dd, J = 1.8, 0.64 Hz, 1 H), 7.67 (dd, J = 8.82, 0.64 Hz, 1 H), 7.56 (dd, J = 8.82, 1.8 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 163.4, 139.8, 135.5, 129.2, 123.8, 123.3, 115.1, 113.3 ppm. IR (KBr): $\tilde{\nu}$ = 3170, 2937, 1689, 1472, 1250 cm^{-1}.

5-Iodoindazole-3-carboxylic Acid (2d): 5-Aminoindazole-3-carboxylic acid (6.1 g, 34.5 mmol) was suspended in sulfuric acid (60%, 25 mL), heated at reflux, and cooled rapidly to 0 °C. With intense stirring, sodium nitrite (7.5 g, 108 mmol) was added in small portions within 45 min at 0 °C, and the mixture was stirred for an additional 30 min. Then, the excess nitrite was destroyed by urea and the solution was adjusted to pH 3–4 with sodium carbonate. Potassium iodide (15 g, 90 mmol) was then added, and the solution was stirred for 24 h. The precipitate was then filtered off and recrystallized from glacial acetic acid. Yield: 6.65 g (67%), m.p. 274–276 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 13.96 (br. s, 1 H), 13.16 (br. s, 1 H), 8.45 (dd, J = 1.66, 0.64 Hz, 1 H), 7.70 (dd, J = 8.7, 1.66 Hz, 1 H), 7.53 (dd, J = 8.7, 0.64 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 163.3, 140.0, 134.9, 134.4, 129.6, 124.6, 113.3, 87.2 ppm. IR (KBr): $\tilde{\nu}$ = 3243, 1688 cm^{-1}.

Methyl 5-Fluoroindazole-3-carboxylate (5a): 5-Fluoroindazole-3-carboxylic acid (**2a**; 968 mg, 5.4 mmol) was heated at reflux for 5 h in methanol (70 mL) and concentrated sulfuric acid (4 mL). Methanol was then distilled off in vacuo. The remaining oil was treated with water (100 mL) and neutralized with $NaHCO_3$. The ester was extracted with dichloromethane and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:2). Yield: 660 mg (63%), m.p. 208 °C. ^{1}H NMR (200 MHz, [D$_6$]-DMSO): δ = 14.10 (s, 1 H), 7.73 (m, 2 H), 7.38 (m, 1 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 162.2, 158.5 (d, J = 235 Hz), 137.9, 135.0 (d, J = 5.8 Hz), 122.3 (d, J = 11.1 Hz), 116.3 (d, J = 27.6 Hz), 113.0 (d, J = 9.9 Hz), 104.8 (d, J = 24.7 Hz), 51.6 ppm. IR (KBr): $\tilde{\nu}$ = 3283, 1727, 1481, 1224 cm^{-1}. MS: m/z (%) = 194 (100). HRESIMS: calcd for $C_9H_8FN_2O_2$ 195.0564; found 195.0565.

Methyl 5-Chloroindazole-3-carboxylate (5b): A sample of 5-chloroindazole-3-carboxylic acid (**2b**; 3 g, 15.2 mmol) in methanol (300 mL) and concentrated sulfuric acid (15 mL) was heated at reflux for 5 h. Methanol was then distilled off in vacuo, and the residue was treated with water (400 mL) and neutralized with $NaHCO_3$. The ester was extracted with dichloromethane and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:2). Yield: 1.8 g (43%), m.p. 212 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 14.14 (s, 1 H), 8.05 (s, 1 H), 7.72 (d, J = 8.9 Hz, 1 H), 7.47 (d, J = 8.9 Hz, 1 H), 3.95 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 162.2, 139.3, 134.6, 127.5, 127.0, 122.9, 119.8, 113.0, 51.7 ppm. IR (KBr): $\tilde{\nu}$ = 3266, 1687, 1492, 1254 cm^{-1}. MS: m/z (%) = 210 (100). HRESIMS: calcd for $C_9H_8ClN_2O_2$ 211.0269; found 211.0252. $C_9H_7ClN_2O_2$ (210.62): calcd. C 51.32, H 3.35, N 13.30; found C 51.38, H 2.97, N 13.21.

Methyl 5-Bromoindazole-3-carboxylate (5c): 5-Bromoindazole-3-carboxylic acid (**2c**; 0.6 g, 2.5 mmol) was dissolved in methanol (50 mL) and concentrated sulfuric acid (4 mL), and the solution was heated at reflux for 5 h. Methanol was then distilled off in vacuo, and the residue was treated with cold water (100 mL) and neutralized with $NaHCO_3$. The ester precipitated and was filtered off. Yield: 0.60 g (96%), m.p. 208–210 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 14.16 (s, 1 H), 8.20 (s, 1 H), 7.60 (m, 2 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 162.2, 139.6, 134.9, 129.5, 123.5, 123.0, 115.6, 113.3, 51.7 ppm. IR (KBr): $\tilde{\nu}$ = 3429, 3183, 2950, 1732, 1479, 1232 cm^{-1}. MS: m/z (%) = 254 (100). HRESIMS: calcd for $C_9H_8BrN_2O_2$ 254.9764; found 255.0952.

Methyl 5-Iodoindazole-3-carboxylate (5d): 5-Iodoindazole-3-carboxylic acid (3.56 g, 12.4 mmol) was suspended in methanol (300 mL) and sulfuric acid (24 mL) and heated at reflux for 6 h.

The solution was concentrated in vacuo, poured into cold water (150 mL), and neutralized with aqueous sodium carbonate solution. The resulting precipitate was then filtered off. Yield: 3.58 g (96%), m.p. 232–235 °C (dec.). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 8.43 (dd, J = 1.66, 0.64 Hz, 1 H), 7.71 (dd, J = 8.82, 1.66 Hz, 1 H), 7.55 (dd, J = 8.82, 0.64 Hz, 1 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 162.3, 139.9, 134.6, 133.9, 129.3, 124.3, 113.5, 87.7, 51.7 ppm. IR (KBr): $\tilde{\nu}$ = 3217, 1689, 1483, 1244 cm^{-1}. MS: *m*/*z* (%) = 302 (100). HRESIMS: calcd for $C_9H_8IN_2O_2$ 302.9625; found 302.9560.

5-Fluoro-1,2-dimethylindazolium-3-carboxylate (7a): A solution of methyl 5-fluoroindazole-3-carboxylate (**5a**; 400 mg, 2.06 mmol) and nitrobenzene (0.1 mL) in xylene (10 mL) was heated at reflux. Dimethyl sulfate (0.6 mL, 6.3 mmol) was then added. Heating was continued for one additional hour, before the solvent was distilled off in vacuo. The resulting brown oil was treated with KOH (1 N in methanol, 60 mL) and stirred overnight. The solution was then neutralized with concentrated HCl, and the solvents were evaporated to dryness. The resulting residue was chromatographed (silica gel, MeOH). Yield: 294 mg (67%), m.p. 126–129 °C (dec.). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.05 (m, 2 H), 7.76 (m, 1 H), 4.67 (s, 3 H), 4.23 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 160.2 (d, J = 239 Hz), 157.6, 140.3 (d, J = 7.3 Hz), 136.7, 123.1 (d, J = 28.4 Hz), 120.1 (d, J = 12.4 Hz), 113.7 (d, J = 9.5 Hz), 108.7 (d, J = 25.5 Hz), 35.7, 33.7 ppm. IR (KBr): $\tilde{\nu}$ = 3021, 1652, 1466, 1241 cm^{-1}. MS: *m*/*z* (%) = 165 (100) [M – CO_2 + H]$^+$, 209 (<1) [M + H]$^+$. HRESIMS: calcd for $C_{10}H_{10}FN_2O_2$ 209.00726; found 209.0724.

5-Chloro-1,2-dimethylindazolium-3-carboxylate (7b): A sample of methyl 5-chloroindazole-3-carboxylate (**5b**; 1.2 g, 5.6 mmol) was heated in nitromethane (35 mL) at reflux, and then treated with dimethyl sulfate (1.6 mL, 16.8 mmol). Heating at reflux was continued for 4 h, and then the solvent was distilled off in vacuo. To the resulting brown oil was added KOH (1 N in methanol, 100 mL). After stirring for 24 h, the KOH was neutralized with concentrated HCl. After evaporation to dryness, the betaine was extracted with ethanol, evaporated to dryness, and chromatographed (MeOH, SiO_2). Yield: 865 mg (69%), m.p. 127–131 °C (dec.). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 8.42 (dd, J = 2.06, 0.78 Hz, 1 H), 8.03 (dd, J = 9.2, 0.78 Hz, 1 H), 7.83 (dd, J = 9.2, 2.06 Hz, 1 H), 4.67 (s, 3 H), 4.22 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 156.9, 139.4, 137.5, 132.5, 128.7, 123.5, 120.2, 112.8, 35.1, 33.1 ppm. IR (KBr): $\tilde{\nu}$ = 3046, 1650, 1329, 739 cm^{-1}. MS: *m*/*z* (%) = 181 (100) [M – CO_2 + H]$^+$, 225 (<1) [M + H]$^+$. HRESIMS: calcd for $C_{10}H_{10}ClN_2O_2$ 225.0431; found: 225.0431.

5-Bromo-1,2-dimethyl-1*H*-indazolium-3-carboxylate (7c): To a solution of methyl 5-bromoindazole-3-carboxylate (**5c**; 523 mg; 2.06 mmol) and nitrobenzene (0.1 mL) in xylene (10 mL)was added dimethyl sulfate (0.25 mL 2.64 mmol) at reflux temperature. Heating was continued for an additional hour. Then, the solvent was distilled off in vacuo. To the remaining brownish oil was added KOH (1 N in methanol, 60 mL), and the mixture was stirred for 24 h, neutralized with concentrated HCl, and the solvents evaporated to dryness. The residue was chromatographed (silica gel, MeOH). Yield: 243 mg (44%), m.p. 131–135 °C, the compound darkens and decomposes at 143–144 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 8.61 (dd, J = 1.66, 1.02 Hz, 1 H), 7.96 (m, 2 H), 4.67 (s, 3 H), 4.22 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 157.4, 139.7, 138.1, 135.4, 127.3, 121.4, 117.2, 113.5, 35.6, 33.6 ppm. IR (KBr): $\tilde{\nu}$ = 3040, 1649, 1327 cm^{-1}. MS: *m*/*z* (%) = 225 (100) [M – CO_2 + H]$^+$, 269 (<1) [M + H]$^+$. HRESIMS: calcd for $C_{10}H_{10}BrN_2O_2$ 268.9920; found 268.9922.

5-Iodo-1,2-dimethylindazolium-3-carboxylate (7d): A boiling solution of methyl 5-iodoindazole-3-carboxylate (3.46 g, 12 mmol) and nitrobenzene (0.1 mL) in xylene (80 mL) was treated with dimethyl sulfate (34 mL, 35 mmol), and the mixture was heated over a period of 1 h. Then, the solvent was distilled off. The resulting brown oil was treated with KOH (1 N in methanol, 150 mL), and the solution was stirred overnight. Then, the solution was neutralized with concentrated HCl and evaporated to dryness, and the residue was chromatographed (silica gel, MeOH). Yield: 1.05 g (28%), m.p. 156–159 °C (dec.). ^{1}H NMR (200 MHz, D_2O): δ = 8.55 (dd, J = 1.66, 0.76 Hz, 1 H), 8.03 (dd, J = 9.2, 1.66 Hz, 1 H), 7.55 (dd, J = 9.2, 0.76 Hz, 1 H), 4.56 (s, 3 H), 4.27 (s, 3 H) ppm. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.81 (dd, J = 1.6, 0.8 Hz, 1 H), 8.00 (dd, J = 9.0, 1.6 Hz, 1 H), 7.62 (dd, J = 9.0, 0.8 Hz, 1 H), 4.63 (s, 3 H), 4.21 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 159.8, 141.1, 138.7, 137.8, 133.3, 121.9, 111.9, 88.6, 34.9, 32.2 ppm. IR (KBr): $\tilde{\nu}$ = 3425, 3007, 1647, 1320, 740 cm^{-1}. MS: *m*/*z* (%) = 273 (100) [M – CO_2 + H]$^+$, 317 (<1) [M + H]$^+$. HRESIMS: calcd for $C_{10}H_{10}IN_2O_2$ 316.9787; found 316.9786.

5-Fluoro-1,2-dihydro-1,2-dimethylindazole-3-thione (10a): 5-Fluoro-1,2-dimethylindazolium-3-carboxylate (7**a**; 84 mg, 4 mmol) and sulfur (150 mg) in toluene (10 mL) was heated at reflux for 1 h. Then, the solvent was distilled off, and the residue was chromatographed (silica gel, EtOAc/petroleum ether, 1:1). Yield: 78 mg (99%), m.p. 158 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.67 (m, 1 H), 7.33 (m, 1 H), 7.19 (m, 1 H), 3.97 (s, 3 H), 3.61 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.9 (d, J = 9.89 Hz), 158.8 (d, J = 240.2 Hz), 141.1, 127.5 (d, J = 9.4 Hz), 120.9 (d, J = 26.8 Hz), 111.3 (d, J = 8.7 Hz), 110.1 (d, J = 24.3 Hz), 35.8, 32.6 ppm. IR (KBr): $\tilde{\nu}$ = 3045, 1584 cm^{-1}. MS: *m*/*z* (%) = 196. HRESIMS: calcd for $C_9H_{10}FN_2S$ 197.0549; found 197.0547.

5-Chloro-1,2-dihydro-1,2-dimethylindazole-3-thione (10b): Under an inert atmosphere, 5-chloro-1,2-dimethylindazolium-3-carboxylate (**7b**; 70 mg, 0.333 mmol) and sulfur (150 mg) were heated at reflux in toluene (10 mL) for 1 h. Then, the solvent was distilled off, and the residue was chromatographed (silica gel, EtOAc/petroleum ether, 1:1). Yield: 70 mg (99%), m.p. 156 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.00 (dd, J = 2.04, 0.64 Hz, 1 H), 7.50 (dd, J = 8.7, 2.0 Hz, 1 H), 7.16 (d, J = 8.7, 0.6 Hz, 1 H), 3.97 (s, 3 H), 3.63 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.3, 142.5, 132.5, 128.4, 127.7, 124.6, 111.0, 35.5, 32.5 ppm. IR (KBr): $\tilde{\nu}$ = 3038, 1469, 1169, 798 cm^{-1}. MS: *m*/*z* = 212. HRESIMS: calcd for $C_9H_{10}ClN_2S$ 213.0253; found 213.0258. $C_9H_9ClN_2S$ (212.70): calcd. C 50.82, H 4.26, N 13.17, S 15.08; found C 50.65, H 4.58, N 13.14, S 15.18.

5-Bromo-1,2-dihydro-1,2-dimethylindazole-3-thione (10c): 5-Bromo-1,2-dimethylindazolium-3-carboxylate (**4c**; 107.6 mg, 0.4 mmol) and sulfur (200 mg) were heated at reflux in toluene (10 mL) for 1 h. The solvent was then distilled off, and the residue was chromatographed (silica gel, EtOAc). Yield: 83 mg (81%), m.p. 177 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.14 (m, 1 H), 7.63 (dd, J = 8.7, 1.8 Hz, 1 H), 7.11 (dd, J = 8.7, 1.8 Hz, 1 H), 3.96 (s, 3 H), 3.63 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.1, 142.7, 135.0, 128.2, 127.8, 115.5, 111.3, 35.3, 32.4 ppm. IR (KBr): $\tilde{\nu}$ = 3341, 1620, 1468, 1223 cm^{-1}. MS: *m*/*z* = 256. HRESIMS: calcd for $C_9H_{10}BrN_2S$ 256.9748; found 256.9740. $C_9H_9BrN_2S$ (257.15): calcd. C 42.04, H 3.53, N 10.89, S 12.47; found C 42.20, H 3.74, N 10.54, S 12.13.

5-Iodo-1,2-dihydro-1,2-dimethylindazole-3-thione (10d): Under an inert atmosphere, 5-iodo-1,2-dimethylindazolium-3-carboxylate (**7d**; 158 mg, 0.5 mmol) and sulfur (250 mg) were heated at reflux in toluene (10 mL) over a period of 1 h. Then, the solvent was

distilled off, and the residue was chromatographed (silica gel, EtOAc/petroleum ether, 1:1). Yield: 100 mg (65%), m.p. 224–226 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 8.05 (dd, J = 1.78, 0.52 Hz, 1 H), 7.87 (dd, J = 8.7, 1.78 Hz, 1 H), 7.50 (dd, J = 8.7, 0.52 Hz, 1 H), 3.93 (s, 3 H), 3.79 (s, 3 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 165.4, 141.3, 139.3, 132.0, 127.2, 112.9, 84.6, 34.2, 31.8 ppm. IR (KBr): $\tilde{\nu}$ = 3441, 1611, 1321 cm^{-1}. MS: m/z = 304. HRESIMS: calcd for $C_9H_{10}IN_2S$ 304.9609; found 304.9585. $C_9H_9IN_2S$ (304.15): calcd. C 35.54, H 2.98, N 9.21, S 10.54; found C 35.61, H 3.12, N 9.14, S 10.74.

***N*-(2,4-Dichlorophenyl)-5-fluoro-1,2-dimethylindazolium-3-amidate (11a):** A sample of mesomeric betaine (**7a**; 156 mg, 0.75 mmol) and 2,4-dichlorophenyl isocyanate (141 mg, 0.75 mmol) were suspended in toluene (12 mL)and heated at reflux for 1 h. After cooling, the precipitate was filtered off and washed with toluene (2 × 5 mL) and ethanol (1 mL). Yield: 100 mg (38%), m.p. 211–212 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.75 (dd, J = 9.38, 2.5 Hz, 1 H), 8.38 (d, J = 8.8 Hz, 1 H), 8.06 (dd, J = 9.38, 4.1 Hz, 1 H), 7.77 (m, 1 H), 7.41 (d, J = 2.5 Hz, 1 H), 7.17 (dd, J = 8.8, 2.5 Hz, 1 H), 4.86 (s, 3 H), 4.25 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.0 (d, J = 238.4 Hz), 158.4, 147.6, 141.7 (d, J = 6.6 Hz), 136.8, 128.8, 128.4, 126.8, 126.1, 123.4, 123.0 (d, J = 28.4 Hz), 119.9 (d, J = 12.4 Hz), 113.5 (d, J = 9.5 Hz), 110.2 (d, J = 26.2 Hz), 36.2, 33.7 ppm. IR (KBr): $\tilde{\nu}$ = 3441, 1593, 1460, 1343 cm^{-1}. HRESIMS: calcd for $C_{16}H_{13}Cl_2FN_3O$ 352.0420; found 352.0421.

5-Chloro-*N*-(2,4-dichlorophenyl)-1,2-dimethylindazolium-3-amidate (11b): Betaine **7b** (105 mg, 0.5 mmol) and 2,4-dichlorophenyl isocyanate (94 mg, 0.5 mmol) were suspended in toluene (10 mL) and heated at reflux for 1 h. After cooling, the precipitate was filtered off and washed with toluene (2 × 5 mL). Yield: 130 mg (73%). ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.16 (dd, J = 2.1, 0.64 Hz, 1 H), 8.38 (d, J = 8.82 Hz, 1 H), 8.03 (dd, J = 9.2, 0.64 Hz, 1 H), 7.83 (dd, J = 9.2, 2.1 Hz, 1 H), 7.41 (d, J = 2.56 Hz, 1 H), 7.18 (dd, J = 8.82, 2.56 Hz, 1 H), 4.86 (s, 3 H), 4.24 (s, 3 H) ppm. ^{13}C NMR not measured because of insufficient solubility. IR (KBr): $\tilde{\nu}$ = 3010, 1564, 1460 cm^{-1}. HRESIMS: calcd for $C_{16}H_{13}Cl_3N_3O$ 368.0119; found 368.0124. $C_{16}H_{12}Cl_3N_3O$ (368.65): calcd. C 52.13, H 3.28, N 11.40; found C 51.81, H 2.853, N 11.33.

5-Bromo-*N*-(2,4-dichlorophenyl)-1,2-dimethylindazolium-3-amidate (11c): A sample of mesomeric betaine **7c** (135 mg, 0.5 mmol) and 2,4-dichlorophenyl isocyanate (94 mg, 0.5 mmol) were suspended in toluene (10 mL) and heated at reflux for 1 h. After cooling, the precipitate was filtered off and washed with toluene (2 × 5 mL) and ethanol (1 mL). Yield: 170 mg (82.3%), m.p. 221 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 8.75 (dd, J = 9.38, 2.52 Hz, 1 H), 8.38 (d, J = 8.8 Hz, 1 H), 8.06 (dd, J = 9.38, 4.1 Hz, 1 H), 7.77 (m, 1 H), 7.41 (d, J = 2.52 Hz, 1 H), 7.17 (dd, J = 8.8, 2.56 Hz, 1 H), 4.86 (s, 3 H), 4.25 (s, 3 H) ppm. ^{13}C NMR not measured because of insufficient solubility. IR (KBr): $\tilde{\nu}$ = 3440, 1587, 1458, 1342 cm^{-1}. HRESIMS: calcd for $C_{16}H_{13}BrCl_2N_3O$ 441.9619; found 441.9622. $C_{16}H_{12}BrCl_2N_3O{\cdot}0.5H_2O$ (422.10): calcd. C 45.53, H 3.10, N 9.95; found C 45.28, H 2.61, N 10.20.

***N*-(2,4-Dichlorophenyl)-5-iodo-1,2-dimethylindazolium-3-amidate (11d):** A sample of mesomeric betaine **7d** (159 mg, 0.5 mmol) and 2,4-dichlorophenyl isocyanate (94 mg, 0.5 mmol) were suspended in toluene (10 mL) and heated at reflux for 1 h. After cooling, the precipitate was filtered off and washed with toluene (2 × 5 mL) and methanol (10 mL). Yield: 107 mg (46%), m.p. 220 °C. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.61 (dd, J = 1.14 Hz, 1 H), 8.40 (d, J = 8.82 Hz, 1 H), 8.04 (dd, J = 8.96, 1.6 Hz, 1 H), 7.81 (d, J = 8.96 Hz, 1 H), 7.41 (d, J = 2.48 Hz, 1 H), 7.17 (dd, J = 8.82, 2.48 Hz, 1 H), 4.85 (s, 3 H), 4.23 (s, 3 H) ppm. ^{13}C NMR not measured because of insufficient solubility. IR (KBr): $\tilde{\nu}$ = 3441, 1585, 1456, 1340 cm^{-1}. HRESIMS: calcd for $C_{16}H_{13}Cl_2IN_3O$ 459.9475; found 459.9480. $C_{16}H_{12}Cl_2IN_3O{\cdot}0.5H_2O$ (469.10): calcd. C 40.97, H 2.79, N 8.96; found C 41.05, H 2.25, N 8.92.

General Procedure for the Preparation of Thiones 10a–d Starting from Amidates 11a–d: To a suspension of amidate **11a**–**d** (0.2 mmol) in toluene (5 mL) was added sulfur (52 mg, 1.6 mmol), and the mixture was then heated at reflux for 3 h. The solvent was then distilled off in vacuo, and the residue was chromatographed (silica gel, EtOAc/petroleum ether, 1:2). Yields: 10–20%. All spectroscopic data are in agreement to those described above.

Supporting Information (see also the footnote on the first page of this article): Drawing of the elemental cell of **7e**, the TGA/DSC curves of **7a**–**d**, and the structure refinement data of **7e**.

Acknowledgments

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support. Dr. Gerald Dräger (University of Hannover, Germany) is gratefully acknowledged for measuring the HRESIMS spectra.

[1] H.-W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75; H.-W. Wanzlick, H.-J. Schönherr, *Angew. Chem.* **1968**, *80*, 154; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141; K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42.
[2] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[3] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.
[4] D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, *107*, 1119; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2021.
[5] A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *Liebigs Ann./Recueil* **1997**, *113*, 365.
[6] A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027.
[7] R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen, *Angew. Chem.* **1996**, *108*, 1211; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1221.
[8] R. W. Alder, C. P. Butts, A. G. Orpen, *J. Am. Chem. Soc.* **1998**, *120*, 11526.
[9] S. Solé, H. Gornitzka, W. W. Schoeller, D. Bourrissou, G. Bertrand, *Science* **2001**, *292*, 1901.
[10] F. Zeng, Z. Yu, *J. Org. Chem.* **2006**, *71*, 5274.
[11] A. Sánchez Pelegrí, M. R. J. Elsegood, V. McKee, G. W. Weaver, *Org. Lett.* **2006**, *8*, 3049; A. W. Waltman, T. Ritter, R. H. Grubbs, *Organometallics* **2006**, *25*, 4238.
[12] I. G. Jung, J. Seo, S. I. Lee, S. Y. Choi, Y. K. Chung, *Organometallics* **2006**, *25*, 4240.
[13] A. P. Dove, R. C. Pratt, B. G. G. Lohmeijer, D. A. Culkin, E. C. Hagberg, G. W. Nyce, R. M. Waymouth, J. L. Hedrick, *Polymer* **2006**, *47*, 4018.
[14] G. C. Lloyd-Jones, R. W. Alder, G. J. J. Owen-Smith, *Chem. Eur. J.* **2006**, *12*, 5361.
[15] A. E. Mattson, A. R. Bharadwaj, A. M. Zuhl, K. A. Scheidt, *J. Org. Chem.* **2006**, *71*, 5715.
[16] A. J. Boydston, C. W. Bielawski, *Dalton Trans.* **2006**, 4073.
[17] Y. Kageyama, S. Murata, *J. Org. Chem.* **2005**, *70*, 3140; K. Zeitler, *Org. Lett.* **2006**, *8*, 637.
[18] J. J. Song, F. Gallou, J. T. Reeves, Z. Tan, N. K. Yee, C. H. Senanayake, *J. Org. Chem.* **2006**, *71*, 1273.
[19] V. Nair, S. Vellalath, M. Poonoth, R. Mohan, E. Suresh, *Org. Lett.* **2006**, *8*, 507.
[20] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815.

[21] H. W. Wanzlick, H. J. Schönherr, *Justus Liebigs Ann. Chem.* **1970**, *731*, 176; H. J. Schönherr, H. W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037.
[22] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561.
[23] W. D. Ollis, S. P. Stanforth, C. A. Ramsden, *Tetrahedron* **1985**, *41*, 2239.
[24] A. Schmidt, *Curr. Org. Chem.* **2004**, *8*, 653.
[25] A. R. Katritzky, R. Awartani, R. C. Patel, *J. Org. Chem.* **1982**, *47*, 498; A. R. Katritzky, H. M. Faid-Allah, *Synthesis* **1983**, 149; P. Haake, J. Mantecón, *J. Am. Chem. Soc.* **1964**, *86*, 5230; K. T. Potts, G. S. Mattingly, *J. Org. Chem.* **1968**, *33*, 3985.
[26] H. Quast, E. Schmitt, *Justus Liebigs Ann. Chem.* **1970**, *732*, 43.
[27] A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 17624; R. H. Crabtree, *J. Organomet. Chem.* **2006**, *691*, 3146; H. A. Duong, T. N. Tekavec, A. M. Arif, J. Louie, *Chem. Commun.* **2004**, 112; P. Haake, L. P. Bausher, J. P. McNeal, *J. Am. Chem. Soc.* **1971**, *93*, 7045.
[28] A. Schmidt, T. Habeck, *Lett. Org. Chem.* **2005**, *2*, 37; A. Schmidt, T. Habeck, L. Merkel, M. Mäkinen, P. Vainiotalo, *Rapid Commun. Mass Spectrom.* **2005**, *19*, 2211.
[29] A. Schmidt, A. Beutler, T. Habeck, T. Mordhorst, B. Snovydovych, *Synthesis* **2006**, 1882; A. Schmidt, L. Merkel, W. Eisfeld, *Eur. J. Org. Chem.* **2005**, 2124.
[30] J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, *Chem. Commun.* **2003**, 28; K. Ishiguro, K. Hirabayashi, T. Nojima, Y. Sawaki, *Chem. Lett.* **2002**, 796; N. Kuhn, M. Steimann, G. Weyers, *Z. Naturforsch., Teil B* **1999**, *54*, 427; N. Kuhn, H. Bohnen, G. Henkel, *Z. Naturforsch., Teil B* **1994**, *49*, 1473; N. Kuhn, E. Niquet, M. Steimann, I. Walker, *Z. Naturforsch., Teil B* **1999**, *54*, 1181; N. Kuhn, M. Steimann, G. Weyers, G. Henkel, *Z. Naturforsch., Teil B* **1999**, *54*, 434; N. Kuhn, H. Bohnen, J. Fahl, D. Blaser, R. Boese, *Chem. Ber.* **1996**, *129*, 1579; N. Kuhn, J. Fahl, R. Fawzi, C. Maichle-Mossmer, M. Steimann, *Z. Naturforsch., Teil B* **1998**, *53*, 720; H.-J. Schönherr, H.-W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037; W. Schössler, M. Regitz, *Chem. Ber.* **1974**, *107*, 1931.
[31] For recent publications, see: A. Schmidt, A. Lindner, M. Nieger, M. C. Ruiz Delgado, F. J. Ramírez, *Org. Biomol. Chem.* **2006**, *4*, 3056; A. Schmidt, A. Gholipour Shilabin, J. C. Namyslo, M. Nieger, S. Hemmen, *Eur. J. Org. Chem.* **2005**, 1781; A. Schmidt, A. Gholipour Shilabin, M. Nieger, *Org. Biomol. Chem.* **2003**, *1*, 4342.
[32] N. P. Buu-Hoi, J. P. Hoeffinger, P. Jacquignon, *J. Heterocycl. Chem.* **1964**, *1*, 239.
[33] K. v. Auwers, H. Lange, *Ber. Dtsch. Chem. Ges.* **1922**, *55B*, 1139.
[34] CCDC-636295 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[35] G. Büchi, G. C. M. Lee, D. Yang, S. R. Tannenbaum, *J. Am. Chem. Soc.* **1986**, *108*, 4115.

Received: March 5, 2007
Published Online: August 10, 2007

