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Reactions on the computer. Geometries and Mechanism Corrado Bacchiocchi H-Bonded Supramolecular architectures Anion binding with biphenyl-bis-urea derivatives

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Anion binding with biphenyl-bis-urea derivatives: solution and solid-state studies[†]

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In this work, we have synthesized and characterized bis-urea derivatives **1–3**, featuring a biphenyl spacer, and studied their anion binding properties in DMSO solution and in the solid state. In solution, 1:1 complexes were observed with association constant K values in the 10^3-10^4 M⁻¹ range with a general preference for acetate over dihydrogenphosphate for all three receptors. We were also able to obtain and characterize, by X-ray diffraction on single crystals, ten receptor–anion complexes including acetate and dihydrogenphosphate, as well as monohydrogenphosphate, halides and the nitrate ion. Linear (anion–receptor)_n arrays, porous frameworks and non-centrosymmetric structures were observed and described in detail.

Introduction

acetate) or two bifurcate HBs to monoatomic anionic species























Mechanisms of catalysis in solution













Fukui reactivity indices

- f⁺: accepting e⁻
- f⁻: donating e⁻

Fukui reactivity indices f⁺: accepting e⁻ f⁻: donating e⁻



Fukui reactivity indices f⁺: accepting e⁻ f⁻: donating e⁻



Fukui reactivity indices f⁺: accepting e⁻ f⁻: donating e⁻









Nitrogen lone pair in the Cu--BnNH₂ coordination



Nitrogen lone pair in the Cu--BnNH₂ coordination





Nitrogen lone pair in the Cu--BnNH₂ coordination

unchanged in the triple-bond coordination

NBO Analysis



NBO Analysis



π coordination of Cu-BnNH₂ with triple bond

NBO Analysis of the C—H bond
NBO Analysis of the C—H bond



NBO Analysis of the C—H bond



Cu(I) acetylide deprotonation

Deprotonation



Deprotonation



Deprotonation



Deprotonation – Reaction Coordinate



Deprotonation Potential Energy Barrier (PM6)



Deprotonation Potential Energy Barrier (DFT)



Fukui reactivity indices f⁺: accepting e⁻ f⁻: donating e⁻



Fukui reactivity indices f⁺: accepting e⁻ f⁻: donating e⁻



Fukui reactivity indices f⁺: accepting e⁻ f⁻: donating e⁻





The **Cu–CCPh bond** has ionic character

The Cu⁺ ion can easily move in and out of the Ph-acetylene axis

+0.49

-0.43

C—C bond formation towards Propargylamine synthesis











key C—C bond formation



C—**C** bond formation Potential Energy Barrier (DFT)



Propargylamine protonation

Propargylamine protonation



Mechanisms of heterogeneous catalysis



X = CI, Br

Scheme 2 Catalytic transformation of halogenated epoxides into the corresponding cyclic carbonates examined in this study.



Catalytic synth. of five-membered cyclic carbonate from epoxide



Catalytic synth. of five-member cyclic carbonate from epoxide

 CO_2 -O attacks the EPO-Cl terminal C on the same side of the detaching O. This is ideal for the subsequent cyclization



Catalytic synth. of five-member cyclic carbonate from epoxide

 CO_2 -O attacks the EPO-Cl terminal C on the same side of the detaching O. This is ideal for the subsequent cyclization



Steric clashes between EPO-Cl and the MOF structure when trying to "insert" a possible TS inside Insertion of EPO-Cl into partially relaxed MOF (only Zn fixed), vdW rendering






C. Cimarelli et al.

Activation of Primary Amines by Copper(I)-Based Lewis Acid Promoters in the Solventless Synthesis of Secondary Propargylamines

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Method A: 9 examples up to 62% yield i) CuSO₄ (30 mol%)/Nal (60 mol%), PhCOOH (5 mol%), solventless, N₂, 80 °C Method B: 20 examples up to 95% yield ii) MgSO₄, CeCl₃•7H₂O (30 mol%), solventless, N₂, r.t., 0.25 h iii) Cul (30 mol%), solventless, N₂, 40 °C

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Abstract Primary amines are activated by copper(I)-based Lewis acid promoters in an A³-coupling one-pot solventless reaction with alde-

Since the pioneering work of Li and Wei²⁵ the issue of the synthesis of propargylamines by direct addition of terminal alkynes to imines, defined in short as A³ coupling, has been addressed in different ways, under solvent or solventless conditions, by metal catalysis or organocatalysis, and also in an enantioselective manner.^{26–29}

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Amino-decorated bis(pyrazolate) metal-organic frameworks for carbon dioxide capture and green conversion into cyclic carbonates†

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The novel Metal–Organic Frameworks (MOFs) $M(BPZNH_2)$ (M = Zn, Ni, Cu) were prepared from the reaction of the corresponding metal acetates $M(OAc)_2 \cdot nH_2O$ and the organic linker 3-amino-4,4'-bipyrazole (H₂BPZNH₂) under solvothermal conditions. H₂BPZNH₂ was obtained straightforwardly from the reduction of the related nitro-compound using hydrazine as a reducing agent. The Zn(II) polymer is characterized by a 3D porous network featuring tetrahedral metallic nodes and bridging BPZNH₂²⁻ anions defining the vertices and edges of square channels. The isostructural Ni(II) and Cu(II) MOFs show square-planar metallic nodes and bridging BPZNH₂²⁻ spacers at the vertices and edges of the rhombic channels of a 3D porous framework. All the MOFs were characterized in the solid state [(VT)-PXRD, IR, TGA-DTG]. The textural property analysis revealed that