C–C Coupling

(*Z*)-Bis(alkylzinc)imido-1,2-di(2-pyridyl)ethene: Intramolecular Stabilization of a Bis(alkylzinc)imide**

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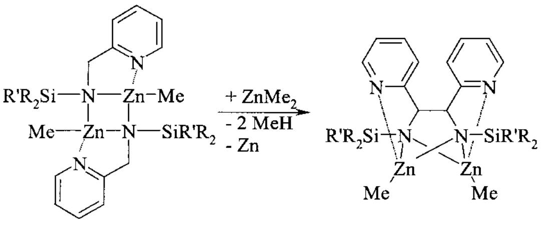
Dedicated to Professor Nils Wiberg
on the occasion of his 70th birthday

The oxidative metal-mediated C–C coupling reaction of (2-pyridylmethyl)(trialkylsilyl)amines succeeds smoothly with dialkylzinc [Eq. (1)] or tin(II) bis[bis(trimethylsilyl)amide].[1] The influence of the standard potential as well as the role of the steric demand of the nitrogen-bonded trialkylsilyl and zinc-bonded alkyl groups have been investigated.[2] The N-bonded trialkylsilyl substituent is obligatory to prevent side reactions. The reaction of dialkylzinc with 2-py-CH_2NH_2 (py = pyridyl) yields several products which can be explained by a combination of oxidative C–C coupling and transamination reactions. After protolysis of this reaction mixture a small amount of *cis*-1,2-di(2-pyridyl)aminoethene (**1**; Scheme 1) can be isolated in a reproducible procedure.[3] However, we were not able to detect the zincated 1,2-di(2-pyridyl)aminoethene during the reaction. Amine **1** crystallized as the eneamine tautomer, an equilibrium with the imine tautomer was not detectable with spectroscopic methods.



(1)

Even 30 years ago, doubly zincated primary amines of the type $[RN(ZnR')_2]$ were of interest as catalysts for polymerization reactions,[4] however, these compounds were poorly characterized and more recent attempts to prepare bis(alkylzinc)alkyl- and -arylimides by zincation of primary alkylamines failed.[5,6] The polymerization reactions are also

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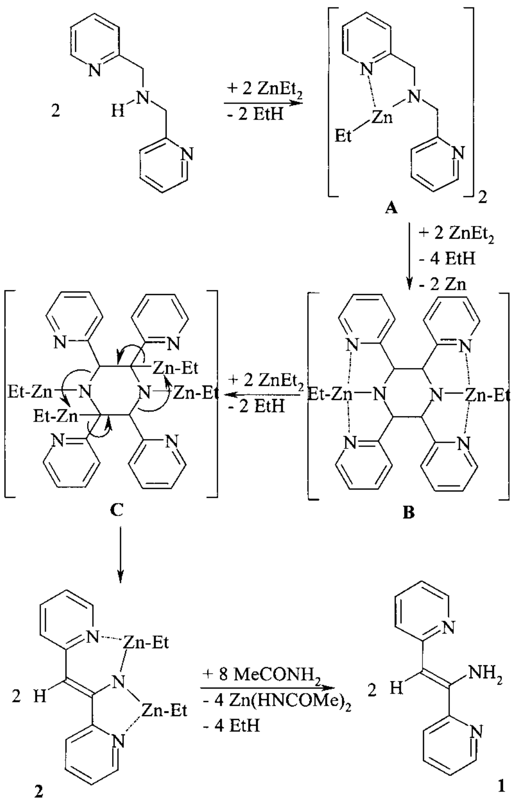
explainable under the assumption that monozincated amines and dialkylzinc coexist during the polymerization reaction, unequivocal data for the biszincated amines were not reported.[4] With stronger metalating reagents imides were synthesized successfully. Thus magnesium phenylimides and related compounds were prepared by Power and co-workers.[7] Similar observations were reported for geminal carbdianions; whereas geminal doubly magnesiated[8] and lithiated[9] carbdianions were characterized by X-ray crystallography, the corresponding zinc derivatives tend to avoid the formation of two Zn–C bonds to one carbon atom.[10] Therefore, to date, only one zinc derivative, which was prepared by a rather complex reaction, has been reported.[11]



Scheme 1. Proposed mechanism for the formation of **2**

The reaction of an excess of diethylzinc with bis(2-pyridylmethyl)amine in toluene yields **2** (Scheme 1). The first reaction step is the zincation of (2-pyCH$_2$)$_2$NH, the resulting compound **A** was identified by NMR spectroscopy.[12] Heating of this reaction solution under reflux for more than twenty hours led to the C–C coupling product **B** under elimination of zinc metal. The excess of dialkylzinc metalated the intermediate **B** at the endocyclic CH moieties giving compound **C** and ethane. Finally, a subsequent deamination (rearrangement) reaction gives **2**. A complex similar to **B** which has AlMe$_2$ fragments instead of the ZnEt moieties has been observed by Trepanier and Wang[13] as a minor dark-brown product in the reaction of AlMe$_3$ and (2-pyCH$_2$)$_2$NH. However, a concise mechanism for its formation was not proposed.

The protolysis of **2** with acetamide led to a nearly quantitative formation of *cis*-1,2-dipyridylaminoethene (**1**). The NMR spectroscopic parameters of **1**[3] and **2** (Table 1) differ remarkably little. This observation can be understood by taking into account that in both compounds the eneamine tautomer is formed and stabilized by N···Zn (**2**) and N···H (**1**) contacts to the pyridyl moieties, respectively.

Table 1: NMR spectroscopic data for **2** (solvent: [D$_8$]THF).[a]

Assignment	^{1}H NMR δ[ppm]	^{13}C{^{1}H} NMR δ[ppm]
δ(pyr 1)	8.23, 7.84–7.80	146.6, 145.9
δ(pyr 2)	7.08–7.01, 6.26	120.5, 111.6
δ(pyr 3)	7.51, 7.08–7.01	138.1, 134.6
δ(pyr 4)	7.84–7.80, 6.67	123.0, 122.5
δ(pyr 5)	–	161.0, 158.9
δ(CH)	5.84	91.0
δ(C$_q$)	–	128.7
δ(NH$_2$)	–	–
δ(ZnC*H*$_2$CH$_3$)	0.30	−1.9
δ(ZnCH$_2$C*H*$_3$)	1.25	12.9

[a] The assignment of the pyridyl (pyr) resonances signals to a specific pyridyl group was not possible.

The asymmetric unit of **2** is represented in Figure 1. The zinc atoms are both bonded to the imide nitrogen atom N2 and fixed by additional bonds to the pyridyl bases which leads to a nearly planar molecule. In the solid state **2** is a dimer (Figure 2) with a crystallographically imposed C_2 axis ($-x$, $-y$, z).

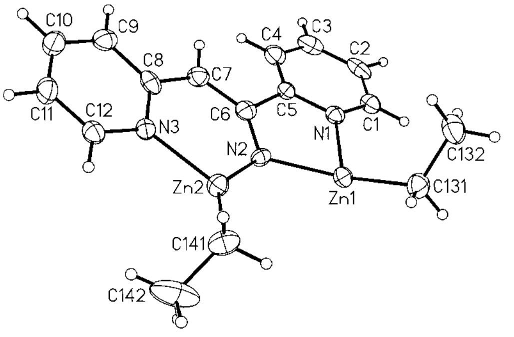


Figure 1. Molecular structure of **2**. Thermal ellipsoids set at 30% probability, the H atoms are drawn with arbitrary radii. Selected bond lengths [pm]: Zn1-N1 209.0(5), Zn1-N2 200.0(4) (Zn1-N2′ 225.4(4)), Zn1-C131 198.1(6), Zn2-N2 192.5(5), Zn2-N3 204.9(4), Zn2-C141 197.4(8), N2-C6 134.2(7), N1-C1 132.4(7), N1-C5 133.3(7), C1-C2 138(1), C2-C3 140(1), C3-C4 136.3(9), C4-C5 134.9(8), C5-C6 156.6(8), C6-C7 138.1(8), C7-C8 141.7(8), C8-C9 141.5(8), C9-C10 136.4(9), C10-C11 136(1), C11-C12 133.7(8), N3-C8 136.9(7), N3-C12 135.9(7).

In **1** an isolated eneamine fragment with characteristic C–C single bonds to the attached pyridyl fragments was found[3] whereas in **2** the ligand's anionic charge is partly delocalized within the neighboring pyridyl moiety (Scheme 2). The consequence of the delocalization is a shortening of the C6–N2 bond of the imide moiety (**1**: 137.8(6) pm;[3] **2**: 134.2(7) pm) and a lengthening of the adjoining C6–C7 double bond (**1**: 129.5(6) pm;[3] **2**: 138.1(8) pm). The C7-C8 bond length of **2** is 141.7(8) pm which supports a multiple-

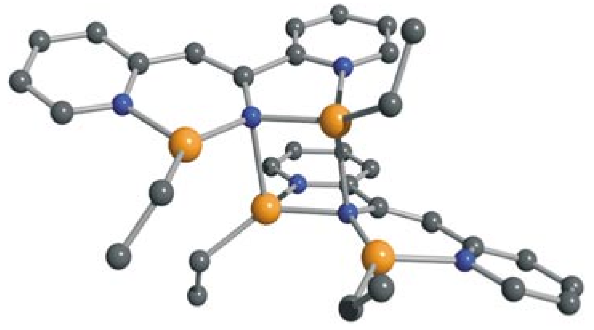
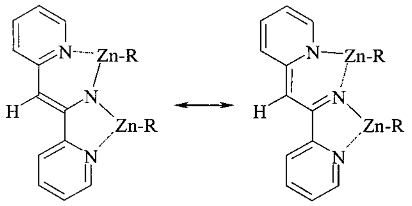


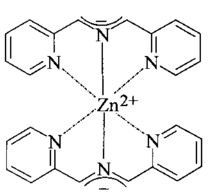
Figure 2. Perspective representation of dimeric **2** (Zn orange, N blue, C black). The hydrogen atoms are omitted for clarity.



Scheme 2. Mesomeric forms of **2**.

bond character and a delocalization of the anionic charge into the pyridyl moiety. This situation weakens the aromaticity of this pyridyl ligand which gives rise to bond lengthening within this heterocycle (N3, C8–C12).

Owing to the dimer formation in which Zn1 and N2 are the bridging atoms the zinc atom Zn1 is four-coordinate whereas Zn2 is in a distorted trigonal planar environment. Owing to the additional electrostatic attraction the Zn1–N2 and Zn2–N2 bond lengths to the imide function are smaller than the Zn1–N1 and Zn2–N3 values of the pyridyl substituents. The intermolecular Zn1–N2′ separation of 225.4(4) pm is large and can be interpreted as an interaction between the occupied nitrogen-centered p orbital with the empty p orbital at the zinc atom. The trans-annular nonbonding Zn1···Zn1′ separation is 290.4(1) pm whereas the Zn1···Zn2′ separation is larger (305.24(9) pm).



D

Scheme 3. Schematic representation of **D**.

The reaction conditions, such as temperature, substituents at N, and stoichiometry play a key role during the formation of **2**. At low temperatures the C–C coupling reaction is extremely slow and **D** (Scheme 3) forms from **A** in an unstirred toluene solution.[14] At elevated temperatures the C–C coupling reaction is favored and **2** becomes the major product.

Experimental Section

All manipulations were carried out in an anhydrous argon atmosphere. The solvents were thoroughly dried and distilled under argon.

Synthesis of **2**: Diethylzinc in n-hexane (20 mL of a 1.0 M solution, 20 mmol) was added slowly to a solution of bis(2-pyridylmethyl)amine (1.8 mL; 10.0 mmol) in toluene (20 mL). The solution turned red-brown. After stirring at room temperature for 1 day the solution was heated under reflux for 22 h. During this time zinc metal precipitated. The hot solution was filtered and the filtrate collected and cooled to room temperature. Then the volume was reduced to a few milliliters. At room temperature 1.24 g of red prisms of **2** (3.2 mmol, 32 %) precipitated. M.p. 264 °C. Elemental analysis calcd (%) for $C_{16}H_{19}N_3Zn_2$, 384.12 g mol^{-1}: C 50.03, H 4.99, N 10.94; found C 50.16, H 4.99, N 10.74. MS (EI, m/z): 383 (M^+–H, 2), 355 (383-Et, 14). NMR data see Table 1.

Crystal data for **2**:[15] red cubes, $C_{16}H_{19}N_3Zn_2$, $M_r = 384.08$, orthorhombic, space group $Fdd2$ (no. 43), $a = 1339.73(7)$, $b = 4211.6(2)$, $c = 1150.00(5)$ pm, $V = 6.4888(5)$ nm^3, $\rho_{calcd} = 1.573$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.953$ mm^{-1}, $Z = 16$ (8 dimers), 5736 reflections were collected on a Siemens P4 diffractometer with a CCD area detector at 193(2) K using graphite monochromated $Mo_{K\alpha}$ radiation, 1797 independent reflections ($R_{int} = 0.0490$), 196 refined parameters, $wR_2 = 0.0743$ (on F^2), $R1 = 0.0293$ (on 1748 reflections with $I > 2\sigma(I)$), $s = 1.079$, residual electron density 426/–332 e nm^{-3}.

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[15] CCDC-244839 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).