Complexes of Group 13 metals with redox-active ligands as catalysts for the hydroamination of carbodiimides

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Complexes of Group 13 elements with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) catalyze the addition of aromatic amines (4-chloroaniline and 1-aminonaphthalene) and diphenylmethylidenehydrazine to carbodiimides.

Key words: boron, aluminum, gallium, diimines, carbodiimides, catalysis.

Nitrogen-containing σ-donating ligands take an important part in the development of modern coordination chemistry. This class of ligands has been used to prepare stable complexes of Main Group elements in low oxidation states, including N-heterocyclic silylenes,[1,2] germylenes,[1,3] stannylenes,[1,3] and phosphenes,[4—6] as well as complexes containing metal—metal bonds.[7] Some transition metal complexes with nitrogen-containing σ-donating ligands catalyze chemical reactions (*e.g.*, alkene and diene polymerizations).[8—12] So-called redox-active ligands capable of reversibly accepting and donating electrons constitute a special subgroup of nitrogen-containing σ-donating ligands. Because of their redox activity, a number of Main Group metal complexes with such ligands have been obtained and involved in uncharacteristic reactions with various organic compounds.[13—17] Gallium and aluminum complexes with redox-active 1,2-bis[(2,6-diisopropylphenyl)-imino]acenaphthene (dpp-bian) have been successfully employed for catalytic hydroamination and hydroarylation of alkynes with aromatic amines.[18—20] Since catalytic systems combining a Main Group metal and a redox-active ligand are highly efficient, we found it possible to extend the range of organic substrates to be functionalized.

In the present work, we tested boron, aluminum, and gallium complexes with 1,2-diiminoacenaphthene for catalytic activity in the hydroamination of carbodiimides with 4-chloroaniline, 1-aminonaphthalene, and diphenylmethylidenehydrazine. It should be noted that the guanidines formed in the hydroamination of carbodiimides are widely used in pharmaceutics,[21—25] food industry,[26,27] agriculture,[28,29] and some other areas.[29]

Results and Discussion

Considering the results of our recent investigations into alkyne functionalization, we decided to study carbodiimides containing, like alkynes, an sp-hybridized C atom. The hydroamination of carbodiimides in the presence of various metal complexes has been described.[30] However, only a few examples refer to compounds of Group 13 elements, *viz.*, guanidinate complexes of aluminum, alkylaluminum compounds, and aluminum trichloride.[30,31] Neither gallium nor boron compounds are so far known to catalyze such reactions. For this reason, we studied the catalytic activity of some mono- and dinuclear bisamide complexes of Group 13 elements with the dpp-bian ligand in the hydroamination of carbodiimides with aromatic amines. 4-Chloroaniline (**1a**) was chosen as an aminating agent because of the most rapid quantitative formation of the product in the hydroamination of phenylacetylene with 4-chloroaniline compared to other aromatic amines.[18] Dicyclohexyl- and diisopropylcarbodiimides were chosen for they are easily accessible and most commonly used substrates.

We found that carbodiimides $R^2N{=}C{=}NR^2$ (**2**, $R^2 = Pr^i$ or Cy) react with such aromatic amines as 4-chloroaniline (**1a**) and 1-aminonaphthene (**1b**) as well as with diphenylmethylidenehydrazine (**1c**) in the presence of 1,2-diiminoacenaphthylene derivatives of Group 13 elements (**A**—**F**) to give substituted guanidines **3** (Scheme 1).

The catalytic activity of compounds **A**—**F** varies broadly. Their activity characteristics and the reaction conditions are given in Table 1. Digallane **A** is the most efficient catalyst (see Table 1). When its concentration is lowered from 2 to 0.5 mol.%, the yields of guanidines decreases. The dicyclohexylcarbodiimide-containing system is the most sensitive to this factor: over the same time interval (1.3 h), the yield of the guanidine derivative drops from 80 to 26% (see Table 1, entries *1* and *3*). At the same time, the yield of the guanidine derived from diisopropylcarbodiimide decreases only by a quarter (from 58 to 43%) when the concentration of the catalyst is lowered by a factor of 4 (see

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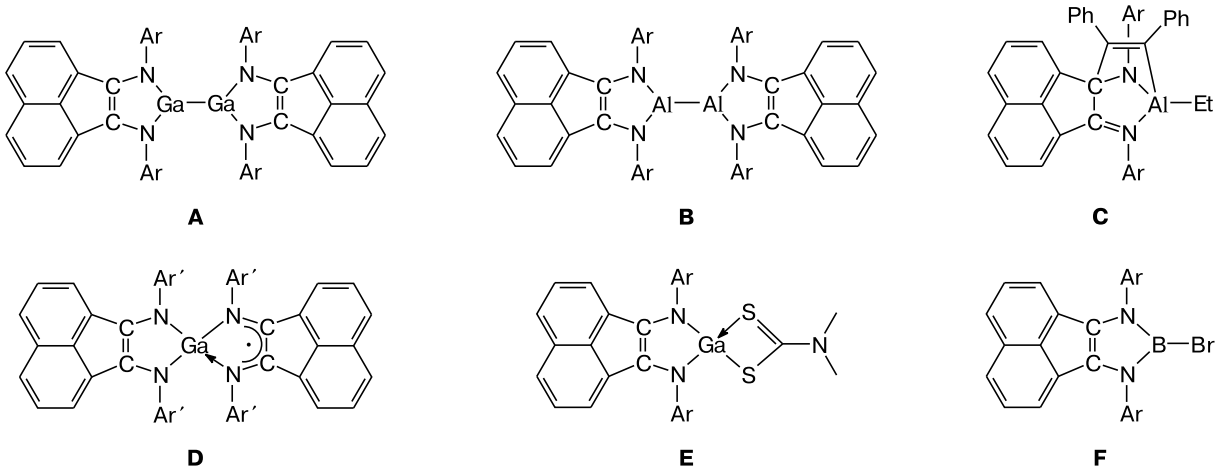


Ar = 2,6-Pr^i_2—C_6H_3; Ar′ = 2,6-Me_2—C_6H_3

Scheme 1

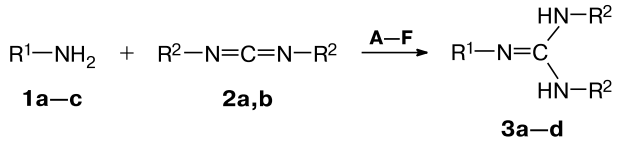
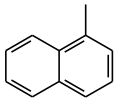
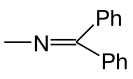


Table 1, entries *2* and *4*). This fact can be explained by a difference in the early kinetics of the reactions of the substrates with digallane, this difference itself being primarily due to steric factors (the size of the alkyl groups of the carbodiimide). In addition, the guanidine product can poison the catalyst. The guanidines containing the isopropyl and cyclohexyl substituents are differently tolerated by the catalyst: the latter interacts with digallane more actively.

The resulting guanidines show limited solubility in nonpolar media, including deuterated benzene and deuterated toluene, in contrast to the starting reaction mixture. In polar THF-d_8, which is a better solvent for the product than aromatic compounds, 4-chloroaniline reacts with dicyclohexylcarbodiimide more slowly (see Table 1, entry *5*).

Table 1. Hydroamination[a] of the carbodiimides in the presence of catalysts **A**—**F**

Entry	Catalyst [Cat]	[Cat] (mol.%)	*T*/°C	R^1	R^2	τ/h	Yields of products **3a**—**d** (%)
1	**A**[a]	2	20	4-ClC_6H_4	Cy	1.3	**3a**, 80
2	**A**[a]	2	20	Same	Pr^i		**3b**, 58
3	**A**[a]	0.5	20	»	Cy		**3a**, 26
4	**A**[a]	0.5	20	»	Pr^i		**3b**, 43
5	**A**[b]	2	20	»	Cy		**3a**, 39
6	**F**[a]	4	80	»	Cy		**3a**, 37
7	**A**[a]	2	20		Cy	1.3	**3c**, 26
8	**A**[a]	2	60	Same	Cy		**3c**, 97
9	**B**[a]	2	20	4-ClC_6H_4	Cy	10	**3a**, 39
10	**B**[a]	2	20	Same	Pr^i		**3b**, 45
11	**C**[a]	4	20	»	Cy		**3a**, 33
12	**C**[a]	4	20	»	Pr^i		**3b**, 41
13	**D**[c]	4	20	4-ClC_6H_4	Cy	100	**3a**, 26
14	**E**[c]	4	20	Same	Cy		**3a**, 69
15	**A**[a]	0.5	80		Cy	100	**3d**, 65

[a] In C_6D_6. [b] In THF-d_8. [c] In toluene-d_8.

This unexpected fact can be explained by competitive coordination of the substrate and THF to the catalyst at one of the reaction steps.

The reaction rate decreases appreciably when moving from digallane to mononuclear gallium complexes: comparable yields are achieved in a much longer period of time (100 h and more; see Table 1, entries *13* and *14*). The lowest rate of guanidine formation was noted for derivative **D** containing two identical ligands (though one as a dianion and the other as a radical anion), which makes the metal atom less accessible to the substrate. In digallane **A**, the Ga—Ga bond length is 2.36 Å. In addition, solvent molecules are not coordinated to the metal atom, so it is less shielded. In dithiocarbamate complex **E**, the metal atom is coordinatively saturated (coordination number 4) and shielded more considerably than that in digallane **A** because of the coordination with two S atoms. The Ga—S bond (2.31 Å) in complex **E** is comparable in length with the Ga—Ga bond in compound **A**. In derivative **D**, the steric hindrances are even greater because of the larger substituents.

For dialane **B**, which is isostructural with digallane **A**, the same reactions under similar conditions proceed at rates 10—20 times lower (see Table 1, entries *9* and *10*). The yield of *N*-(4-chlorophenyl)-*N′*,*N″*-dicyclohexylguanidine in the presence of dialane **B** over 10 h is half that achieved in an analogous reaction catalyzed by digallane **A** over 1.3 h (39 and 80%, respectively). Earlier, we have demonstrated that dialane **B**, unlike digallane **A**, exhibit some properties of a Lewis acid, including coordination with pyridine.[20] The lower catalytic activity of dialane **B** compared to digallane **A** can be explained by the formation of a kinetically inert, coordinatively saturated adduct *via* coordination of anilines with dialane **B**. Within the series of aluminum derivatives, the reaction rate remains virtually unchanged when moving from dialane **B** to mononuclear ethyl complex **C** (see Table 1, entries *11* and *12*). In this complex, the attached diphenylacetylene molecule is mobile and promptly eliminated in reactions of the complex with basic substrates. This elimination is accompanied by a color change observed when a mixture of aniline and carbodiimide is added to complex **C**. The red-brown color characteristic of the addition complex of diphenylacetylene turns blue, which is inherent in aluminum complexes with the dpp-bian dianion. Compounds **B** and **C** are both less active for dicyclohexylcarbodiimide than for diisopropylcarbodiimide. The yields of product **3a** in the presence of catalysts **B** and **C** are lower than those of product **3b** by 6 and 8%, respectively (see Table 1, entries *9—12*).

Mononuclear boron complex **F** does not catalyze a room-temperature reaction of 4-chloroaniline with dicyclohexylcarbodiimide. However, the same reaction at 80 °C affords a guanidine product in 37% yield over 1.3 h, which is comparable with the guanidine yields achieved in the presence of digallane **A** (see Table 1, entry *6*). Thus, we were the first to do gallium- and boron-catalyzed hydroamination of carbodiimides with substituted anilines.

Earlier, we have demonstrated that a reaction of 1-aminonaphthalene with phenylacetylene in the presence of digallane **A** gives both hydroamination and hydroarylation products.[18] To find out whether the hydroarylation of dicyclohexylcarbodiimide is possible, we studied a reaction of the latter with 1-aminonaphthalene in the presence of a catalytic amount of digallane **A**. It turned out that this reaction yields the corresponding guanidine as the only product. It can be seen in Table 1 (entries *1* and *7*) that the replacement of 4-chloroaniline by 1-aminonaphthalene decreases the yield of the hydroamination product from 80 to 26 %. The same reaction at 60 °C afforded *N′*,*N″*-dicyclohexyl-*N*-(1-naphthyl)guanidine in 97% yield over 1.3 h (see Table 1, entry *8*).

Digallane **A** catalyzes reactions of carbodiimides not only with aromatic amines but also with diphenylmethylidenehydrazine. A similar reaction with (9*H*-fluoren-9-ylidene)hydrazine instead of diphenylmethylidenehydrazine is catalyzed by titanium complexes.[32] We found that dicyclohexylcarbodiimide reacts with diphenylmethylidenehydrazine in the presence of digallane **A** (0.5 mol.%) at 80 °C to give a guanidine derivative in 65% yield over 100 h (see Table 1, entry *15*). With the titanium complex Cp*[N(CH_2)CHNXyl]Ti=N—NR_2(L) (5 mol.%) as a catalyst, a 96% yield is achieved at 80 °C in 24 h. Therefore, the activity of digallane **A** in this reaction is comparable with that of titanium catalysts. The reaction between dicyclohexylcarbodiimide and diphenylmethylidenehydrazine in the presence of a gallium complex with dpp-bian provides a first documented example of the gallium-catalyzed hydroamination of carbodiimides with hydrazines.

To gain insight into the mechanism of the catalytic action of complexes of Group 13 elements with the dpp-bian ligand in the hydroamination of carbodiimides, we conducted a series of experiments using the system dicyclohexylcarbodiimide—4-chloroaniline—catalyst **A**. A ^{1}H NMR study of the reaction mixture containing no catalyst revealed that the reactants remain inert at both room temperature and 90 °C for 24 h (Fig. 1).

Clearly, the first step of the hydroamination of dicyclohexylcarbodiimide with 4-chloroaniline involves an interaction of either substrate with the catalyst. We found that addition of a fivefold excess of 4-chloroaniline to digallane **A** in C_6D_6 causes no changes in the mixture kept at room temperature for 19 h. Only upon heating at 90 °C for several hours does the NMR spectrum show weak signals indicating minor transformations of the catalyst in contact with 4-chloroaniline (Fig. 2). For instance, a singlet at δ 5 can be due to the diamine dpp-bianH_2 formed by protonation of the catalyst with 4-chloroaniline. However, this interaction does not occur unless at elevated temperature, and its rate is much lower than that of the

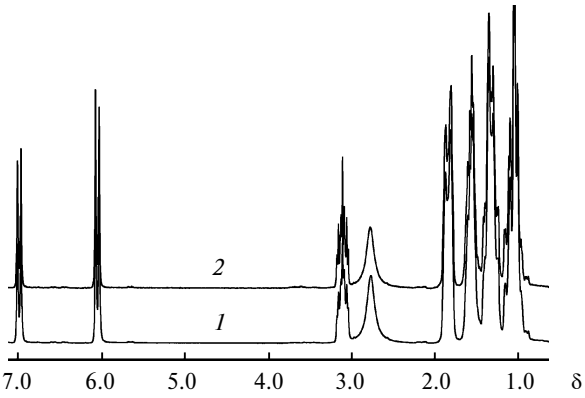


Fig. 1. ^{1}H NMR spectra (200 MHz, C_6D_6, 20 °C) of the system dicyclohexylcarbodiimide—4-chloroaniline 5 min after the mixing of the reagents (*1*) and after 24-h heating at 90 °C (*2*).

catalytic hydroamination in question. This obviously rules out the formation of a catalyst—4-chloroaniline adduct as a first step of the catalytic cycle. Nor do dicyclohexylcarbodiimide and catalyst **A** form an adduct between 20 and 90 °C for several hours (or its amount is below the detection limit of ^{1}H NMR spectroscopy). We assumed that a digallane—carbodiimide cycloadduct (similar to digallane—alkyne adducts[18]) can be detected at low temperatures. However, such a cycloadduct remains undetectable even at −50 °C. The low-temperature NMR spectrum of the system dicyclohexylcarbodiimide—catalyst **A** only shows some broadened signals, probably because of the retardation of some dynamic processes in the molecules of both compounds (Fig. 3).

Nevertheless, we do assume that the formation of a digallane—carbodiimide cycloadduct is possible and is actually the first step of the catalytic cycle. The equilibrium constant of adduct formation is probably very low. This complexation is suggested by the decreased yield of *N*-(4-chlorophenyl)-*N′*,*N″*-dicyclohexylguanidine in THF-d_8 (see Table 1, entries *1* and *5*), which seems to

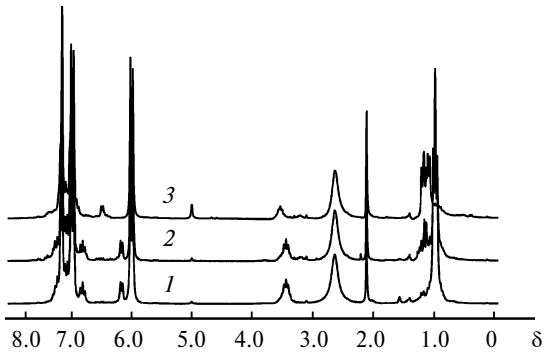


Fig. 2. ^{1}H NMR spectra (200 MHz, C_6D_6, 20 °C) of the system 4-chloroaniline—catalyst **A** (5 : 1) 5 min after their mixing (*1*), after 19-h keeping at room temperature (*2*), and after 14-h heating at 90 °C (*3*).

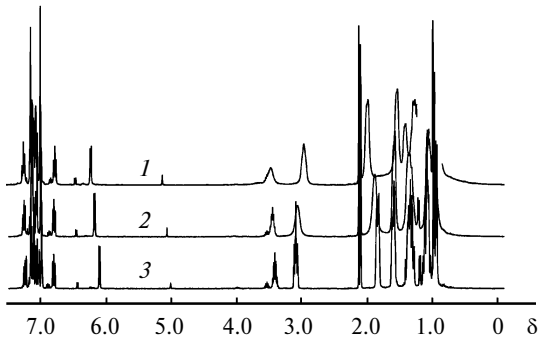


Fig. 3. ^{1}H NMR spectra (400 MHz, C_7D_8) of the system dicyclohexylcarbodiimide—catalyst **A** at −50 (*1*), −20 (*2*), and 25 °C (*3*).

compete with carbodiimide molecules for a coordination site of the catalyst.

To gain a deeper insight into the transformations of the catalyst, we monitored the reaction mixture in two parallel ways: the transformations of the substrates were monitored by ^{1}H NMR spectroscopy and the presence of digallane **A** was detected by electronic absorption spectroscopy. In this experiment, the content of catalyst **A** did not exceed 0.1 mol.% with respect to the substrates used in equimolar amounts. The initial electronic absorption spectrum of the reaction mixture features an intense band with λ_{max} = 580 nm due to catalyst **A** (Fig. 4). Nineteen hours after all three components were mixed at room temperature, the yield of the guanidine product was 60%. Over this period of time, the band corresponding to digallane **A** became much weaker. In addition, the spectrum shows a new band with λ_{max} = 535 nm due to the diamine dpp-bianH_2 (Fig. 4), and the hydroamination rate decreases sharply (Fig. 5).

A number of conclusions can be drawn from the results obtained. First, digallane **A** catalyzes the hydroamination

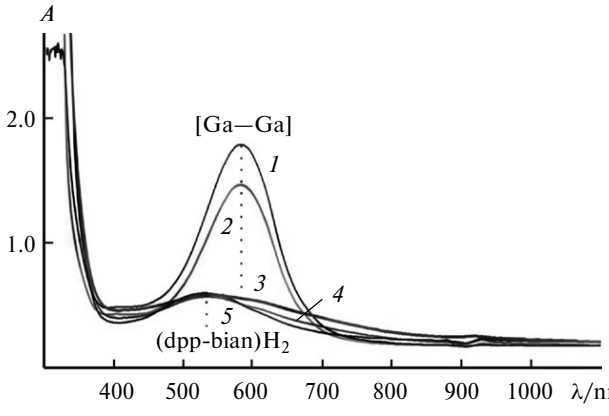


Fig. 4. Changes with time in the electronic absorption spectrum of the system dicyclohexylcarbodiimide—4-chloroaniline—catalyst **A** in deuterated toluene: immediately after the mixing (*1*), after 40 min (*2*), and after 19 (*3*, 60% conversion), 43 (*4*), and 140 h (*5*).

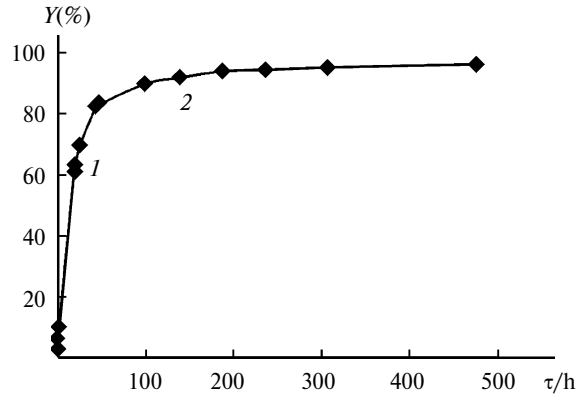


Fig. 5. Yields *Y* of the guanidine derivative in the reaction of dicyclohexylcarbodiimide with 4-chloroaniline in the presence of catalyst **A** at different reaction times τ: (*1*) τ = 19 h (60% yield) and (*2*) τ = 140 h (94% yield).

of carbodiimide with aniline. However, the graph of guanidine accumulation with time is no longer linear above a guanidine yield of 60%. The subsequent conversion of the substrates into the product occurs with a decreasing rate, and the 94% yield is achieved only after 140 h. Hence, the second conclusion is that the catalyst seems to be poisoned by the guanidine formed. Third, the guanidinate derivatives of gallium resulting from the reaction of digallane **A** with guanidine are also catalytically active, though much less active than digallane **A**.

To sum up, we demonstrated that the hydroamination of carbodiimides can be catalyzed by Group 13 metal complexes with redox-active ligands. The catalytic activity of the complexes depends on a number of factors, primarily, on the coordination unsaturation of the metal atom. The low activity of aluminum complexes versus gallium ones can also be explained by the formation of more stable complexes with carbodiimide and aniline substrates. In the case of (dpp-bian)B—Br, the HOMO energy seems to be too low for an effective interaction of this orbital with the LUMO of carbodiimide. This precludes the formation of a cycloadduct that is a first intermediate in the catalytic cycle. The present work will be followed by studying the catalytic properties of the complexes in question (notably, gallium derivatives) in intra- and intermolecular hydroamination of alkenes.

Experimental

All manipulations were carried out *in vacuo* using the Schlenk equipment. Compounds **A**,[18] **B**,[20] **C**,[19] **E**,[33] and **F**[34] were synthesized according to known procedures. Complex **D** was prepared by reduction of 1,2-bis[(2,6-dimethylphenyl)imino]-acenaphthene (dmp-bian) with excess gallium metal in boiling toluene for 20 h and isolated as dark brown crystals by crystallization from toluene. The deuterated solvents C_6D_6, toluene-d_8, THF-d_8, and $CDCl_3$ (Aldrich) were dried over sodium benzophenone ketyl and distilled into an NMR tube containing a substrate and a catalyst. 4-Chloroaniline, 1-aminonaphthalene, diphenylmethylidenehydrazine, dicyclohexylcarbodiimide, and diisopropylcarbodiimide (Aldrich) were used as purchased.

Catalytic reactions were carried out in sealed NMR tubes. An NMR sample was prepared as follows: an aminating agent (4-chloroaniline (0.087 g, 0.7 mmol), 1-aminonaphthalene (0.100 g, 0.7 mmol), or diphenylmethylidenehydrazine (0.137 g, 0.7 mmol)) and dicyclohexylcarbodiimide (0.144 g, 0.7 mmol) were placed in an NMR tube. Diisopropylcarbodiimide (0.088 g, 0.7 mmol) was distilled into an NMR tube. Then a catalyst was added; its amount had been calculated from the molar percentage specified in Table 1. A deuterated solvent (0.7 mL) was distilled in the NMR tube, whereupon the tube was sealed. The reactions were monitored by ^{1}H NMR spectroscopy. The concentration of the catalyst for the mononuclear complexes equals their molar concentrations. For dinuclear complexes **A** and **B**, the concentration is twice as high as their molar concentrations because they contain two metal centers per molecule. The yields of the reaction products were calculated from the ratio of the integral intensities of the signals for the reactants and the products.

^{1}H NMR spectra were recorded on Bruker DPX-200 and Bruker Advance III 400 spectrometers. Electronic absorption spectra were recorded on a PerkinElmer λ 25 spectrometer.

The products obtained by hydroamination of dicyclohexyl- and diisopropylcarbodiimides with 4-chloroaniline and 1-aminonaphthalene were isolated in the individual state, characterized by NMR spectroscopy, and identified by comparing their NMR spectra with the literature data.

***N*-(4-Chlorophenyl)-*N′*,*N″*-dicyclohexylguanidine (3a).** ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ: 7.13 (d, 2 H, arom., J = 8.5 Hz); 6.72 (d, 2 H, arom., J = 8.4 Hz); 3.56 (br.s, 2 H); 3.34 (br.s, 2 H); 1.95—1.01 (m, 20 H, 2 *cyclo*-CH—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—).

***N*-(4-Chlorophenyl)-*N′*,*N″*-diisopropylguanidine (3b).** ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ: 7.14 (d, 2 H, arom., J = 8.3 Hz); 6.72 (d, 2 H, arom., J = 8.3 Hz); 3.69 (br.s, 2 H); 3.51 (br.s, 2 H); 1.10 (d, 12 H, 2 CH$\underline{Me}_2$, J = 6.2 Hz).

***N′*,*N″*-Dicyclohexyl-*N*-(1-naphthyl)guanidine (3c).** ^{1}H NMR (200 MHz, $CDCl_3$, 298 K), δ: 7.99 (d, 1 H, arom., J = 7.3 Hz); 7.73 (d, 1 H, arom., J = 7.1 Hz); 7.36 (m, 4 H, arom.); 6.88 (d, 1 H, J = 6.2 Hz); 3.69 (br.s, 2 H); 3.43 (br.s, 2 H); 1.99—0.82 (m, 20 H, 2 *cyclo*-CH—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—).

***N′*,*N″*-Dicyclohexyl-*N*-(diphenylmethaniminyl)guanidine (3d).** ^{1}H NMR (200 MHz, C_6D_6, 298 K), δ: 7.89 (d, 2 H, arom., J = 7.0 Hz); 7.60 (d, 2 H, arom., J = 6.8 Hz); 7.30—7.03 (m, 6 H, arom.); 6.48 (d, 1 H, NH, J = 9.0 Hz); 3.76—3.61 (br.m, 1 H, CH); 3.47 (d, 1 H, NH, J = 7.3 Hz); 2.88—2.84 (br.m, 1 H, CH); 1.95—0.82 (m, 20 H, 2 *cyclo*-CH—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—C$\underline{H}_2$—).

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