Influence of copper(I) halides on the reactivity of aliphatic carbodiimides

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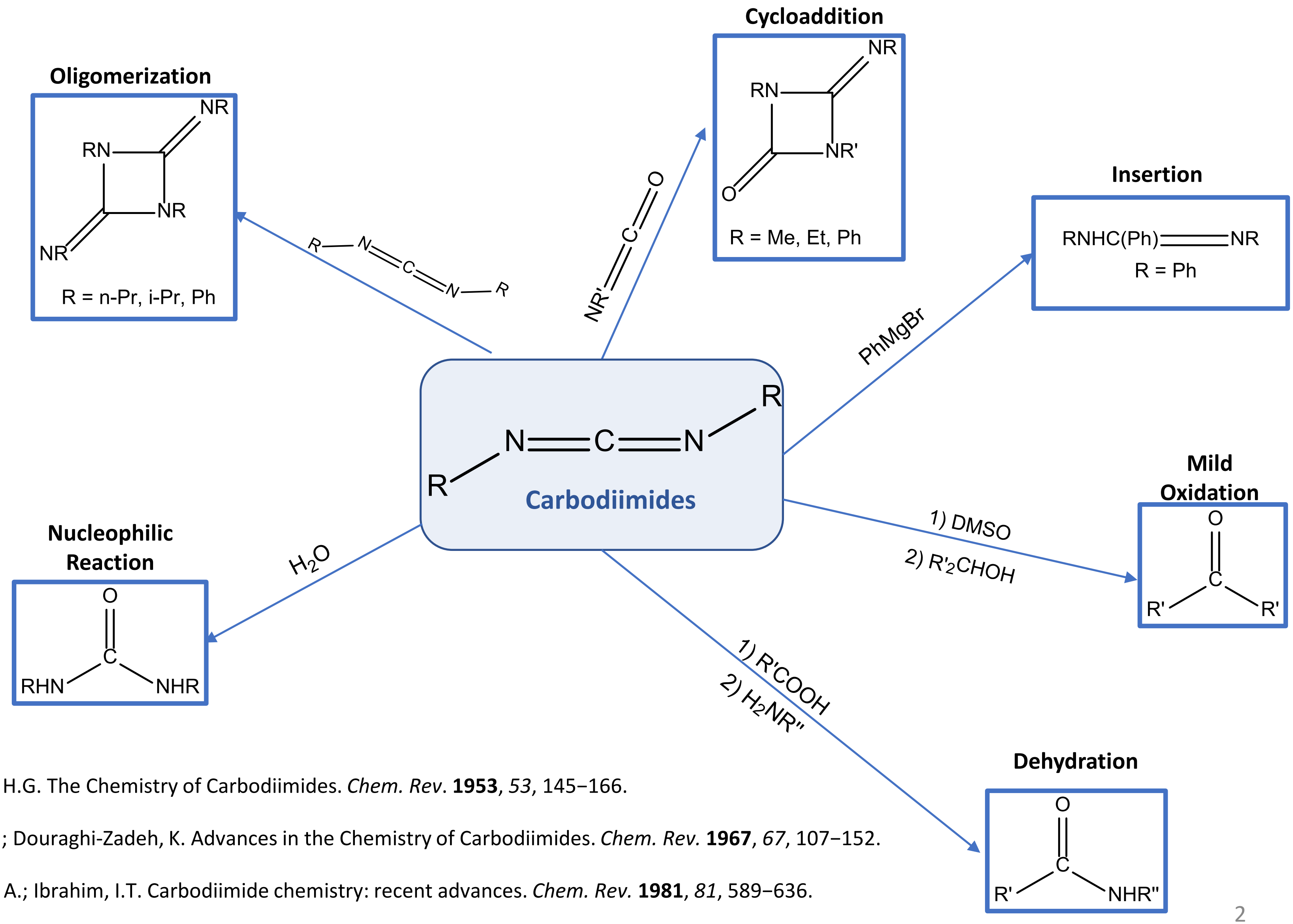
Carbodiimides main reactions



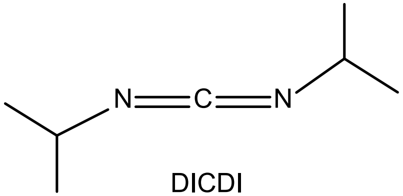
Khorana, H.G. The Chemistry of Carbodiimides. *Chem. Rev*. **1953**, *53*, 145−166.

Kurzer, F.; Douraghi-Zadeh, K. Advances in the Chemistry of Carbodiimides. *Chem. Rev.* **1967**, *67*, 107−152.

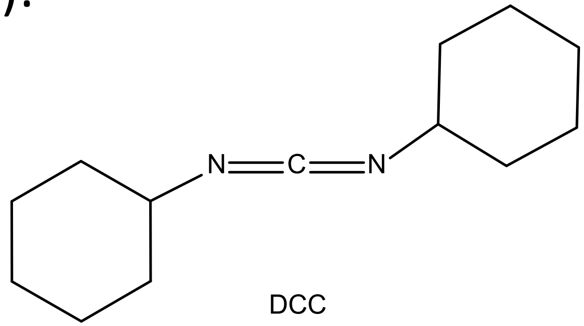
Williams, A.; Ibrahim, I.T. Carbodiimide chemistry: recent advances. *Chem. Rev.* **1981**, *81*, 589−636.

Ulrich, A. *Chemistry and Technology of Carbodiimides*. Wiley, Chichester, **2007**.

The two most used carbodiimides are diisopropylcarbodiimide (DICDI) and dicyclohexylcarbodiimide (DCC):



DICDI



DCC

Their electrophilicity can be enhanced by the addition of copper(I) halides to the reaction medium.

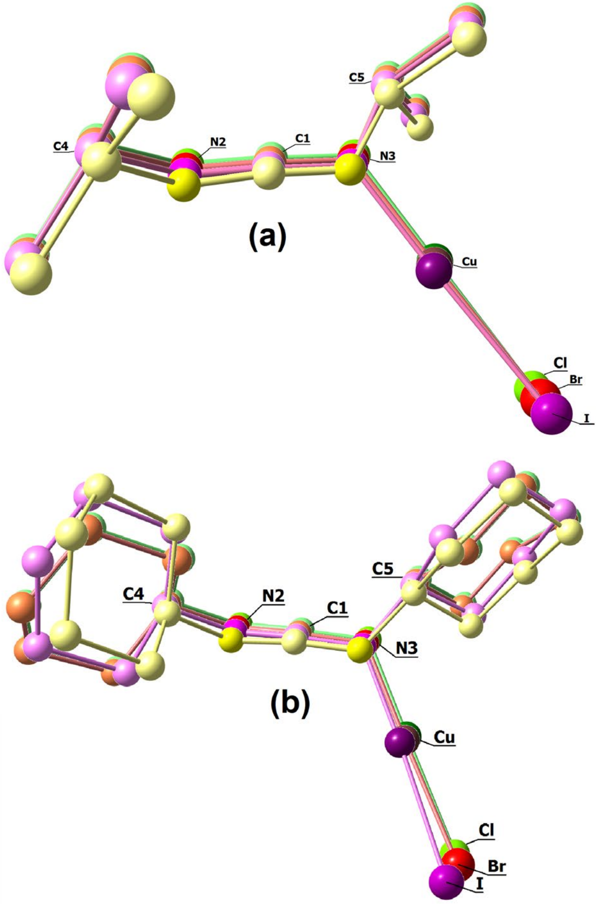
Isoureas are commonly obtained from the reaction between carbodiimides and alcohols in presence of CuX.

R = i-Pr, Cy

The interaction of DICDI and DCC with CuX (X = Cl, Br, I) was investigated by means of DFT calculations, and the influence of coordination on the electronic structure of carbodiimides was studied by several population analyses.

Results and Discussion

Superimposition of the DFT-optimized geometries for DICDI and [CuX(DICDI)] **(a)**, DCC and [CuX(DCC)] **(b)**.



Selected computed bond lengths (Å) for carbodiimides and CuX complexes.

Bond	DICDI	[CuCl(DICDI)]	[CuBr(DICDI)]	[CuI(DICDI)]
C1-N2	1.217	1.193	1.193	1.193
C1-N3	1.215	1.243	1.243	1.243
N2-C4	1.478	1.470	1.470	1.470
N3-C5	1.471	1.494	1.494	1.494

Bond	DCC	[CuCl(DCC)]	[CuBr(DCC)]	[CuI(DCC)]
C1-N2	1.216	1.192	1.192	1.191
C1-N3	1.217	1.243	1.244	1.244
N2-C4	1.469	1.465	1.464	1.464
N3-C5	1.470	1.489	1.489	1.488

C-PCM/ωB97X/def2-SVP

(CH_2Cl_2 as continuous medium, hydrogen atoms are omitted for clarity).

Selected computed Mayer bond orders and Wiberg bond orders in parenthesis:

Bond	DICDI	[CuCl(DICDI)]	[CuBr(DICDI)]	[CuI(DICDI)]
C1-N2	2.107 (2.393)	2.217 (2.490)	2.217 (2.490)	2.216 (2.491)
C1-N3	2.112 (2.377)	1.692 (2.085)	1.693 (2.086)	1.683 (2.088)
N2-C4	0.864 (1.196)	0.842 (1.164)	0.842 (1.164)	0.842 (1.165)
N3-C5	0.804 (1.179)	0.711 (1.096)	0.710 (1.097)	0.714 (1.098)

Bond	DCC	[CuCl(DCC)]	[CuBr(DCC)]	[CuI(DCC)]
C1-N2	2.072 (2.386)	2.196 (2.487)	2.198 (2.489)	2.199 (2.493)
C1-N3	2.083 (2.379)	1.700 (2.078)	1.700 (2.078)	1.682 (2.077)
N2-C4	0.859 (1.200)	0.867 (1.171)	0.868 (1.171)	0.842 (1.172)
N3-C5	0.837 (1.181)	0.629 (1.102)	0.627 (1.102)	0.664 (1.104)

Energy density (ρ) values at carbon-nitrogen (3,-1) bond critical points (b.c.p.). Potential energy density (V) values in parenthesis.

Bond	DICDI	[CuCl(DICDI)]	[CuBr(DICDI)]	[CuI(DICDI)]
C1-N2	0.436 (-1.340)	0.450 (-1.506)	0.450 (-1.505)	0.450 (-1.505)
C1-N3	0.435 (-1.325)	0.418 (-1.159)	0.419 (-1.161)	0.419 (-1.161)
N2-C4	0.248 (-0.410)	0.241 (-0.443)	0.241 (-0.442)	0.241 (-0.443)
N3-C5	0.248 (-0.404)	0.236 (-0.374)	0.236 (-0.374)	0.236 (-0.375)

Data in a.u.

Bond	DCC	[CuCl(DCC)]	[CuBr(DCC)]	[CuI(DCC)]
C1-N2	0.435 (-1.330)	0.449 (-1.507)	0.450 (-1.509)	0.451 (-1.513)
C1-N3	0.435 (-1.327)	0.418 (-1.153)	0.418 (-1.152)	0.419 (-1.142)
N2-C4	0.249 (-0.414)	0.243 (-0.459)	0.243 (-0.461)	0.243 (-0.463)
N3-C5	0.248 (-0.412)	0.239 (-0.385)	0.239 (-0.385)	0.239 (-0.385)

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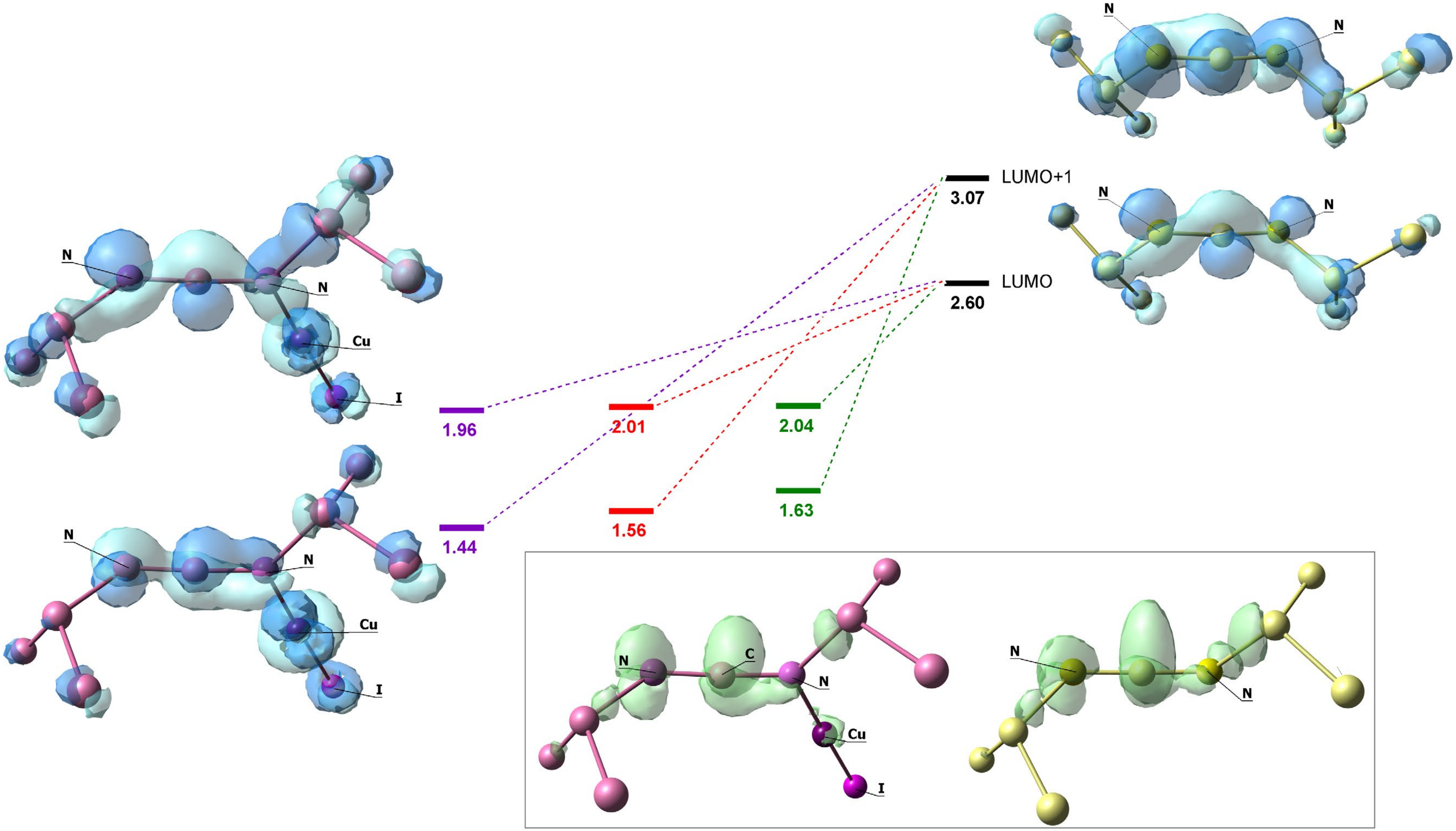


Energy values (eV) of LUMO and LUMO+1 orbitals of **DICDI** and of its **CuCl**, **CuBr** and **CuI** complexes. Plots of the LUMO and LUMO+1 molecular orbitals of **DICDI** and of **[CuI(DICDI)]**. Molecular orbitals surfaces in blue tones, isovalue = 0.05 a.u. Inset: plots of the Fukui $f_+(r)$ functions for DICDI and [CuI(DICDI)], surfaces in green, isovalue = 0.005 a.u. Hydrogen atoms are omitted for clarity.

Selected Hirshfeld partial charges and Mulliken charges in parenthesis.

Atom	DICDI
C1	0.152 (0.219)
N2	-0.184 (-0.346)
N3	-0.184 (-0.339)
C4	0.040 (0.103)
C5	0.039 (0.105)

[CuCl(DICDI)]	[CuBr(DICDI)]	[CuI(DICDI)]
0.199 (0.345)	0.199 (0.345)	0.199 (0.355)
-0.110 (-0.211)	-0.110 (-0.211)	-0.110 (-0.212)
-0.142 (-0.303)	-0.141 (-0.289)	-0.142 (-0.275)
0.054 (0.071)	0.054 (0.071)	0.054 (0.071)
0.048 (0.073)	0.048 (0.074)	0.048 (0.074)

Data in a.u.

Data in a.u.

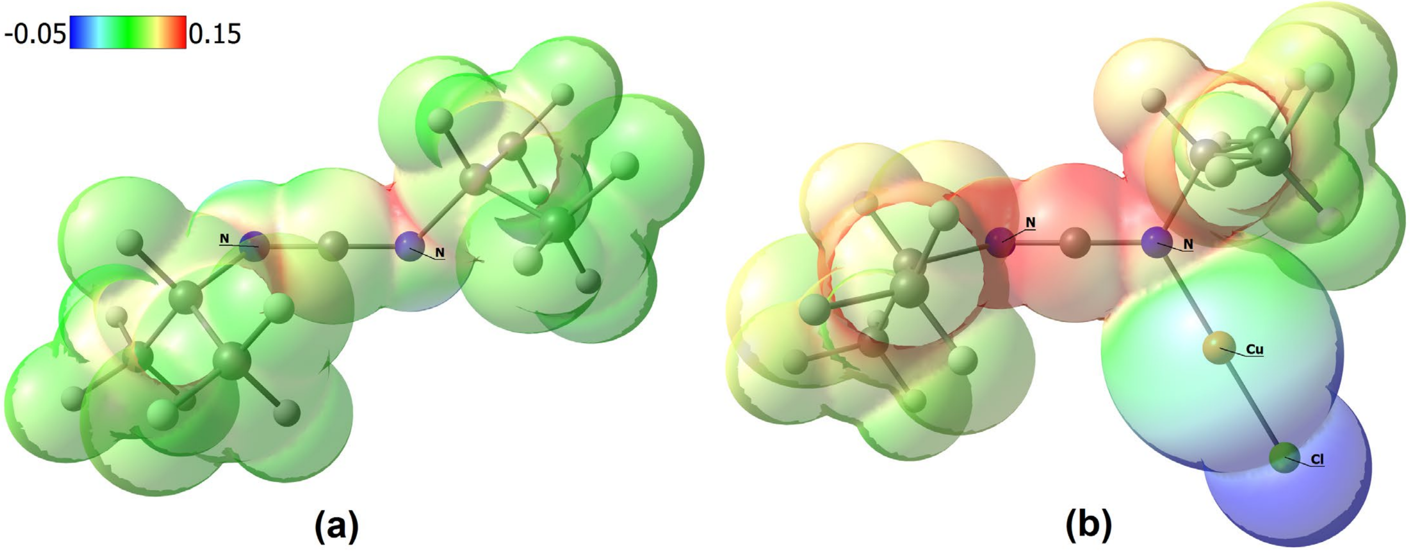
Atom	DCC
C1	0.154 (0.210)
N2	-0.189 (-0.354)
N3	-0.182 (-0.329)
C4	0.032 (0.118)
C5	0.034 (0.074)

[CuCl(DCC)]	[CuBr(DCC)]	[CuI(DCC)]
0.199 **(0.327)**	0.200 (0.326)	0.199 (0.325)
-0.108 **(-0.206)**	-0.107 (-0.205)	-0.107 (-0.205)
-0.142 **(-0.325)**	-0.142 (-0.311)	-0.144 (-0.287)
0.046 **(0.041)**	0.046 (0.041)	0.046 (0.069)
0.041 **(0.110)**	0.040 (0.112)	0.040 (0.098)

CDA values for the [CuX(carbodiimide)] complexes and ECDA values in parenthesis.

Carbodimmide	CuCl	CuBr	CuI
DICDI	0.237 (0.374)	0.248 (0.391)	0.255 (0.415)
DCC	0.240 (0.379)	0.251 (0.398)	0.254 (0.415)

Data in a.u.



Overlapping spheres plots of DICDI **(a)** and [CuCl(DICDI)] **(b)** with mapped electrostatic potentials (a.u.).

Conclusion

- DFT calculations confirm that DICDI and DCC can coordinate Cu(I) halides and that the interaction alters the orbital structure, the bond orders and the electrophilicity, enhancing the reactivity towards nucleophiles.
- The CuX fragments essentially behave as Lewis acids, and the nature of X influences the Cu-N bond strength, the carbodiimide→CuX donation and the energies of frontier unoccupied orbitals.
- Despite the fact that CuCl is actually the most employed catalyst, the reactivity could be yet more enhanced by its replacement with CuI.