Diphenyldipyridinezinc(II): partial spontaneous resolution of an organometallic reagent

Anders Lennartson* and Mikael Håkansson

Department of Chemistry, University of Gothenburg, SE-412 96 Gothenburg, Sweden
Correspondence e-mail: anle@chem.gu.se

The title compound, $[Zn(C_6H_5)_2(C_5H_5N)_2]$, (I), forms conformationally chiral molecules residing on a twofold axis. The molecules are stacked along c, and these stacks are associated by edge-to-face π–π interactions. Crystals of (I) belong to the Sohncke space group $P2_12_12$ and the crystal lattice of (I) is chiral. The crystal batch that was examined consisted of a mixture of enantiomerically pure crystals and crystals twinned by inversion.

Comment

Optical resolution is usually time consuming (Faigl *et al.*, 2008), but in a few rare cases spontaneous resolution may occur. It has been estimated to occur for less than 10% of crystalline racemates (Jacques *et al.*, 1981) and involves the crystallization of a racemate in one of the 65 Sohncke space groups (Flack, 2003). Chiral molecules which are stereochemically labile in solution may undergo total spontaneous resolution, also known as crystallization-induced asymmetric transformation (Jacques *et al.*, 1984). This is a phenomenon where the whole batch of crystals originates from a single nucleus and a fast enantiomerization in the solution converts all material in solution into the crystallizing enantiomer. Under favourable circumstances, the entire amount of racemate may be converted to a pure enantiomer in quantitative yield. It has been observed that slow stirring may be beneficial for crystallization-induced asymmetric transformation (Kondepudi *et al.*, 1990; McBride & Carter, 1991; Pagni & Compton, 2002). Since a racemic mixture is transformed into an optically active substance without the use of chiral reagents or catalysts, crystallization-induced asymmetric transformation is an important strategy for absolute asymmetric synthesis, *i.e.* the creation of optically active substances from achiral or racemic starting materials only (Feringa & Van Delden, 1999).

Over the years, we have studied the total spontaneous resolution of stereochemically labile chemical reagents (Lennartson *et al.*, 2009; Vestergren *et al.*, 2000, 2003;

Håkansson *et al.*, 1999) and potential substrates (Johansson & Håkansson, 2005; Lennartson, Salo *et al.*, 2005; Andersson *et al.*, 1986, Lennartson *et al.*, 2007). During a study of diphenylzinc complexes, it was found that diphenyldipyridinezinc(II), (I), crystallizes in the Sohnke space group $P2_12_12$.


(I)
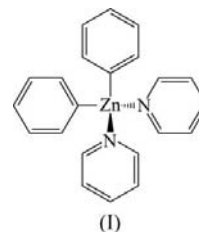
The molecules of (I) are located on a twofold axis, and the molecules are therefore C_2 symmetric. The coordination geometry around atom Zn1 is distorted tetrahedral (Fig. 1). The molecules of (I) are conformationally chiral due to the orientations of the aromatic rings surrounding the central Zn atom, as shown in Fig. 2. The enantiomerization barrier between the two enantiomers can be expected to be very low, and the conformational chirality of (I) will be immediately lost upon dissolution of the crystals, one of the requirements for total spontaneous resolution.
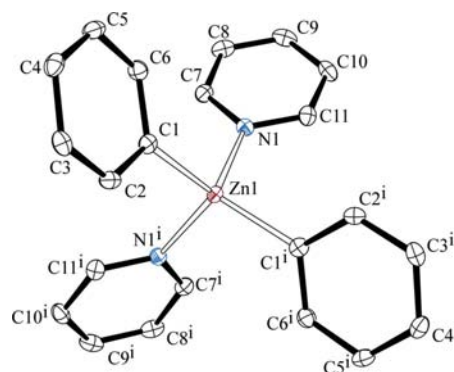
Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted. The central Zn atom displays a distorted tetrahedral coordination geometry. [Symmetry code: (i) $1 - x$, $1 - y$, z.]
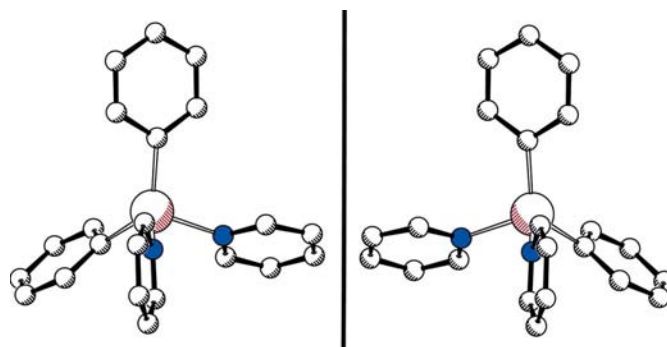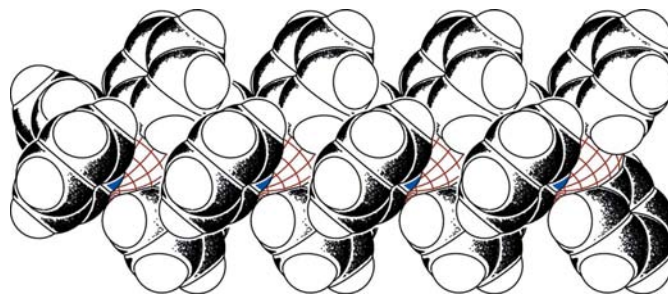

Figure 2
A molecule of (I) and its mirror image, illustrating the conformational chirality of the molecules.

metal-organic compounds

Only a limited number of diphenylzinc structures are reported in the Cambridge Structural Database (CSD, Version 5.30 of February 2009; Allen, 2002). Unsolvated diphenylzinc forms a dimer with two three-coordinate Zn atoms bridged by two phenyl groups (Markies *et al.*, 1990). There are another five structures where diphenylzinc coordinates crown ethers (Markies *et al.*, 1991; Fabicon *et al.*, 1999; Kooijman *et al.*, 2007), two examples of coordination to glyme ligands (Markies *et al.*, 1992) and a complex with thiophene (Dickson *et al.*, 2000). The thiophene complex is dimeric with two distorted tetrahedral Zn atoms bridged by two phenyl groups, and the structure is therefore very different from that of (I). The other seven complexes also differ from (I), since the C—Zn—C angles are considerably larger, approximately 140–150° compared with 125.65 (8)° in (I). The C—Zn—C angle in the diphenylzinc–18-crown-6 rotaxane is 174.5 (1)° (Fabicon *et al.*, 1999). These differences are rational, since pyridine appears to coordinate more strongly than the ligands previously employed. The Zn—N distances in (I) are 2.1505 (12) Å, while the Zn—O distances in the rotaxane approach 3 Å. Monomeric Lewis base free dialkylzinc compounds are reported to be linear (Almenningen *et al.*, 1982; Lewinski *et al.*, 2007), and this rule also applies to monomeric diarylzinc compounds, *viz.* dimesitylzinc (Cole *et al.*, 2003). Weaker coordinating ligands would therefore be expected to give rise to larger C—Zn—C angles. A few structures with one phenyl group attached to Zn have also been published, *e.g.* di-μ-phenoxido-bis[[(diethyl ether)phenyl-zinc(II)], which we recently reported (Lennartson & Håkansson, 2008). The dinuclear phenylzinc amide bis[μ_2-phenyl-*C*,*C*-{μ_2-4,6-bis(dimethylamino)ethylamido}dibenzo-furan-*N*,*N*′,*N*″,*N*‴]dizinc (Hlavinka & Hagadorn, 2005) is also related to (I), since it has an *N*-donor ligand rather than the *O*-donor ligands which appear to be more abundant among the structures reported in the CSD.

The molecules in (I) are stacked along *c*, and molecules of the same chiral sense will fit perfectly on top of each other. There are no unambiguous indications of interactions within these stacks, although there is one intermolecular distance (2.89 Å) within the sum of the van der Waals radii between H8 and C6(x, y, $1 + z$). Each stack is surrounded by four adjacent stacks, and these stacks appear to be held together by means of edge-to-face π–π interactions, resulting in a network structure (Fig. 3). Each aromatic ring acts both as a donor and as an acceptor. There are two independent sets of interactions in (I), the shortest intermolecular distances being H9···C5($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $2 - z$) with a distance of 2.87 Å and H4···C10($\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$) with a distance of 2.90 Å. Due to the molecular symmetry, each molecule will be engaged in eight interactions, four of each kind.

Organozinc reagents readily undergo nucleophilic addition to aldehydes and ketones, and the reaction of (I) with a prochiral aldehyde is expected to give rise to a chiral product. If crystallization-induced asymmetric transformation of (I) could be performed, it would perhaps be possible to use (I) as a chiral reagent and to obtain an optically active alcohol. This would be similar to the reaction of octahedral 'chiral-at-Mg'

Figure 3
The molecules of (I) forming stacks along *c*. The figure shows a stack of four molecules viewed along *b*.

Grignard reagents with prochiral aldehydes, which give up to 22% enantiomeric excess (e.e.) (Vestergren *et al.*, 2003). Reaction conditions that prevent the reagent from dissolving are required, *e.g.* a solid-state reaction with an aldehyde. The formation of a solid-state melt could, however, be a potential problem. A problem encountered during crystallization of (I), compared to the Grignard reagents, is a tendency for twinning by inversion. Three crystals from the same crystal batch were picked for absolute structure determination, and two of these crystals were found to be twinned, and almost racemic. Complete spontaneous resolution of (I) would therefore require rigorously controlled crystallization conditions (Gervais *et al.*, 2002; Perez-Garcia & Amabilino, 2002). Determination of an e.e. in a microcrystalline bulk sample of (I) using solid-state circular dichroism (CD) spectroscopy (Lennartson, Vestergren *et al.*, 2005) would be very difficult due to the high air sensitivity of (I).

Experimental

Bromobenzene (4.1 ml, 0.039 mol) was added to a stirred mixture of magnesium (1.1 g, 0.045 mol) and diethyl ether (40 ml). The mixture was stirred overnight at ambient temperature. The solution was then added dropwise to a suspension of zinc chloride (2.6 g, 0.019 mol) in diethyl ether (10 ml) at 273 K. The reaction mixture was stirred at ambient temperature overnight, evaporated and sublimed at 10^{-2} mbar (1 mbar = 100 Pa). The white product was dissolved in toluene (4 ml). An excess of pyridine (1 ml) was added, whereupon a precipitate formed. The mixture was heated to reflux and slowly allowed to reach ambient temperature, whereupon colourless crystals of (I) formed.

Crystal data

[Zn(C$_6$H$_5$)$_2$(C$_5$H$_5$N)$_2$]	$V = 912.6$ (3) Å^3
$M_r = 377.79$	$Z = 2$
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation
$a = 11.931$ (2) Å	$\mu = 1.35$ mm^{-1}
$b = 12.157$ (2) Å	$T = 100$ K
$c = 6.2921$ (13) Å	$0.4 \times 0.3 \times 0.2$ mm

Data collection

Rigaku R-AXIS IIC image-plate system diffractometer	5959 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)	1672 independent reflections
	1644 reflections with $I > 2\sigma(I)$
$T_{min} = 0.551$, $T_{max} = 0.767$	$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.046$
$S = 1.04$
1672 reflections
124 parameters
H-atom parameters constrained

$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983), 678 Friedel pairs
Flack parameter: 0.061 (10)

Table 1
Selected geometric parameters (Å, °).

C1—Zn1	2.0158 (15)	N1—Zn1	2.1505 (12)
C1—Zn1—C1^i	125.65 (8)	C1—Zn1—N1	107.60 (5)
C1—Zn1—N1^i	107.11 (5)	N1^i—Zn1—N1	98.45 (7)

Symmetry code: (i) $-x + 1, -y + 1, z$.

Table 2
Shortest intermolecular contact geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H9$\cdots$C5^{ii}	0.93	2.87	3.765 (2)	162
C4—H4$\cdots$C10^{iii}	0.93	2.90	3.703 (2)	146

Symmetry codes: (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 2$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$.

All H atoms were included in calculated positions and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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