doi.org/10.1002/hlca.202200152

RESEARCH ARTICLE

HELVETICA chimica acta

Preparation and Characterization of *N,N′*-Dialkyl-1,3-propanedialdiminium Chlorides, *N,N′*-Dialkyl-1,3-propanedialdimines, and Lithium *N,N′*-Dialkyl-1,3-propanedialdiminates

Claire E. Schmit[a] and Gregory S. Girolami*[a]

[a] School of Chemical Sciences, University of Illinois, 600 South Mathews Avenue, Urbana, IL, 61801, United States of America, e-mail: ggirolam@illinois.edu

Dedicated to a great colleague and friend, *Scott Denmark*, on the occasion of his 70th birthday

We describe convenient preparations of *N,N′*-dialkyl-1,3-propanedialdiminium chlorides, *N,N′*-dialkyl-1,3-propanedialdimines, and lithium *N,N′*-dialkyl-1,3-propanedialdiminates in which the alkyl groups are methyl, ethyl, isopropyl, or *tert*-butyl. For the dialdiminium salts, the N_2C_3 backbone is always in the *trans*-s-*trans* configuration. Three isomers are present in solution except for the *tert*-butyl compound, for which only two isomers are present; increasing the steric bulk of the *N*-alkyl substituents shifts the equilibrium away from the (*Z,Z*) isomer in favor of the (*E,Z*), and (*E,E*) isomers. For the neutral dialdimines, crystal structures show that the methyl and isopropyl compounds adopt the (*E,Z*) form, whereas the *tert*-butyl compound is in the (*E,E*) form. In aprotic solvents all four dialdimines (as well as the lithium dialdiminate salts) adopt *cis*-s-*cis* conformations in which there presumably is either an intramolecular hydrogen bond (or a lithium cation) between the two nitrogen atoms.

Keywords: conformation analysis, crystal structures, dialdiminium, dialdimine, dialdiminate, isomers.

Introduction

Since their introduction in the 1960s, β-diketimines, the nitrogen analogues of β-diketones (*Figure 1*, R^2, $R^4 \neq H$), have been used extensively in their deprotonated form (colloquially known as NacNacs) as ligands in a wide variety of coordination complexes.[1–8] β-Diketimines can be synthesized by several classical[9,10] and modern[11,12] methods; the latter make it possible to vary independently all five substituents on the 1,3-propanediimine backbone. For example, symmetrical *N,N′*-diaryl-β-diketimines can be isolated in their protonated (iminium) form by treating a β-diketone with a primary arylamine in refluxing acid; the resulting salts can be isolated as tetrafluoroborate, chloride, or perchlorate salts, or can be neutralized to yield the *N,N′*-diaryl-β-diketimine.[9,11,13]

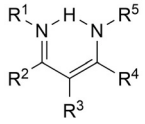


Figure 1. A generic β-diimine.

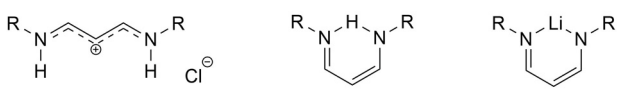
Compared with the methods that successfully afford *N,N′*-diaryl-β-diketimines, the synthesis of *N,N′*-dialkyl analogues often requires different conditions because the second transamination reaction of the β-diketone is slow; in such cases, the first transamination step is best followed by alkylation of the remaining ketone group by reagents such as *Meerwein*'s salt.[9] The resulting enol ether usually reacts readily with a second equivalent of a primary amine to

Supporting information for this article is available on the WWW under https://doi.org/10.1002/hlca.202200152

form the β-diketimine.[9] Recent work has shown that the synthesis of *N,N′*-dialkyl-β-diketimines can often be improved by replacing *Meerwein*'s salt with stronger alkylating agents such as dimethyl sulfate,[14] or through the azeotropic removal of water.[15,16] With these optimizations, neutral *N,N′*-dialkyl-β-diketimines can be synthesized in yields of 44–77% depending on the substituents and the method chosen.[14–16] But because these compounds are more reactive than their *N,N′*-diaryl analogues, isolated yields of *N,N′*-dialkyl-β-diketimines are often lower than desired due to hydrolysis or thermal decomposition during the reaction or purification steps.[16]

Neutral β-diketimines can be deprotonated to make lithium complexes, which have been used to make coordination complexes.[13,17] The vast majority of the known coordination complexes contain *N,N′*-diaryl-β-diketiminate ligands, and in contrast relatively few coordination complexes of *N,N′*-dialkyl-β-diketiminates have been reported; among these are several manganese(II) and copper(II) compounds that are of interest as potential chemical vapor deposition (CVD) precursors.[17,18] In addition, alkylaluminum complexes bearing *N,N′*-dialkyl-β-diketiminate ligands show activity towards ring-opening polymerization of lactones.[19]

Here we are interested in the closely related β-dialdimines, which have hydrogen substituents on the two imine carbon atoms (*Figure 2*, R^2=R^4=H); such molecules are also known as 1,3-propanedialdimines, 1,5-diaza-1,4-pentadienes, alkylamino-alkyliminio-propenes, malonaldehyde bis-imines, and vinylogous amidines. *N,N′*-Diaryl-β-dialdimines, which were studied in the 1900s as intermediates for the preparation of sensitized dyes,[20,21] can be prepared by a method similar to one used to obtain *N,N′*-diaryl-1,3-diketimines: *viz.*, by treating an acetal of malondialdehyde (such as 1,1,3,3-tetramethoxypropane) with a primary arylamine in an acid medium.[10,20,22] For example, *N,N′*-dimesityl-1,3-propanedialdimine hydrochloride can be synthesized in 85% yield by this method.[23]



1a R = Me
1b R = Et
1c R = ^{i}Pr
1d R = ^{t}Bu

2a R = Me
2b R = Et
2c R = ^{i}Pr
2d R = ^{t}Bu

3a R = Me
3b R = Et
3c R = ^{i}Pr
3d R = ^{t}Bu

Figure 2. The compounds discussed in this article.

Few *N,N′*-dialkyl-β-dialdimines of simple aliphatic amines have been reported, however, and characterization has been scanty.[1] Owing in part to their sensitivity to water and (in some cases) their thermal instability, they are often difficult to purify and there are many discrepancies in the reported chemical properties, such as the color, melting point, boiling point, and room temperature state (*i.e.*, liquid *vs.* solid). Most studies of the *N,N′*-dialkyl-β-dialdimines have dealt with their protonated form, the β-dialdiminium salts. In 1959 *Arnold* claimed that treatment of sodium malondialdehyde with methylammonium iodide in boiling *n*-butanol formed *N,N′*-dimethyl-1,3-propanedialdiminium iodide (an analogue of **1a** with iodide as the counterion) in 70% yield, but no spectroscopic data were given that would have proven the identity of the product.[25] In 1968, *Hirsch et al.* reported the synthesis of **1a** with methyl sulfate as the counterion by the reaction of β-(methylamino)acrolein with dimethyl sulfate, followed by treatment of the O-alkylated salt with excess methylamine.[26] Again, no spectroscopic data were reported for the product, which was an oil. In 1975, *Dähne et al.* claimed that bis(*N*-methylanilino)trimethine perchlorate (*i.e.*, *N,N′*-diphenyl-*N,N′*-dimethyl-1,3-propanedialdiminium perchlorate) reacts with an excess of neat methyl- or ethylamine to form the perchlorate analogs of **1a** and **1b**, which were reported to be a colorless crystalline solid and an oil, respectively.[27] The only spectroscopic characterizations given were the UV-vis absorption maxima.

For the neutral β-dialdimines, even less information is available. In his 1968 paper, *Hirsch* reported that deprotonation of the methylsulfate analog of **1a** with aqueous hydroxide afforded a yellow oil supposed to be **2a**, but no spectroscopic data were given. Since then, **2a** has been reported a few other times: in 1973 from the reaction of propargyl aldehyde (2-propynal) and methylamine,[28] and in 1978 through the reaction of β-aziridinylacroleins with methylamine.[29] The latter paper reported the ^{1}H-NMR spectrum of **2a** along with other characterization data. A 1974 paper on electrochemical and spectroscopic studies of simple polymethine dyes included some data for **2a**, but no synthetic details were given.[30] A more recent paper on **2a** by *de la Hoz et al.* will be discussed below.[31]

[1] Some macrocyclic compounds can also be considered as elaborated *N,N′*-dialkyl-β-dialdimines,[24] but we have excluded these compounds from this discussion.

The *N*,*N*′-diethyl compound **2b** was briefly mentioned in 1979 as a yellow oil that was said to decompose at room temperature, and so was characterized only in its protonated form by NMR spectroscopy.[32]

N,*N*′-Dibenzyl-1,3-propanedialdimine can be made from 1,5-di-*p*-tolyl-1,5-diazapenta-1,3-dienium perchlorate and benzylamine in ethanol, followed by deprotonation of the resulting dialdiminium salt with sodium hydride.[31] *N*,*N*′-Dialkyl-β-dialdimines bearing a cyano substituent at the 3-position have been synthesized in good yields (85–87%) from 1,3,3-tributoxy-2-cyanopropene and certain alkyl amines (alkyl = benzyl, cyclohexyl, (*R*)-1-phenylethyl).[24] The *N*,*N*′-diadamantyl-β-dialdimine in which the central methine position is substituted with a formyl group has been made from triformylmethane and 1-aminoadamantane.[33]

The deprotonated form of the β-dialdimines (*i.e.*, the anionic β-dialdiminates) are also rare and the few examples known all have aryl groups on nitrogen. These examples include alkali metal salts of *N*,*N*′-diaryl-β-dialdiminates where aryl = phenyl,[34,35] *m*-(CF_3)phenyl,[34] *p*-tolyl,[34] or 2,6-$C_6H_3R_2$.[36] Some alkali metal *N*,*N*′-diaryl-β-dialdiminates salts are also known in which the central (3-position) atom of the ligand backbone bears an aryl substituent.[36–38]

There are only a few coordination complexes of *N*,*N*-dialkyl-β-dialdiminates. Among these are compounds of divalent Co, Ni, Cu, Zn, and Pd in which the central methine (3-position) is substituted with a nitro group, and the nitrogen atoms bear methyl, ethyl, isopropyl, isopentyl (3-methylbutyl), or cyclohexyl substituents.[39,40] In addition, there are some transition metal complexes of tetradentate ligands that incorporate *N*,*N*-dialkyl-β-dialdiminate units.[41–44] None of these complexes, however, contains unsubstituted *N*,*N*-dialkyl-β-dialdiminate ligands with small aliphatic alkyl groups on nitrogen.

In general, *N*,*N*′-dialkyl-β-dialdimines have been investigated far less often than their *N*,*N*′-diaryl or β-diketimine analogues, especially (in their deprotonated form) as ligands in coordination chemistry. In the context of chemical vapor deposition, however, *N*,*N*′-dialkyl-β-dialdimines have at least one attractive feature: lower molecular masses due to the lack of alkyl groups on the R^2 and R^4 positions. As a result, transition metal β-dialdiminates should be more volatile than the analogous β-diketiminate with the same substituents on the nitrogen atoms; higher vapor pressures are advantageous in the design and use of precursors for chemical vapor deposition. Here we describe convenient preparations of *N*,*N*′-dialkyl-1,3-propanedialdiminium chlorides, *N*,*N*′-dialkyl-1,3-propanedialdimines, and lithium *N*,*N*′-dialkyl-1,3-propanedialdiminates in which the alkyl groups are methyl, ethyl, isopropyl, or *tert*-butyl.

Results and Discussion

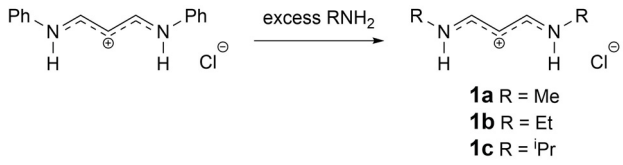
N,*N*′-Dialkyl-1,3-propanedialdiminium Chloride Salts

In 1995, *de la Hoz et al.* used a modification of *Dähne*'s method[27] to prepare 1,5-dimethyl-1,5-diazapenta-1,3-dienium perchlorate (*i.e.*, *N*,*N*′-dimethyl-1,3-propanedialdiminium perchlorate) in 93% yield by transamination of 1,5-di-*p*-tolyl-1,5-diazapenta-1,3-dienium perchlorate with methylamine in ethanol.[31] This β-dialdiminium salt is the perchlorate analog of **1a**.

To avoid working with potentially explosive perchlorate salts, we adapted this procedure to prepare the analogous chlorides. Thus, *N*,*N*′-diphenyl-1,3-propanedialdiminium chloride (a commercially available and inexpensive starting material that is also known as malonaldehyde bis(phenylimine) monohydrochloride) readily transaminates with a solution of methylamine, ethylamine, or isopropylamine in THF at room temperature. The desired compounds **1a**, **1b**, and **1c** precipitate from solution and can be obtained pure simply by filtration; the aniline byproduct is removed with the supernatant (*Scheme 1*).

Interestingly, these three transamination reactions occur in high yield (94–98%) even though neither the starting material nor the desired product has any appreciable solubility in THF. The transaminations can also be carried out in ethanol but the purification is more complicated because the products do not precipitate from this solvent, so that the aniline byproduct has to be removed in a separate step (such as removal of the solvent by distillation and washing out the aniline with diethyl ether).

In contrast to the reactions above, treatment of *N*,*N*′-diphenyl-1,3-propanedialdiminium chloride with *tert*-butylamine in THF results in transamination and deprotonation, resulting in the formation of *tert*-



Scheme 1. Synthesis of dialdiminium salts **1a**, **1b**, and **1c**.

butylammonium chloride and the neutral β-dialdimine **2d** (which is soluble in THF). The deprotonation reaction probably occurs for reasons related to the greater solubility of the β-dialdiminium salt **1d** in THF relative to salts with smaller alkyl groups. Although the transamination reaction proceeds in high yield, the separation of **2d** from the aniline byproduct is difficult.

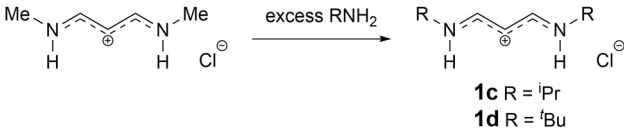
To circumvent these issues, we investigated whether **1d** could be obtained by transamination of the easily-prepared *N*,*N*′-dimethyl compound **1a**, with the expectation that the methylamine byproduct (a gas at room temperature) would be easy to remove. The reaction of **1a** with neat *tert*-butylamine is slow at room temperature, but heating this mixture to reflux affords the desired product **1d**, which can be isolated in 95% yield by simply removing the solvent in vacuum and washing the resulting solid with pentane. We also find that stirring **1a** in neat isopropylamine at room temperature affords the *N*,*N*′-di(isopropyl) compound **1c**; similar work-up affords this salt as pure material in 95% yield (*Scheme 2*).

All four of the chloride **1a**–**1d** salts are stable at room temperature in air for weeks to months but eventually hydrate and hydrolyze. They are best stored under inert atmosphere or in a vacuum desiccator; under such conditions they are stable indefinitely. The *N*,*N*′-dimethyl compound **1a** is insoluble in hydrocarbons, ethers, acetonitrile, benzonitrile, ethyl acetate, and chlorocarbons. In contrast, the *N*,*N*′-diethyl, -di(isopropyl) and -di(*tert*-butyl) compounds **1b**, **1c**, and **1d** dissolve slowly in dichloromethane and chloroform, and are moderately soluble in THF and diethyl ether. All four compounds are soluble in DMSO, water, and short-chain alcohols. The IR spectra of **1a**–**1d** contain a broad N–H stretching band near 3200 cm^{-1}, and a broad C=C and C=N stretching band near 1600 cm^{-1}. Complete ^{1}H- and $^{13}C\{^{1}H\}$-NMR data can be found in the *Experimental Section* and in *Tables S1.1*, *S1.2*, and *S1.3*.

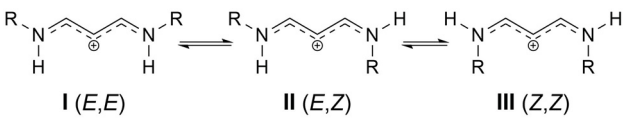
As has been discussed previously,[31] the N_2C_3 backbone in these compounds is always in the *trans*-s-*trans* configuration (also referred to as the all-*trans* or open-chain configuration) as shown in the ^{1}H-NMR spectrum by the *ca.* 12 Hz $^{3}J_{HH}$ coupling constants between the central CH group and the flanking CH groups (if one of the –CH–CH– units were in a *cis* configuration, the $^{3}J_{HH}$ coupling constant would be 6–8 Hz). Although the N_2C_3 backbone in these compounds is fixed in the *trans*-s-*trans* configuration, there are three possible isomers that differ in the locations of the two *N*-alkyl substituents, because of restricted rotation about the carbon-nitrogen bonds (*Scheme 3*).

The unsymmetrical (*E*,*Z*) isomer **II** can be easily identified by NMR spectroscopy because the two methine CH groups alpha to nitrogen are chemically inequivalent, but the symmetrical (*E*,*E*), and (*Z*,*Z*) isomers **I** and **III** can be distinguished only if couplings to the NH protons are observable (which is not the case in dry DMSO). For the perchlorate salts with R = methyl or benzyl, *de la Hoz* observed that all three isomers were present in solution, but when R = *p*-tolyl only one isomer was present; *de la Hoz* proposed that the latter existed exclusively as the (*E*,*E*) isomer **I** owing to steric and conjugation effects.[31]

For the chloride salts **1a**–**1c**, we find that all three isomers are indeed present in DMSO solution whereas only two isomers (one symmetrical isomer and very small amounts of **II**) are present for the *N*,*N*′-di(*tert*-butyl) compound **1d**. From steric considerations, we can confidently decide which symmetrical isomer of **1d** is likely present in solution: in the (*Z*,*Z*) configuration **III** there would be very short contacts of about 2.1 Å between some of the *tert*-butyl hydrogen atoms and the hydrogen atom on the central CH methine unit (as calculated by molecular modeling). These short H···H interactions are energetically unfavorable because they are significantly shorter than the 2.4 Å sum of the *van der Waals* radii for two hydrogen atoms.[45] In contrast, in the (*E*,*E*) configuration **I** the shortest H···H contacts are about 2.4 Å; this must be the isomer that the *N*,*N*′-di(*tert*-butyl) compound **1d** adopts in solution. *De la Hoz* assumed that the majority species in solution for the *N*,*N*′-dimethyl compound **1a** was also the (*E*,*E*) isomer **I**, but we will demonstrate in the following experiments that this assignment is incorrect. In these experiments, we make use of the observation that in imines (as in alkenes) the $^{3}J_{HH}$ coupling constant between the two hydrogen atoms in a RNH=CHR unit is larger for an (*E*)



Scheme 2. Synthesis of dialdiminium salts **1c** and **1d**.



Scheme 3. Isomers of the dialdiminium cations.

(*trans*) configuration than for a (*Z*) (*cis*) arrangement.[46,47]

In rigorously dried DMSO, the NH protons of **1a**–**1d** give broad ^{1}H-NMR resonances (*Figure 3*) with no observable couplings to the hydrogen atoms in the C_3H_3 backbone, suggesting that the NH protons are exchanging with one another. Intermolecular exchange of the NH protons is likely promoted by the DMSO solvent, which serves as a weak base that reversibly deprotonates a small amount of the β-dialdiminium salt to its β-dialdimine form: DMSO is a considerably stronger base than water (by about 1.5 p*K* units), and it is known that organic ammonium salts are stronger acids in DMSO than in water.[48,49]

We confirmed this hypothesis by adding trifluoroacetic acid (TFA) in excess to solutions of each compound in dry DMSO (*Figure 3*); by inhibiting deprotonation the exchange process should be greatly slowed. Consistent with this expectation, sharp NH resonances are seen for each isomer in the presence of excess acid, instead of the broad NH resonances seen in pure DMSO. For the *N*,*N*′-dimethyl compound **1a**, the major symmetrical isomer has a $^3J_{HH}$ coupling constant between the NH proton and the NCH proton of only 8 Hz, which shows that these two hydrogen atoms are in a (*Z*) (*cis*) relationship; therefore, the major symmetrical isomer has the (*Z*,*Z*) configuration **III**. For the minor symmetrical isomer of **1a**, this same $^3J_{HH}$ coupling constant is much larger, 14 Hz, as expected for the (*E*,*E*) configuration **I**. For the *N*,*N*′-diethyl and *N*,*N*′-di(isopropyl) compounds **1b** and **1c** a similar analysis of the couplings to the NH protons enables us to determine which resonances are due to isomer **I** and which are due to **III**. The spectrum of the *N*,*N*′-di(*tert*-butyl) compound **1d** in the presence of excess TFA confirms our expectation from steric considerations that the dominant species in solution has the (*E*,*E*) configuration **I**: the NH resonance for the major species is a doublet with a large $^3J_{HH}$ coupling to the NH proton of 16 Hz.

These experiments show that, in DMSO, the three isomers **I**, **II**, **III** (*i.e.*, (*E*,*E*), (*E*,*Z*), and *Z*,*Z*), resp.) are present in a ratio of 6:29:65 for **1a**, 14:41:45 for **1b**, 29:45:26 for **1c**, and 95:5:0 for **1d**. For compounds **1a**, **1b**, and **1c**, the relative free energies of isomers **I**, **II**, and **III** at room temperature can be calculated from their relative concentrations at equilibrium using the reaction isotherm equation. For the *N*,*N*′-dimethyl compound **1a**, the (*Z*,*Z*) isomer **III** is the most stable and the (*E*,*Z*) and (*E*,*E*) isomers are 0.48 and 1.41 kcal mol^{-1} higher in energy, respectively. For the *N*,*N*′-diethyl compound **1b**, the (*Z*,*Z*) isomer is again the most stable and the (*E*,*Z*) and (*E*,*E*) isomers are 0.06 and 0.69 kcal mol^{-1} higher in energy, respectively. For

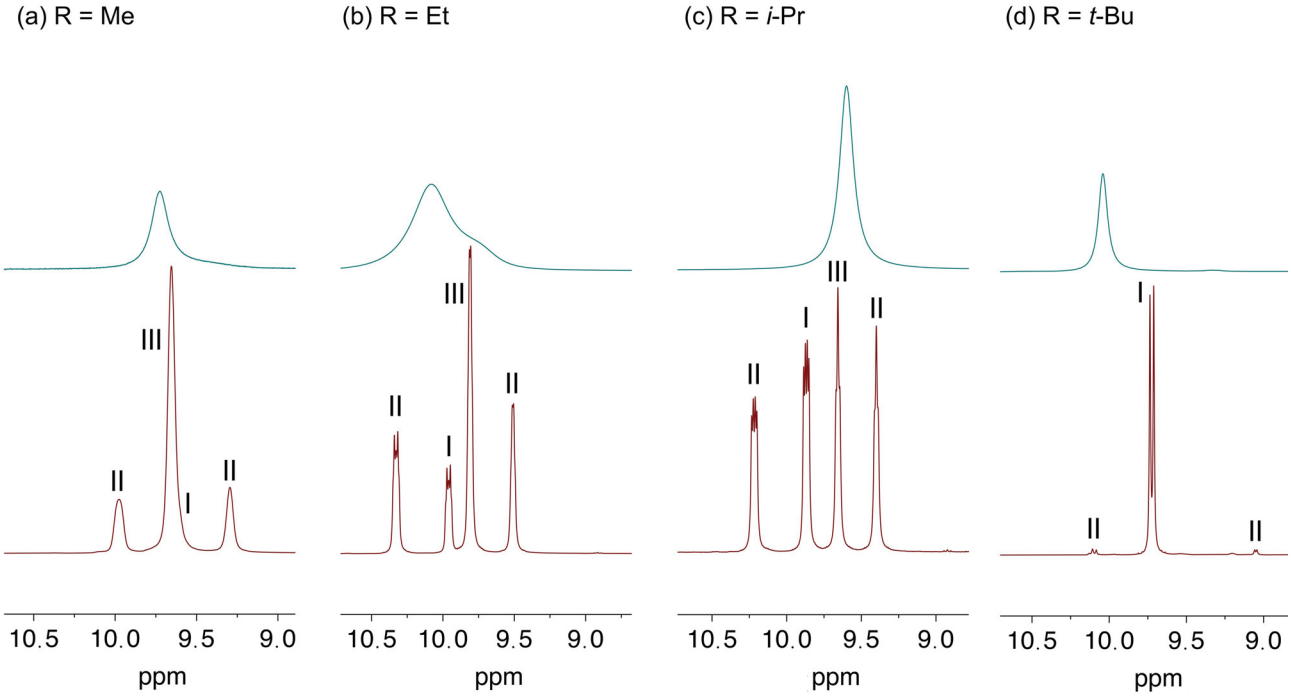


Figure 3. ^{1}H-NMR resonances for the NH groups in compounds (a) **1a** (b) **1b** (c) **1c** (d) **1d** in dry DMSO (top) and acidified dry DMSO (bottom).

the *N*,*N*′-di(isopropyl) compound **1c**, the unsymmetrical (*E*,*Z*) isomer **II** has the lowest free energy and the (*Z*,*Z*) and (*E*,*E*) isomers are 0.26 and 0.32 kcal mol^{-1} higher in energy, respectively; (alternatively, referenced to the energy of the (*Z*,*Z*) isomer, the (*E*,*Z*) and (*E*,*E*) isomers have energies of −0.26 and 0.06 kcal mol^{-1}, resp.). For the *N*,*N*′-di(*tert*-butyl) compound **1d** there is no evidence of the (*Z*,*Z*) isomer; instead, the (*E*,*E*) isomer is the most stable with the (*E*,*Z*) isomer being 1.74 kcal mol^{-1} higher in energy. A plot of the relative free energies can be found in the *Supporting Information* (*Figure S1.1*).

Overall, as the *N*-alkyl group becomes larger in size, the (*Z*) configurations at each end of the molecule are increasingly disfavored and the equilibrium shifts in favor of the (*E*) configurations. Thus, for small *N*-alkyl groups (methyl, ethyl), the preferred β-dialdiminium species in DMSO solution is the (*Z*,*Z*) isomer **III**, in which the R and R′ groups in the RNH=CHR′ units are *cis* (here, of course, the N–C bond is a partial double bond). This preference is the opposite of that seen in alkenes of the type RCH=CHR′, for which the *trans* (*E*) isomer is energetically preferred even when R and R′ are small groups such as methyl.[50] Although the lower free energy of *trans*-alkenes is often ascribed to repulsive steric effects (and this is certainly the reason when the substituents are large), for R=Me the reasons behind the preference for the *trans* configuration are complex.[51] There have been a number of studies of the (*E*/*Z*) preferences in a variety of other species (such as the RCO–XR′ units in carboxylic esters, thioesters, secondary amides, and acids, in which the C–X bond has partial multiple bond character).[52–55] These studies have ascribed the observed preference to a variety of factors, including steric effects, dipole interactions, hyperconjugation, and solvation effects.

We have carried out some calculations (see *Supporting Information* for computational details) of the three isomers of the *N*,*N*′-dimethyl compound **1a**. We find that (as has been seen in some other systems)[55] the observed stability trend can be reproduced only with certain choices of functional/theory and solvent corrections (see *Supporting Information*). Finding reasons to explain why a compound preferentially adopts a particular structure becomes difficult when alternative structures have only slightly higher free energies, as is the case here: the free energies of the three isomers of **1a** in solution differ by 1.5 kcal mol^{-1} or less. The best conclusion from our calculations is that there is no simple explanation for why **1a** prefers to adopt the (*Z*,*Z*) configuration **III**, but that solvation effects enhance the preference for this isomer.

N,*N*′-Dialkyl-1,3-propanedialdimines

De la Hoz reported that deprotonation of *N*,*N*′-dimethyl-1,3-propanedialdiminium perchlorate with NaH in dichloromethane afforded the neutral *N*,*N*′-dimethyl-1,3-propanedialdimine **2a**, which decomposed on attempted recrystallization. In our hands, this method does not work for **1a** (the yield was very poor), most likely because this chloride salt is insoluble in dichloromethane.

We have found two methods to deprotonate all four compounds **1a**–**1d** that best combine convenience with a reasonable yield of the corresponding neutral β-dialdimine. The first is a modification of *Hirsch's* method[26] in which deprotonation of the β-dialdiminium salt is carried out in water, the β-dialdimine product is extracted into dichloromethane, the extract is dried, the solvent is removed, and after an additional drying step the isolated yields of sublimed **2a**–**2d** are 31–51% depending on the R group (with the yield of **2a** being the lowest). Although this method is easily scalable, it is important to minimize the amount of time that the product is exposed to water (30 min or less) because hydrolytic decomposition of the desired product occurs over time and the product yields suffer accordingly.

The second deprotonation method, which is also a modification of a literature method,[9] involves addition of the β-dialdiminium salt to one equivalent of sodium methoxide (or ethoxide) in methanol. The resulting solution is filtered from the NaCl precipitate, the solvent is removed, the resulting oil is treated with molecular sieves to remove residual methanol, and the product is sublimed to obtain the β-dialdimine **2a**–**2d** in yields ranging from 44–73% depending on the R group.

For both deprotonation methods, vacuum removal of the solvent is best carried out at 0 °C in order to minimize the loss of the β-dialdimine products (especially for the more volatile compounds **2a** and **2b**).

The β-dialdimines **2a**–**2d** are all colorless low-melting solids that sublime readily at or near room temperature under moderate vacuum. They are soluble in hydrocarbons, chlorocarbons, ethers, alcohols, acetonitrile, and DMSO. Compounds **2a** and **2b** are thermally unstable: they will decompose if left at or near room temperature overnight. Compounds **2c** and

2d are much less thermally sensitive and can be left at room temperature for at least a week.

Upon exposure to air, the *N*,*N*′-dimethyl and *N*,*N*′-diethyl compounds **2a** and **2b** hydrate rapidly and become yellow oils that further decompose over the course of a few hours. As mentioned in the *Introduction*, **2a** and **2b** (which in our hands are crystalline solids) have usually been described as oils; it is now clear that these oils were the hydrated, impure, or decomposed form of these compounds. Compounds **2c** and **2d** can be handled in air for half an hour to several days (depending on the humidity) before hydration or decomposition occurs. All four compounds are best stored in a freezer in an inert atmosphere; under these conditions the compounds can be kept for at least several weeks or months.

We have determined the crystal and molecular structures of three of the β-dialdimines: the *N*,*N*′-dimethyl compound **2a**, the *N*,*N*′-di(isopropyl) compound **2c**, and the *N*,*N*′-di(*tert*-butyl) compound **2d** (*Table 1*). In the solid state, all three compounds adopt the open-chain conformation (*Figure 4*). The NH hydrogen atom is localized on one of the two nitrogen atoms, and accordingly the backbone is desymmetrized and consists of localized C–C and C–N single and double bonds (RN=C–C=C–NHR). In **2a**, the NH groups form intermolecular hydrogen bonds to adjacent molecules in a head-to-tail fashion; the result is that the molecules form zig-zag chains along the *c*-axis (*Figure 5*). Similarly, the molecules of **2c** and **2d** are connected into head-to-tail chains by intermolecular hydrogen bonds, except that for **2c** and for **2d** the chains form helices parallel to the *b*- and *a*-axes, respectively (*Figures 6* and *7*) instead of forming a zig-zag pattern.

As seen in enamines and in crystallographically characterized β-diketimines and β-dialdimines,[56–61] the amine nitrogen (which forms three single bonds, to the *N*-alkyl group, a hydrogen atom, and one CH group of the three-carbon backbone) shows no stereochemically active lone pair and instead is almost exactly planar (sp^2 hybridized): the sum of the three angles around this nitrogen atom is 359.97°, 359.5°, and 358.98° for **2a**, **2c**, and **2d**, respectively.

An interesting aspect of the crystal structures is that molecules of the *N*,*N*′-dimethyl and *N*,*N*′-di-

Table 1. Crystallographic data for *N*,*N*′-dimethyl-1,3-propanedialdimine (**2a**), *N*,*N*′-di(isopropyl)-1,3-propanedialdimine (**2c**), and *N*,*N*′-di(*tert*-butyl)-1,3-propanedialdimine (**2d**).

	2a	**2c**	**2d**
Formula	$C_5H_{10}N_2$	$C_9H_{18}N_2$	$C_{11}H_{22}N_2$
Formula weight	98.15	154.25	182.30
T [K]	100	100	100
λ [Å]	0.71073 (Mo Kα)	1.54178 (Cu Kα)	0.71073 (Mo Kα)
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	9.9058(5)	15.7037(4)	5.9214(3)
b [Å]	6.1227(3)	17.6342(4)	12.1100(7)
c [Å]	10.9624(6)	31.2951(9)	17.1077(10)
β [°]	109.960(2)	90	90
V [Å^3]	624.93(6)	8666.3(4)	1226.76(12)
Z	4	32	4
ϱ_{calc} [g cm^{-3}]	1.043	0.946	0.987
μ [mm^{-1}]	0.066	0.431	0.059
F(000)	216.0	2752.0	408.0
Crystal size [mm]	0.275×0.235×0.154	0.462×0.21×0.07	0.448×0.158×0.144
2θ range [°]	4.374 to 56.564	5.648 to 149.272	4.762 to 50.716
R(int)	0.0235	0.0679	0.0344
Abs. corr. type	Multi-scan	Multi-scan	Multi-scan
Max, min transmission factors	0.7457, 0.6857	0.7538, 0.6566	0.7452, 0.6612
Data/restraints/parameters	1547/0/79	210439/0/850	2244/0/127
GOF on F^2	1.123	1.008	1.108
R_1 [$I>2\sigma(I)$][a]	0.0354	0.0559	0.0408
wR_2 (all data)[b]	0.0922	0.1407	0.1045
Max, min $\Delta\varrho_{elect}$ [e Å^{-3}]	0.23/−0.19	0.29/−0.22	0.21/−0.16
Flack parameter	NA	0.03(7)	−0.1(7)

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

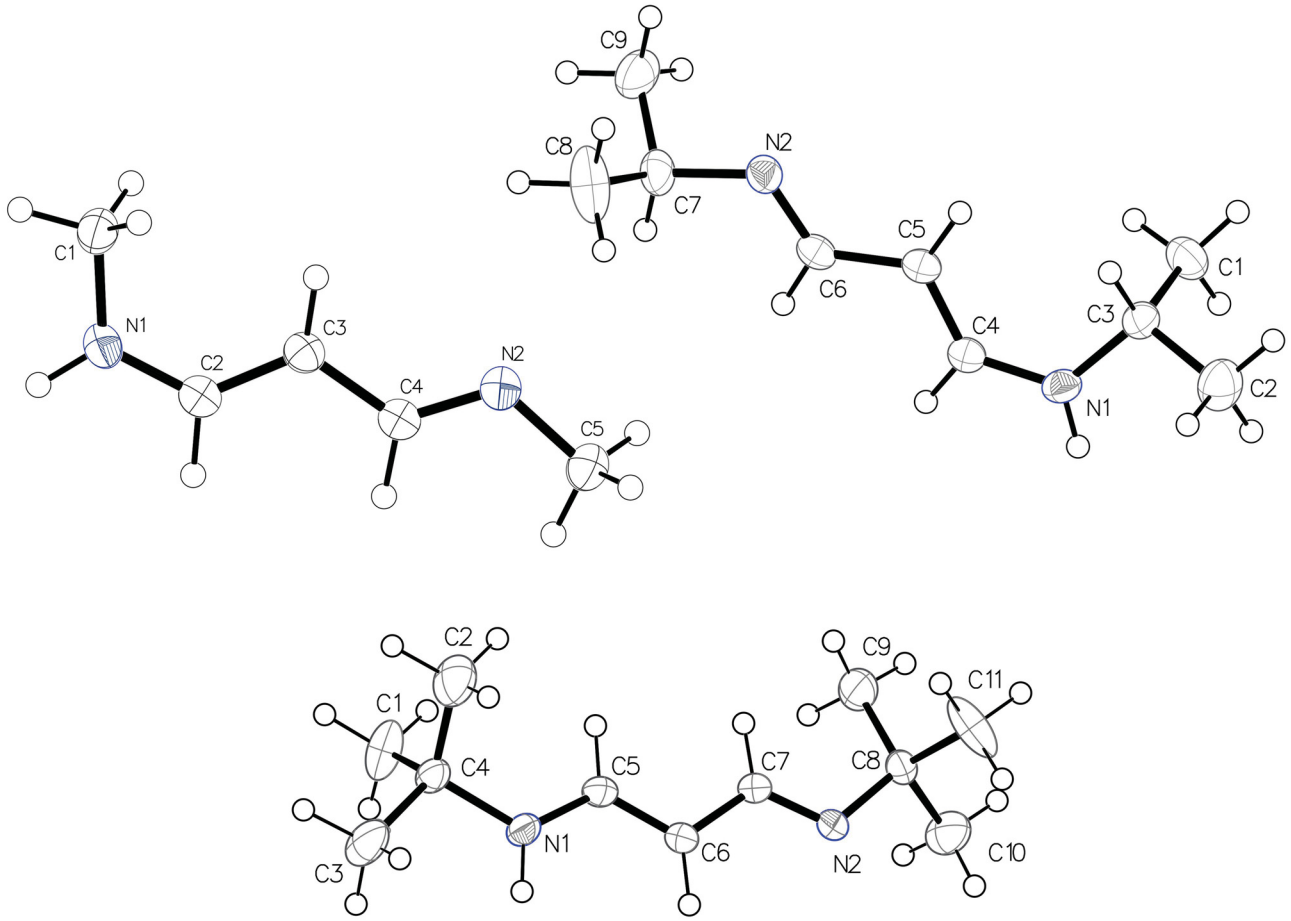


Figure 4. Molecular structures of **2a**, **2c**, **2d**. Thermal ellipsoids drawn at the 50% probability density level except for hydrogen atoms, which are represented by arbitrarily-sized spheres.

(isopropyl) compounds **2a** and **2c** both adopt the (*E*,*Z*) configuration, whereas molecules of the *N*,*N*′-di(*tert*-butyl) compound **2d** adopt the (*E*,*E*) configuration. The geometries of the neutral β-dialdimines will be influenced by the same steric repulsions between the *N*-alkyl groups and the central CH hydrogen atom seen for the protonated β-dialdiminium salts **1a**–**1d** discussed above. Thus, for **2c** and **2d**, the isomer seen in the solid state ((*E*,*Z*) and (*E*,*E*), respectively) is the analog of the isomer that is most prevalent in solution for the protonated analogs **1c** and **1d**. For **2a**, the (*E*,*Z*) solid state structure corresponds to the isomer of **1a** with the second-lowest energy seen in solution.

The current crystal structures are the first for *N*,*N*′-dialkyl-β-dialdimines, but they can usefully be compared with those of *N*,*N*′-dialkyl-β-diketimines, *N*,*N*′-diaryl-β-diketimines, and *N*,*N*′-diaryl-β-dialdimines (all these compounds have localized single and double bonds along the backbone, and this aspect will not be discussed further). There is one known crystal structure (and a correction) of an *N*,*N*′-dialkyl-β-diketimine[62,63] and many dozen crystal structures of *N*,*N*′-diaryl-β-diketimines.[3,13,57–61] Unlike **2a**, **2c**, and **2d**, all of these compounds – including those with fluorinated substituents, extremely bulky substituents, non-hydrogen substituents on the central methine carbon, or different substituents at the two imine carbon atoms – crystallize in the closed U-shaped conformation with an intramolecular hydrogen bond. Evidently, for β-diketimines the open chain structure is disfavored because steric repulsions involving the substituents attached to the imino carbon atoms cause a significant energy penalty.

In contrast, in β-dialdimines the substituents on the imino carbon atoms are hydrogen atoms, and the steric repulsions involving these groups are small. Of the roughly twenty *N*,*N*′-diaryl-β-dialdimines that have been crystallographically characterized, two[56,64] crystallize in the open-chain conformation (R^1=R^5=Ph, R^2=R^3=R^4=H and R^1=R^5=2,6-di(isopropyl)phenyl=

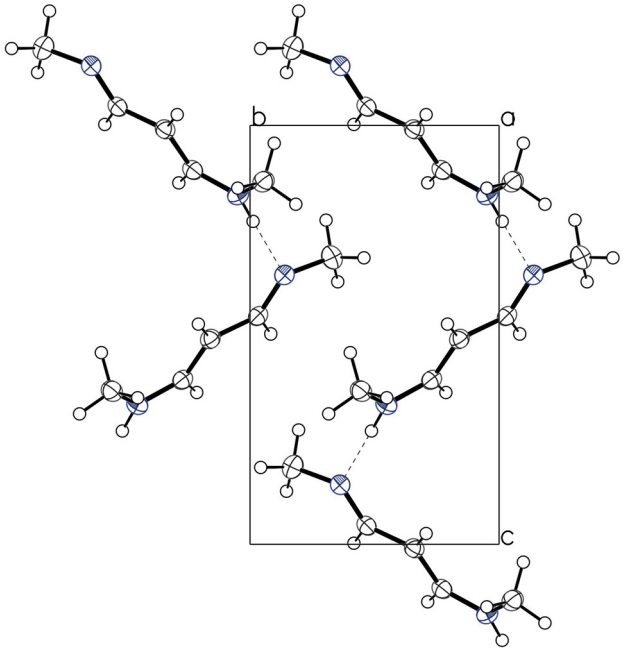


Figure 5. Packing diagram for **2a** showing the hydrogen-bonded zig-zag chains.

Dipp, R^2=R^4=H, R^3=Me; see *Figure 1*) whereas the remainder adopt the closed U-shaped conformation.[37] Of the two compounds that adopt the open-chain conformation, *N,N′*-diphenyl-β-dialdimine shows intermolecular hydrogen bonding in a head-to-tail manner similar to the pattern seen for **2a**,[64] whereas the *N,N′*-bis(Dipp)-β-dialdimine compound with R^3=Me is hydrogen-bonded to co-crystallized methanol molecules.[56] For the latter compound, the relative energies of the two conformations have been calculated by semiempirical methods, and for isolated molecules the closed U-shaped form is more stable. Hydrogen bonding networks, however, can stabilize the open-chain conformation.[56]

In benzene solution, the N_2C_3 backbones in all four compounds **2a**–**2d** adopt the *cis*-s-*cis* (*i.e.*, closed, U-shaped) conformation, as shown by the 6 Hz $^3J_{HH}$ coupling constants between the methine hydrogen atoms in the ^{1}H-NMR spectra (for comparison, $^3J_{HH}$ coupling constants of 8.6 and 10.7 Hz were seen for the methine resonances of **2a** in CCl_4[29] and **2b** in acetone-d_6,[32] resp.). In benzene (an aprotic solvent), the adoption of the *cis*-s-*cis* backbone structure is most likely due to the presence of an intramolecular hydrogen bond between the two nitrogen atoms. The consequent ability of the NH proton to jump rapidly between the two nitrogen atoms accounts for the NMR equivalence of the two halves of the molecules in benzene solution (and for the lack of observable couplings in the NH resonances, which are broad). Although the ^{1}H-NMR resonances for the backbone methine groups of **2a**–**2d** are sharp in benzene, they are broad in methanol and DMSO, most likely due to dynamic equilibria involving the isomers in which the N_2C_3 backbone adopts an open-chain conformation; in such solvents, these conformers are stabilized with respect to the closed U-shaped conformer because they can engage in intermolecular hydrogen bonding with solvent molecules. Broad resonances for the methine protons were also seen in ^{1}H-NMR spectrum of **2a** in $CDCl_3$.[31]

The IR spectra of compounds **2a**–**2d** all show two strong peaks near 1575 and 1645 cm^{-1} due to C=C and C=N stretching vibrations.

Lithium N,N′-Dialkyl-1,3-propanedialdiminates

Unlike the deprotonation of β-diketimines, which readily affords pentane-soluble lithium β-diketiminate salts that are useful synthetically,[17] deprotonation of the β-dialdimines often gives orange-colored gelatinous precipitates that proved ineffective in salt metathesis reactions with transition metal starting materials. Eventually, we found that the β-dialdiminate salts could be prepared successfully by slow addition of a slight (10%) excess of an alkyllithium reagent (preferably *sec*-butyllithium) to a pentane solution of the β-dialdimine at 0 °C. For **3a**, **3b**, and **3c**, it is important to keep the solution cold even after the addition step; isolation of the product is best achieved by cooling the resulting solution to −78 °C and collecting the precipitated product at that temperature by filtration. The *N,N′*-di(*tert*-butyl) compound **3d** is less heat-sensitive, and the deprotonation can be carried out successfully at room temperature. The isolated yields of the lithium β-dialdiminates are 81% for the *N,N′*-dimethyl compound **3a**, 69% for the *N,N′*-diethyl and *N,N′*-di(isopropyl) compounds **3b** and **3c**, and 82% for the *N,N′*-di(*tert*-butyl) compound **3d**.

Interestingly, once the lithium salts are collected by filtration and dried, they can be kept under argon as solids at room temperature for at least several weeks. Compounds **3a**–**3d** are insoluble in benzene but soluble in diethyl ether and THF; they decompose in chlorocarbons. The NMR spectra of **3a**–**3d** in THF show that the $^3J_{HH}$ couplings are all near 6 Hz, so that these compounds adopt the closed U-shaped conformation in solution; presumably, the β-dialdiminate anions coordinate in a chelating fashion to the lithium

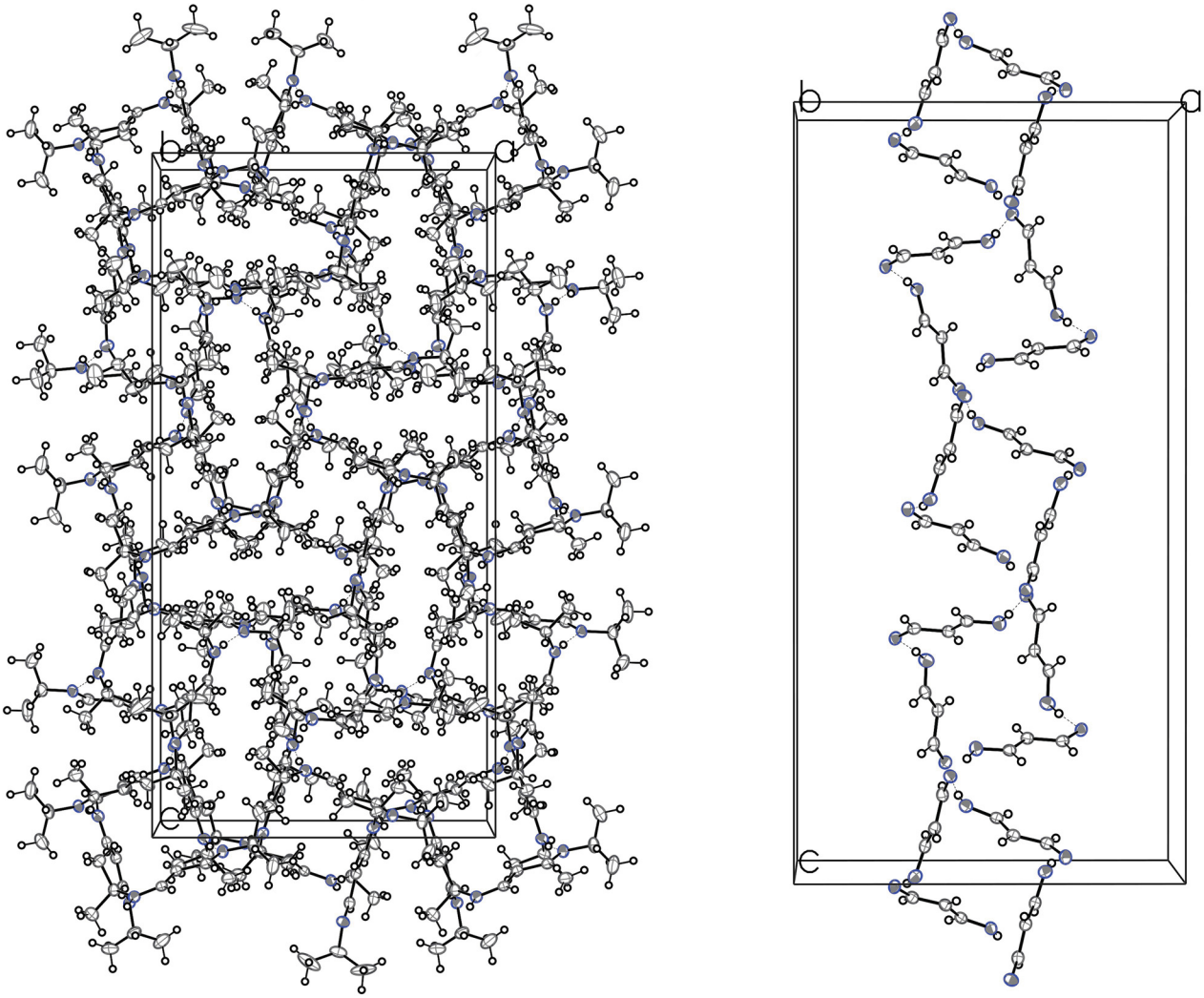


Figure 6. Packing diagram for **2c** showing the hydrogen-bonded helices. In the right diagram, the isopropyl groups have been omitted for clarity.

cations, as seen in lithium β-diketiminates[13,15,65,66] and lithium β-dialdiminates.[35,37]

Conclusions

We have developed convenient preparations of *N*,*N*′-dialkyl-1,3-propanedialdiminium chlorides, *N*,*N*′-dialkyl-1,3-propanedialdimines, and lithium *N*,*N*′-dialkyl-1,3-propanedialdiminates in which the alkyl groups are methyl, ethyl, isopropyl, or *tert*-butyl. For the dialdiminium salts, when the *N*-alkyl group is methyl or ethyl the preferred species in DMSO solution is the (*Z*,*Z*) isomer **III** in which the R and R′ groups in the RNH=CHR′ units are *cis*; this conclusion differs from earlier work, which assumed that these compounds adopted the (*E*,*E*) structure. The reason for the preference for the (*Z*,*Z*) isomer is not clear; the energy differences are small enough that DFT calculations provide no insights. For larger *N*-alkyl groups, the (*Z*,*Z*) isomer is disfavored owing to steric repulsions, and in solution the equilibrium increasingly consists of the (*E*,*Z*), and (*E*,*E*) isomers. We also found that in dry DMSO the ^{1}H-NMR resonances for the NH protons are broad owing to exchange through a deprotonation mechanism, but that this exchange can be inhibited (and the NH resonances can be sharpened) by addition of an acid.

For the neutral dialdimines, previous reports described the *N*,*N*′-dimethyl and *N*,*N*′-diethyl compound

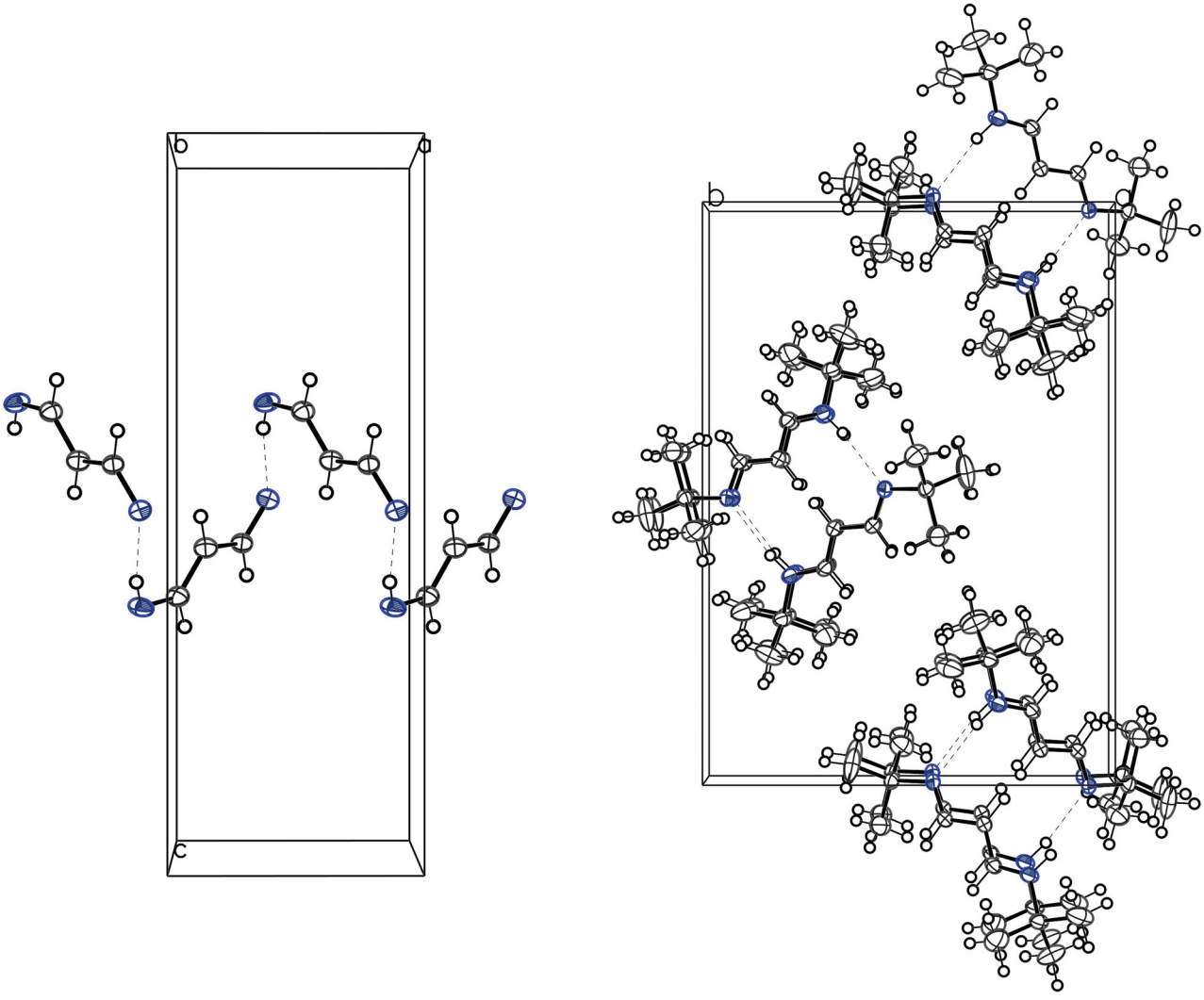


Figure 7. Packing diagram for **2d**, showing two views of the hydrogen-bonded helices. In the left diagram, the *tert*-butyl groups have been omitted for clarity.

as oils, but we find that these compounds are crystalline solids; it is now clear that the oils were the hydrated, impure, or decomposed form of these compounds. Crystal structures, which are the first for *N*,*N*′-dialkyl-β-dialdimines, show that the *N*,*N*′-dimethyl and *N*,*N*′-di(isopropyl) compounds both adopt the (*E*,*Z*) configuration, whereas the *N*,*N*′-di(*tert*-butyl) compound adopts the (*E*,*E*) configuration. In all three crystal structures, the molecules are linked by hydrogen bonds into chains. Interestingly, whereas in the solid state the N_2C_3 backbone of the neutral dialdimines is in the open *trans*-s-*trans* configuration, in benzene solution the backbone is in the closed (or U-shaped) *cis*-s-*cis* configuration, in which almost certainly there is an intramolecular hydrogen bond between the two nitrogen atoms. Deprotonation of the neutral dialdimines with *sec*-butyllithium affords the corresponding lithium dialdiminate salts, which were isolated as colorless or pale-colored solids. We have already begun to employ these lithium salts as reagents for the preparation of coordination complexes with metals; such compounds are potentially of interest as precursors for the chemical vapor deposition of thin films. These results will be communicated separately.

Experimental Section

General Considerations

All operations were carried out in vacuum or under argon using standard *Schlenk* and glove box techniques unless otherwise stated. All glassware was oven dried before use. Solvents were distilled under nitrogen from sodium/benzophenone (pentane, diethyl ether, and THF), calcium hydride (dichloromethane), or magnesium/iodide (methanol) before use. Malonaldehyde bis(phenylimine) monohydrochloride, methylamine (2.0 M solution in THF), ethylamine (2.0 M solution in THF), sodium hydride (60 wt-% in oil), isopropylamine, *tert*-butylamine, *sec*-butyllithium (1.4 M solution in cyclohexane), and *n*-butyllithium (1.6 M solution in hexanes) were purchased from *Sigma–Aldrich* and used as received. Deuterated benzene and THF (*Cambridge Isotope Laboratories*) were distilled from calcium hydride (benzene) or sodium/benzophenone (THF) and stored over 3 Å molecular sieves; deuterated dimethyl sulfoxide (*Cambridge Isotope Laboratories*) was distilled from calcium hydride under vacuum and stored over 4 Å molecular sieves. The 3 Å and 4 Å molecular sieves (*Alfa Aesar*) were dried in a vacuum oven overnight (*ca.* 130 °C, *ca.* 10 mTorr) before use and stored under argon. All other compounds were purchased as reagent grade and used as received.

Elemental analyses were performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. FT-IR spectra were acquired on a *Thermo Nicolet IR200* spectrometer as Nujol mulls between KBr plates and processed using the Omnic software package. NMR spectra were recorded on a *Varian Unity Inova 400* spectrometer at 9.4 T, a *Varian Unity Inova 500NB* spectrometer at 11.75 T, a V*arian VXR 500* spectrometer with *Unity Inova 500* console at 11.75 T, a *Varian Unity Inova 500* spectrometer at 11.75 T, or a *B600 Bruker NEO* spectrometer at 14.1 T. Chemical shifts are reported in δ units, more positive shifts to higher frequency relative to TMS, as referenced to residual solvent peaks; coupling constants are reported in Hz. Melting points and decomposition temperatures were determined in closed capillaries under argon on a *Thomas-Hoover Unimelt* apparatus.

N*,*N*′-Dimethyl-1,3-propanedialdiminium Chloride** (=N*-Methyl-3-(methylamino)prop-2-en-1-iminium Chloride**; **1a**). This preparation can be conducted in air, but dry THF must be employed. To a suspension of malonaldehyde bis(phenylimine) monohydrochloride (50.30 g, 193 mmol) in THF (200 mL) was added methylamine (300 mL of a 2.0 M solution in THF, 600 mmol). The cloudy yellow solution was stirred vigorously for 12 h at room temperature (if stirring is inefficient, more THF can be added). The precipitate was collected by filtration, washed with diethyl ether (4×100 mL), and dried in vacuum to afford a colorless powder. Yield: 25.73 g (98 %). M.p. *ca.* 200 °C (dec). IR: 3205 br., 3148 br., 1618 m, 1330 m, 1297 m, 1224 m, 1034 w, 975 w, 767 m. ^{1}H-NMR (500 MHz, dry DMSO-d_6, 25 °C): isomer **I**: 9.72 (br., 2H, NH), 5.58 (br., 1H, β-CH), 3.01 (s, 6H, CH_3), all other peaks obscured; isomer **II**: 9.72 (br., 2H, NH), 7.90 (d, ^{3}J(H,H) = 12, 1H, N=CH), 7.71 (d, ^{3}J(H,H) = 12, 1H, N=CH′), 5.42 (t, ^{3}J(H,H) = 12, 1H, β-CH), 3.05 (s, 3H, CH_3), 2.81 (s, 3H, CH_3); isomer **III**: 9.72 (br., 2H, NH), 7.90 (d, ^{3}J(H,H) = 12, 2H, N=CH), 5.47 (t, ^{3}J(H,H) = 12, 1H, β-CH), 2.92 (s, 6H, CH_3). ^{1}H-NMR (500 MHz, dry DMSO-d_6 in the presence of excess TFA, 25 °C): isomer **I**: 9.59 (br., 2H, NH), 7.66 (dd, ^{3}J(H,H) = 14, 12, 2H, N=CH), 5.57 (t, ^{3}J(H,H) = 12, 1H, β-CH), 3.00 (d, ^{3}J(H,H) = 5, 6H, CH_3); isomer **II**: 9.98 (br., 1H, NH), 9.29 (br., 1H, NH′), 7.90 (dd, ^{3}J(H,H) = 14, 11, 1H, N=CH), 7.70 (dd, ^{3}J(H,H) = 12, 8, 1H, N=CH′), 5.42 (t, ^{3}J(H,H) = 12, 1H, β-CH), 3.04 (d, ^{3}J(H,H) = 5, 3H, CH_3), 2.81 (d, ^{3}J(H,H) = 5, 3H, CH_3′); isomer **III**: 9.66 (br., 2H, NH), 7.90 (dd, ^{3}J(H,H) = 12, 8, 2H, N=CH), 5.45 (t, ^{3}J(H,H) = 12, 1H, β-CH), 2.91 (d, ^{3}J(H,H) = 5, 6H, CH_3). ^{13}C{^{1}H}-NMR (600 MHz, DMSO-d_6, 25 °C): isomer **I**: 164.40 (s, N=CH), 92.15 (s, β-CH), 35.03 (s, CH_3); isomer **II**: 166.19 (s, N=CH), 160.38 (s, N=CH′), 90.00 (s, β-CH), 35.36 (s, CH_3), 29.73 (s, CH_3′); isomer **III**: 162.21 (s, N=CH), 88.54 (s, β-CH), 30.09 (s, CH_3). The NMR data matched those previously reported for the perchlorate salts.[31] Anal. calc. for $C_5H_{11}N_2Cl$ (134.61): C 44.6, H 8.24, N 20.8; found: C 44.5, H 8.12, N 20.4.

N*,*N*′-Diethyl-1,3-propanedialdiminium Chloride** (=N*-Ethyl-3-(ethylamino)prop-2-en-1-iminium Chloride**; **1b**). To a suspension of malonaldehyde bis(phenylimine) monohydrochloride (10.82 g, 42 mmol) in THF (125 mL) was added ethylamine (100 mL of a 2.0 M solution in THF, 200 mmol), which causes the yellow color of the suspension to lighten. After an hour, solids begin to precipitate; it is important that vigorous stirring be maintained to ensure complete conversion to product. The cloudy yellow suspension was stirred for 12 h at room temperature. Subsequent manipulations can be carried out in air. The precipitate was collected by filtration, washed with diethyl ether (3×100 mL), and dried by vacuum to afford a colorless powder. Yield:

6.41 g (94%). M.p. 131 °C. IR: 3200 br., 3136 br., 1609 m, 1574 m, 1549 m, 1299 m, 1269 m, 1226 m, 1140 w, 1087 m, 1017 w, 806 w. ^{1}H-NMR (500 MHz, dry DMSO-d_6, 25 °C): isomer **I**: 10.08 (br., 2H, NH), 7.70 (d, ^3J(H,H) = 12, 2H, N=CH), 5.67 (t, ^3J(H,H) = 12, 1H, β-CH), 3.29 (q, ^3J(H,H) = 7, 4H, CH_2), 1.16 (t, ^3J(H,H) = 7, 6H, CH_3); isomer **II**: 10.08 (br., 2H, NH), 8.06 (d, ^3J(H,H) = 11, 1H, N=CH), 7.66 (d, ^3J(H,H) = 12, 1H, N=CH′), 5.51 (t, ^3J(H,H) = 12, 1H, β-CH), 3.34 (q, ^3J(H,H) = 7.2, 2H, CH_2), 3.16 (q, ^3J(H,H) = 7.5, 2H, CH_2′), 1.11 (t, ^3J(H,H) = 7.3, 3H, CH_3), the second triplet is obscured; isomer **III**: 10.08 (br., 2H, NH), 7.86 (d, ^3J(H,H) = 12, 2H, N=CH), 5.55 (t, ^3J(H,H) = 12, 1H, β-CH), 3.31 (q, ^3J(H,H) = 7.3, 4H, CH_2), 1.14 (t, ^3J(H,H) = 7.3, 6H, CH_3). ^{1}H-NMR (500 MHz, dry DMSO-d_6 in the presence of excess TFA, 25 °C): isomer **I**: 9.96 (dt, ^3J(H,H) = 16, 5, 2H, NH), 7.75 (dd, ^3J(H,H) = 15, 12, 2H, N=CH), 5.63 (t, ^3J(H,H) = 12, 1H, β-CH), 3.29 (quintet, ^3J(H,H) = 6, 4H, CH_2), 1.16 (t, ^3J(H,H) = 7, 6H, CH_3); isomer **II**: 10.33 (dt, ^3J(H,H) = 15, 6, 1H, NH), 9.51 (q, ^3J(H,H) = 6, 1H, NH′), 8.00 (dd, ^3J(H,H) = 15, 12, 1H, N=CH), 7.65 (dd, ^3J(H,H) = 12, 8, 1H, N=CH′), 5.48 (t, ^3J(H,H) = 12, 1H, β-CH), 3.33 (quintet, ^3J(H,H) = 6, 2H, CH_2), 3.16 (quintet, ^3J(H,H) = 6, 2H, CH_2′), 1.12 (t, ^3J(H,H) = 6, 3H, CH_3), 1.11 (t, ^3J(H,H) = 7, 3H, CH_3′); isomer **III**: 9.81 (q, ^3J(H,H) = 6, 2H, NH), 7.84 (dd, ^3J(H,H) = 12, 8, 2H, N=CH), 5.53 (t, ^3J(H,H) = 12, 1H, β-CH), 3.30 (quintet, ^3J(H,H) = 7, 4H, CH_2), 1.13 (t, ^3J(H,H) = 7, 6H, CH_3). ^{13}C{^{1}H}-NMR (600 MHz, DMSO-d_6, 25 °C): isomer **I**: 162.99 (s, N=CH), 92.05 (s, β-CH), 43.30 (s, CH_2), 15.29 (s, CH_3); isomer **II**: 164.85 (s, N=CH), 159.17 (s, N=CH′), 89.88 (s, β-CH), 43.59 (s, CH_2), 37.94 (s, CH_2′), 15.16 (s, CH_3), 13.03 (s, CH_3′); isomer **III**: 161.13 (s, N=CH), 88.38 (s, β-CH), 38.20 (s, CH_2), 13.15 (s, CH_3). Anal. calc. for $C_7H_{15}N_2Cl$ (162.66): C 51.7, H 9.29, N 17.2; found: C 51.5, H 9.08, N 17.0.

***N*,*N*′-Di(isopropyl)-1,3-propanedialdiminium Chloride** (= ***N*-(Propan-2-yl)-3-[(propan-2-yl)amino]-prop-2-en-1-iminium Chloride**; **1c**). This preparation can be conducted in air. To a suspension of malonaldehyde bis(phenylimine) monohydrochloride (10.18 g, 39 mmol) in THF (110 mL) was added isopropylamine (10 mL, 116 mmol). The cloudy yellow solution was stirred vigorously for 12 h at room temperature (if stirring is inefficient, more THF can be added). The precipitate was collected by filtration, washed with diethyl ether (5 × 50 mL), and dried in vacuum to afford a colorless powder. Yield: 7.07 g (94%). M.p. 205–210 °C (dec). IR: 3144 br., 1631 br., 1314 m, 1274 m, 1216 m, 1162 m, 1145 m, 1066 m, 851 m. ^{1}H-NMR (500 MHz, dry DMSO-d_6, 25 °C): isomer **I**: not observed in dry DMSO, but even the smallest amount of water will show the presence of isomer **I** with resolved peaks; isomer **II**: 9.60 (br., 2H, NH), 8.20 (br., 1H, N=CH), 7.60 (br., 1H, N=CH′), 5.54 (br., 1H, β-CH), 3.62 (sept, ^3J(H,H) = 7, 1H, N–CH), 3.62 (sept, ^3J(H,H) = 7, 1H, N–CH′), 1.18 (d, ^3J(H,H) = 6, 6H, CH_3), 1.18 (d, ^3J(H,H) = 6, 6H, CH_3′); isomer **III**: 9.60 (br., 2H, NH), 7.77 (d, ^3J(H,H) = 12, 2H, N=CH), 5.60 (t, ^3J(H,H) = 12, 1H, β-CH), 3.90 (sept, ^3J(H,H) = 7, 2H, N–CH), 1.17 (d, ^3J(H,H) = 7, 12H, CH_3). ^{1}H-NMR (500 MHz, nearly-dry DMSO-d_6, 25 °C): isomer **I**: 10.10 (br., 2H, NH), 7.86 (dd, ^3J(H,H) = 12, 5, 2H, N=CH), 5.68 (t, ^3J(H,H) = 11, 1H, β-CH), 3.59 (sept, ^3J(H,H) = 7, 2H, N–CH), 1.17 (d, ^3J(H,H) = 7, 12H, CH_3); isomer **II**: 10.56 (br., 1H, NH), 9.64 (br., 1H, NH′), 8.09 (d, ^3J(H,H) = 11, 1H, N=CH), 7.61 (dd, ^3J(H,H) = 11, 5, 1H, N=CH′), 5.55 (t, ^3J(H,H) = 11, 1H, β-CH), 3.3 (sept, ^3J(H,H) = 7, 1H, N–CH), 3.61 (sept, ^3J(H,H) = 7, 1H, N–CH′), 1.19 (d, ^3J(H,H) = 7, 6H, CH_3), 1.16 (d, ^3J(H,H) = 7, 6H, CH_3′); isomer **III**: 9.89 (br., 2H, NH), 7.78 (d, ^3J(H,H) = 12, 2H, N=CH), 5.61 (t, ^3J(H,H) = 11, 1H β-CH), 3,90 (sept, ^3J(H,H) = 7, 2H, N–CH), 1.15 (d, ^3J(H,H) = 7, 12H, CH_3). ^{1}H-NMR (500 MHz, dry DMSO-d_6 in the presence of excess TFA, 25 °C): isomer **I**: 9.87 (dd, ^3J(H,H) = 15, 7, 2H, NH), 7.79 (dd, ^3J(H,H) = 14, 12, 2H, N=CH), 5.61 (t, ^3J(H,H) = 12, 1H, β-CH), 3.61 (d sept, ^3J(H,H) = 7, 2H, N–CH), 1.17 (d, ^3J(H,H) = 7, 12H, CH_3); isomer **II**: 10.22 (dd, ^3J(H,H) = 15, 7, 1H, NH), 9.40 (t, ^3J(H,H) = 7, 1H, NH′), 8.01 (dd, ^3J(H,H) = 15, 11, 1H, N=CH), 7.59 (dd, ^3J(H,H) = 13, 8, 1H, N=CH′), 5.48 (t, ^3J(H,H) = 12, 1H, β-CH), 3.64 (d sept, ^3J(H,H) = 7, 1H, N–CH), 3.63 (d sept, ^3J(H,H) = 7, 1H, N–CH′), 1.20 (d, ^3J(H,H) = 7, 6H, CH_3), 1.16 (d, ^3J(H,H) = 7, 6H, CH_3′); isomer **III**: 9.66 (t, ^3J(H,H) = 7, 2H, NH), 7.76 (dd, ^3J(H,H) = 12, 8, 2H, N=CH), 5.60 (t, ^3J(H,H) = 12, 1H, β-CH), 3.90 (d sept, ^3J(H,H) = 7, 2H, N–CH), 1.17 (d, ^3J(H,H) = 7, 12H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, DMSO-d_6, 25 °C): isomer **I**: 161.46 (s, N=CH), 92.13 (s, β-CH), 50.36 (s, N–CH), 22.58 (s, CH_3); isomer **II**: 163.33 (s, N=CH), 158.17 (s, N=CH′), 89.94 (s, β-CH), 50.71 (s, N–CH), 45.20 (s, N–CH′), 22.47 (s, CH3), 21.21 (s, CH_3′); isomer **III**: 160.17 (s, N=CH), 88.35 (s, β-CH), 45.28 (s, N–CH), 21.29 (s, CH_3). Anal. calc. for $C_9H_{19}N_2Cl$ (190.71): C 56.7, H 10.0, N 14.7; found: C 56.6, H 10.1, N 14.7. Compound **1c** can also be prepared in 95% yield by treating *N*,*N*′-dimethyl-1,3-propanedialdiminium chloride (**1a**; 5.72 g, 37 mmol) with isopropylamine (50 mL, excess), stirring the mixture for 12 h at room temperature, followed by removal of the excess solvent (along with the methylamine byproduct) on a rotary evaporator to give a colorless solid.

***N*,*N*′-Di(*tert*-butyl)-1,3-propanedialdiminium Chloride** (= ***N*-*tert*-Butyl-3-(*tert*-butylamino)prop-2-

en-1-iminium Chloride; **1d**). This preparation can be conducted in air. To *N*,*N*′-dimethyl-1,3-propanedialdiminium chloride (**1a**; 3.11 g, 23 mmol) was added *tert*-butylamine (25 mL, excess) and the mixture was heated to reflux at 65 °C for 12 h. The solution was cooled and evaporated to dryness on a rotary evaporator. The resulting colorless solid was washed with pentane (4×50 mL) and dried in vacuum. Yield: 4.79 g (95 %). M.p. 225–230 °C (dec). IR: 3150 br., 3104 br., 3064 br., 1630 br., 1354 m, 1316 w, 1298 w, 1252 m, 1221 m, 1184 m, 1064 m, 1036 w, 915 w, 861 m, 808 w, 776 w. ^{1}H-NMR (500 MHz, dry DMSO-d_6, 25 °C): 10.04 (br. s, 2H, NH), 8.03 (d, ^{3}J(H,H) = 12, 2H, N=CH), 5.75 (t, ^{3}J(H,H) = 12, 1H, β-CH), 1.26 (s, 18H, CH_3). ^{1}H-NMR (500 MHz, dry DMSO-d_6 in the presence of excess TFA, 25 °C): isomer **I**: 9.73 (d, ^{3}J(H,H) = 16, 2H, NH), 7.94 (dd, ^{3}J(H,H) = 12, 15, 2H, N=CH), 5.62 (t, ^{3}J(H,H) = 12, 1H, β-CH), 1.23 (s, 18H, CH_3); isomer **II**: 10.10 (d, ^{3}J(H,H) = 15, 1H, NH), 9.05 (d, ^{3}J(H,H) = 9, 1H, NH′), 7.47 (dd, ^{3}J(H,H) = 13, 9, 1H, N=CH), the second aldiminate resonance is obscured, 5.76 (dd, ^{3}J(H,H) = 13, 11, 1H, β-CH), 1.29 (s, 9H, CH_3), 1.26 (s, 9H, CH_3′). ^{13}C{^{1}H}-NMR (600 MHz, DMSO-d_6, 25 °C): 159.78 (s, N=CH), 92.93 (s, β-CH), 53.89 (s, N–C), 28.97 (s, CH_3). Anal. calc. for $C_{11}H_{23}N_2Cl$ (218.77): C 60.4, H 10.6, N 12.8; found: C 60.6, H 10.8, N, 12.7.

N*,*N*′-Dimethyl-1,3-propanedialdimine** (=N*-Methyl-3-(methylimino)prop-1-en-1-amine**; **2a**). *Method A*. To a mixture of dichloromethane (50 mL) and a 20 % solution of KOH saturated with K_2CO_3 (50 mL; stock solution prepared by dissolving 20 g of KOH in 100 mL of DI water, then adding *ca*. 100 g of K_2CO_3 with stirring until no more solids dissolve) was added *N*,*N*′-dimethyl-1,3-propanedialdiminium chloride (**1a**) (24.28 g, 180 mmol). The mixture was stirred vigorously at 0 °C until all the solid dissolved (about 30 min). The dichloromethane layer was decanted off and the aqueous layer was rinsed with dichloromethane (3×10 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed from the filtrate in vacuum at 0 °C to give a yellow oil. Pentane (150 mL) and 3 Å molecular sieves (19 g) were added, and the mixture was stirred for 12 h. The solution was filtered, and the filtrate was evaporated to dryness in vacuum at 0 °C to give an off-white solid that was sublimed in vacuum (10 mTorr) at 45 °C to yield the product as highly-hygroscopic colorless crystals. Yield: 5.48 g (31 %).

Method B. To a stirred solution of *N*,*N*′-dimethyl-1,3-propanedialdiminium chloride (**1a**; 9.18 g, 68 mmol) in methanol (45 mL) was added a solution of sodium ethoxide (4.96 g, 74 mmol) in methanol (10 mL), and the cloudy solution was stirred for 1 h. The solution was filtered, and the filtrate was evaporated in vacuum at 0 °C to give a yellow viscous oil, to which pentane (150 mL) and 4 Å molecular sieves (19 g) were added. The mixture was stirred for 12 h, the solution was filtered, and the filtrate was evaporated to dryness in vacuum at 0 °C to give an off-white solid, which was sublimed in vacuum (10 mTorr) at 45 °C to yield the product as highly-hygroscopic colorless crystals. Yield: 2.94 g (44 %). M.p. 37 °C. IR: 3160 w, 1648 m, 1580 m, 1299 m. ^{1}H-NMR (600 MHz, C_6D_6, 25 °C): 9.47 (br. s, 1H, NH), 6.95 (d, ^{3}J(H,H) = 5.9, 2H, N=CH), 4.59 (t, ^{3}J(H,H) = 5.9, 1H, β-CH), 2.78 (s, 6H, CH_3). ^{13}C{^{1}H}-NMR (600 MHz, C_6D_6, 25 °C): 154.86 (s, N=CH), 90.29 (s, β-CH), 40.87 (s, CH_3). Anal. calc. for $C_5H_{10}N_2$ (98.15): C 61.2, H 10.3, N 28.5; found: C 61.1, H 10.2, N 28.2. Upon exposure to air, the compound hydrates and becomes oily. The hydrated oil can be dehydrated (if caught before decomposition begins) by stirring it overnight in dry pentane together with molecular sieves (3 or 4 Å), filtering the pentane, evaporating the pentane in vacuum at 0 °C, and finally subliming the residue to recover the colorless crystalline compound.

N*,*N*′-Diethyl-1,3-propanedialdimine** (=N*-Ethyl-3-(ethylimino)prop-1-en-1-amine**; **2b**). This compound can be prepared by the same method as for **2a**, with a sublimation temperature of 45 °C to yield a colorless crystalline solid. *Method A*. Prepared from **1b** (5.74 g, 35 mmol) in dichloromethane (35 mL) and a 20 % solution of KOH saturated with K_2CO_3 (11 mL). Yield: 1.92 g (43 %). *Method B*. Prepared from **1b** (2.97 g, 18.3 mmol) in methanol (15 mL). Yield: 1.29 g (56 %). M.p. 59 °C. IR: 3180 w, 1643 m, 1577 m, 1258 w, 1139 w. ^{1}H-NMR (500 MHz, C_6D_6, 25 °C): 9.75 (br. s, 1H, NH), 7.04 (d, ^{3}J(H,H) = 6.0, 2H, N=CH), 4.60 (t, ^{3}J(H,H) = 6.0, 1H, β-CH), 3.04 (q, ^{3}J(H,H) = 7.3, 4H, CH_2), 1.01 (t, ^{3}J(H,H) = 7.2, 6H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, C_6D_6, 25 °C): 153.10 (s, N=CH), 90.08 (s, β-CH), 49.28 (s, CH_2), 17.43 (s, CH_3). Anal. calc. for $C_7H_{14}N_2$ (126.20): C 66.6, H 11.2, N 22.2; found: C 66.5, H 11.1, N 22.0. Upon exposure to air, the salt hydrates and becomes oily. The hydrated oil can be dehydrated in the same manner as described for compound **2a**.

N*,*N*′-Di(isopropyl)-1,3-propanedialdimine** (=N*-(Propan-2-yl)-3-[(propan-2-yl)imino]prop-1-en-1-amine**; **2c**). This compound can also be prepared by the same method as for **2a**. *Method A*. Prepared from **1c** (7.76 g, 40 mmol) in dichloromethane (30 mL) and

a 20% KOH solution saturated with K_2CO_3 (10 mL). Yield: 3.20 g (51%). *Method B.* Prepared from **1c** (3.08 g, 16 mmol) in methanol (20 mL). Yield: 1.69 g (68%). M.p. 68 °C. IR: 3165 br., 1641 m, 1573 m, 1311 w, 1280 w, 1185 w, 1152 w, 1023 w, 976 w, 946 w. ^{1}H-NMR (500 MHz, C_6D_6, 25 °C): 9.87 (br. s, 1H, NH), 7.10 (d, ^3J(H,H) = 6, 2H, N=CH), 4.60 (t, ^3J(H,H) = 6, 1H, β-CH), 3.05 (sept, ^3J(H,H) = 6.5, 2H, N–CH), 1.08 (d, ^3J(H,H) = 6.4, 12H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, C_6D_6, 25 °C): 151.06 (s, N=CH), 89.97 (s, β-CH), 55.06 (s, N–CH), 24.92 (s, CH_3). Anal. calc. for $C_9H_{18}N_2$ (154.25): C 70.1, H 11.8, N 18.2; found: C 70.0, H 11.7, N 18.1.

***N,N′*-Di(*tert*-butyl)-1,3-propanedialdimine** (= ***N*-*tert*-Butyl-3-(*tert*-butylimino)prop-1-en-1-amine**; **2d**). This compound can also be prepared by the same method as for **2a**. *Method A.* Prepared from **1d** (5.50 g, 25 mmol) in dichloromethane (20 mL) and a 20% KOH solution saturated with K_2CO_3 (10 mL). Yield: 1.50 g (33%). *Method B.* Prepared from **1d** (3.00 g, 13.7 mmol) in methanol (10 mL). Yield: 1.83 (73%). M.p. 78 °C. IR: 3177 br., 3068 m, 1641 s, 1616 m, 1601 m, 1577 s, 1299 m, 1220 m, 1174 m, 1044 w, 1028 w, 1009 w, 990 m, 945 w, 912 w, 810 w, 720 m. ^{1}H-NMR (600 MHz, C_6D_6, 25 °C): 10.70 (br. s, 1H, NH), 7.25 (d, ^3J(H,H) = 6, 2H, N=CH), 4.75 (t, ^3J(H,H) = 6, 1H, β-CH), 1.13 (s, 18H, CH_3). ^{13}C{^{1}H}-NMR (600 MHz, C_6D_6, 25 °C): 148.31 (s, N=CH), 90.57 (s, β-CH), 53.00 (s, N–C), 30.58 (s, CH_3). Anal. calc. for $C_{11}H_{22}N_2$ (182.30): C 72.5, H 12.2, N 15.4; found: C 72.4, H 12.1, N, 15.5.

Lithium *N,N′*-Dimethyl-1,3-propanedialdiminate (= **[*N*-Methyl-3-(methylimino-κ*N*) prop-1-en-1-aminato-κ*N*]lithium**; **3a**). To obtain good yields, the temperature must be kept cold throughout this procedure, including the filtration step. To a solution of *N,N′*-dimethyl-1,3-propanedialdimine (**2a**; 1.21 g, 12.4 mmol) in pentane (250 mL) at 0 °C was added *sec*-butyllithium (10 mL of a 1.4 M solution in cyclohexanes, 14 mmol) dropwise over 75 min. After the addition was complete, the cloudy solution was stirred for 1 h at 0 °C, and then the mixture was cooled to −78 °C and allowed to stand undisturbed for 30 min. The precipitate was collected by filtration and dried in vacuum at −78 °C to give the product as a pale orange powder. Yield: 1.04 g (81%). M.p. 80–90 °C (dec). IR: 3341 br., 3162 br., 2776 m, 1634 m, 1582 m, 1512 s, 1409 w, 1350 m, 1318 m, 1203 w, 1122 w, 1081 w, 961 w, 802 w, 764 w, 689 w. ^{1}H-NMR (500 MHz, THF-d_8, 25 °C): 6.96 (d, ^3J(H,H) = 6, 2H, N=CH), 3.59 (t, ^3J(H,H) = 6, 1H, β-CH), 3.03 (s, 6H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, THF-d_8, 25 °C): 160.42 (s, N=CH), 84.40 (s, β-CH), 46.97 (s, CH_3). Anal. calc. for $C_5H_9N_2Li$ (104.08): C 57.7, H 8.72, N 26.9; found: C 59.2, H 9.30, N 26.4; the microanalysis suggests that some alkane solvent is retained in the isolated solid.

Lithium *N,N′*-Diethyl-1,3-propanedialdiminate (= **[*N*-Ethyl-3-(ethylimino-κ*N*)prop-1-en-1-aminato-κ*N*]lithium**; **3b**). Prepared from **2b** (1.06 g, 8.4 mmol) in pentane (200 mL) as described for **3a**. The product is a pale pink powder. Yield: 0.76 g (69%). M.p. 55–60 °C (dec). IR: 1631 m, 1564 m, 1516 m, 1325 m, 1261 m, 1203 m, 1132 w, 1081 w, 989 w, 864 w. ^{1}H-NMR (500 MHz, THF-d_8, 25 °C): 7.01 (d, ^3J(H,H) = 6, 2H, N=CH), 3.55 (t, ^3J(H,H) = 6, 1H, β-CH), 3.15 (q, ^3J(H,H) = 7, 4H, CH_2), 1.03 (t, ^3J(H,H) = 7, 6H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, THF-d_8, 25 °C): 158.59 (s, N=CH), 83.91 (s, β-CH), 55.28 (s, CH_2), 18.86 (s, CH_3). Anal. calc. for $C_7H_{13}N_2Li$ (132.13): C 63.6, H 9.92, N 21.2; found: C 62.2, H 10.2, N 19.3; moisture sensitivity prohibited a better microanalysis.

Lithium N,N′-Di(isopropyl)-1,3-propanedialdiminate (= **{*N*-(propan-2-yl)-3-[(propan-2-yl)imino-κ*N*]prop-1-en-1-aminato-κ*N*}lithium**; **3c**). Prepared from **2c** (1.28 g, 8.3 mmol) in pentane (90 mL) as described for **3a**. The product is a colorless powder. Yield: 0.78 g (59%). M.p. 148 °C. IR: 2599 w, 1583 s, 1569 m, 1332 m, 1301 m, 1283 m, 1208 m, 1154 m, 1135 m, 1118 m, 990 w, 961 w, 843 w, 736 m. ^{1}H-NMR (500 MHz, THF-d_8, 25 °C): 7.04 (d, ^3J(H,H) = 6.4, 2H, N=CH), 3.53 (t, ^3J(H,H) = 6, 1H, β-CH), 3.01 (sept, ^3J(H,H) = 6.4, 2H, N–CH), 1.03 (d, ^3J(H,H) = 6.4, 12H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, THF-d_8, 25 °C): 157.29 (s, N=CH), 83.91 (s, β-CH), 61.00 (s, N–CH), 26.32 (s, CH_3). Anal. calc. for $C_9H_{17}N_2Li$ (160.19): C 67.5, H 10.7, N 17.5; found: C 67.3, H 10.9, N 17.2.

Lithium *N,N′*-Di(*tert*-butyl)-1,3-propanedialdiminate (= **[*N*-*tert*-butyl-3-(*tert*-butylimino-κ*N*)prop-1-en-1-aminato-κ*N*]lithium**; **3d**). This preparation is less sensitive to heat than those used to make the other lithium salts. To a solution of *N,N′*-di(*tert*-butyl)-1,3-propanedialdimine (**2d**; 1.34 g, 7.4 mmol) in pentane (30 mL) at 0 °C was added *sec*-butyllithium (5.8 mL of a 1.4 M solution in cyclohexanes, 8 mmol) dropwise. After the addition was complete, the cloudy yellow solution was stirred for 2 h, and then the mixture was cooled to −78 °C and allowed to stand undisturbed for 30 min. The solid was collected by filtration and dried in vacuum at room temperature to give the product as a pale yellow powder. Yield: 1.13 g (82%). M.p. > 270 °C. IR: 1639 m, 1572 s, 1347 m, 1331 m, 1293 m,

1239 m, 1211 m, 1175 m, 1159 m. ^{1}H-NMR (500 MHz, THF-d_8, 25 °C): 7.18 (d, ^{3}J(H,H) = 7, 2H, N=CH), 3.71 (t, ^{3}J(H,H) = 7, 1H, β-CH), 1.08 (s, 18H, CH_3). ^{13}C{^{1}H}-NMR (500 MHz, THF-d_8, 25 °C): 154.02 (s, N=CH), 85.13 (s, β-CH), 53.90 (s, N–C), 31.56 (s, CH_3). Anal. calc. for $C_{11}H_{21}N_2Li$ (188.24): C 70.2, H 11.2, N 14.9; found: C 70.1, H 11.2, N 14.7. Note: In this procedure, *n*-butyllithium can be used in place of *sec*-butyllithium with no reduction in yield.

Supplementary Material

Supporting information for this article is available on the WWW under https://doi.org/10.1002/MS-number. CCDC-2217130, CCDC-2217131, and CCDC-2217132 contain the supplementary crystallographic data for this work. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

We thank the National Science Foundation (CHE 1954745) and the University of Illinois (fellowship for C. E. S.) for support of this research. We thank Dr. Danielle Gray and Dr. Toby Woods of the Clark X-ray Laboratory at the University of Illinois in Urbana-Champaign for collecting the X-ray diffraction data. We thank Nathan Edmonsond and Joe Lastowski for useful suggestions and assistance.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1] J. E. Parks, R. H. Holm, 'Synthesis, Solution Stereochemistry, and Electron Delocalization Properties of Bis(β-iminoamino)nickel(II) Complexes', *Inorg. Chem.* **1968**, *7*, 1408–1416.
[2] C. P. Richards, G. A. Webb, 'A Spectroscopic and Magnetic Study of Some Metal Complexes of Malonaldehydedianil', *J. Inorg. Nucl. Chem.* **1969**, *31*, 3459–3464.
[3] L. Bourget-Merle, M. F. Lappert, J. R. Severn, 'The Chemistry of β-Diketiminatometal Complexes', *Chem. Rev.* **2002**, *102*, 3031–3066.
[4] M. Xue, R. Jiao, Y. Zhang, Y. Yao, Q. Shen, 'Syntheses and Structures of Tris-β-Diketiminate Lanthanide Complexes and Their High Activity for Ring-Opening Polymerization of ε-Caprolactone and L–Lactide', *Eur. J. Inorg. Chem.* **2009**, 4110–4118.
[5] C. Chen, S. M. Bellows, P. L. Holland, 'Tuning Steric and Electronic Effects in Transition-Metal β-Diketiminate Complexes', *Dalton Trans.* **2015**, *44*, 16654–16670.
[6] A. Causero, G. Ballmann, J. Pahl, C. Färber, J. Intemann, S. Harder, 'β-Diketiminate Calcium Hydride Complexes: the Importance of Solvent Effects', *Dalton Trans.* **2017**, *46*, 1822–1831.
[7] R. L. Webster, 'β-Diketiminate Complexes of the First Row Transition Metals: Applications in Catalysis', *Dalton Trans.* **2017**, *46*, 4483–4498.
[8] M. Zhong, S. Sinhababu, H. W. Roesky, 'The Unique β-Diketiminate Ligand in Aluminum(I) and Gallium(I) Chemistry', *Dalton Trans.* **2020**, *49*, 1351–1364.
[9] S. G. McGeachin, 'Synthesis and Properties of Some β-Diketimines Derived from Acetylacetone, and their Metal Complexes', *Can. J. Chem.* **1968**, *46*, 1903–1912.
[10] C. L. Honeybourne, G. A. Webb, 'Some Metal Complexes of 1,3-Di-imines', *Chem. Commun. (London)* **1968**, 739–740.
[11] D. J. Mindiola, P. L. Holland, T. H. Warren, 'Complexes of Bulky β-Diketiminate Ligands', in 'Inorganic Syntheses, Vol. 35', Ed. T. B. Rauchfuss, 2010, pp. 1–55.
[12] D. C. H. Do, A. Keyser, A. V. Protchenko, B. Maitland, I. Pernik, H. Niu, E. L. Kolychev, A. Rit, D. Vidovic, A. Stasch, C. Jones, S. Aldridge, 'Highly Electron-Rich β-Diketiminato Systems: Synthesis and Coordination Chemistry of Amino-Functionalized "*N*-nacnac" Ligands', *Chem. Eur. J.* **2017**, *23*, 5830–5841.
[13] M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky, P. P. Power, 'The Synthesis and Structure of Lithium Derivatives of the Sterically Encumbered β-Diketiminate Ligand [{(2,6-$Pr^{i}_2H_3C_6$)N(CH_3)C}$_2$CH]$^-$, and a Modified Synthesis of the Aminoimine Precursor', *J. Chem. Soc., Dalton Trans.* **2001**, 3465–3469.
[14] A. Z. Bradley, D. L. Thorn, G. V. Glover, 'Efficient Synthesis of Alkyl β-Diketimines', *J. Org. Chem.* **2008**, *73*, 8673–8674.
[15] K. Chand, C.-L. Tsai, H.-Y. Chen, W.-M. Ching, S.-P. Hsu, J. R. Carey, S. C. N. Hsu, 'Improved Synthesis of Unsymmetrical *N*-Aryl-*N'*-alkylpyridyl β-Diketimines Using Molecular Sieves and their Lithium Complexes', *Eur. J. Inorg. Chem.* **2018**, 1093–1098.
[16] I. El-Zoghbi, A. Ased, P. O. Oguadinma, E. Tchirioua, F. Schaper, 'One-pot Synthesis of β-Diketimine Ligands', *Can. J. Chem.* **2010**, *88*, 1040–1045.
[17] M. M. Stalzer, T. L. Lohr, T. J. Marks, 'Synthesis, Characterization, and Thermal Properties of *N*-alkyl β-Diketiminate Manganese Complexes', *Inorg. Chem.* **2018**, *57*, 3017–3024.
[18] K.-H. Park, W. J. Marshall, 'Remarkably Volatile Copper(II) Complexes of *N,N'*-Unsymmetrically Substituted 1,3-Diketimines as Precursors for Cu Metal Deposition via CVD or ALD', *J. Am. Chem. Soc.* **2005**, *127*, 9330–9331.
[19] D. Li, Y. Peng, C. Geng, K. Liu, D. Kong, 'Well-controlled Ring-opening Polymerization of Cyclic Esters Initiated by Dialkylaluminum β-Diketiminates', *Dalton Trans.* **2013**, *42*, 11295–11303.

[20] C. F. Jelinek, R. F. Kleinschmidt, U. S. 'Preparation of Malonaldehyde Dianils', Patent 2 549 097, 1951.
[21] F. Reitzenstein, G. Bönitsch, 'Farbwirkung und Absorption der Dirosanilidine des β-Oxyacroleins und der Ameisensäure', *J. Prakt. Chem.* **1912**, *86*, 1–58.
[22] V. Zatka, J. Holzbecher, D. E. Ryan, 'Heterocyclic *N,N'*-Disubstituted 1-amino-3-iminopropenes as Analytical Reagents', *Anal. Chim. Acta* **1971**, *55*, 273–278.
[23] C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, 'Rapid, Regioconvergent, Solvent-Free Alkene Hydrosilylation with a Cobalt Catalyst', *J. Am. Chem. Soc.* **2015**, *137*, 13244–13247.
[24] S. Takamura, T. Yoshimiya, S. Kameyama, A. Nishida, H. Yamamoto, M. Noguchi, 'An Efficient Preparation of Macrocycles Bearing Vinamidine Moieties by the Cyclocondensation of Malonaldehyde Derivatives and 1,ω-Diaminoalkanes', *Synthesis* **2000**, 637–639.
[25] Z. Arnold, 'The Preparation of Tetramethylformamidinium Salts and Their Vinylogues', *Collect. Czech. Chem. Commun.* **1959**, *24*, 760–765.
[26] H. Bredereck, F. Effenberger, D. Zeyfang, K.-A. Hirsch, 'Orthoamide, VII Synthese vinyloger Amidacetale, Aminalester und Amidaminale', *Chem. Ber.* **1968**, *101*, 4036–4047.
[27] B. Grimm, S. Dähne, G. Bach, 'Synthese einfachster Polymethinfarbstoffe', *J. Prakt. Chem.* **1975**, *317*, 161–165.
[28] A. P. Arendaruk, T. M. Godzhello, V. N. Mel'yantseva, T. V. Protopopova, A. P. Skoldinov, 'Synthesis of Functional Malondialdehyde Derivatives from Propargyl Aldehyde', *Pharm. Chem. J.* **1973**, *7*, 545–549.
[29] A. V. Eremeev, D. A. Tikhomirov, V. A. Tyusheva, É. É. Liepin'sh, 'β-Aziridinylacroleins in Reactions with Nucleophilic Reagents', *Chem. Heterocycl. Compd.* **1978**, *14*, 394–398.
[30] O. Gürtler, S. Dähne, 'Elektrochemische Studien an Polymethinfarbstoffen', *Z. Phys. Chem.* **1974**, *255*, 501–508.
[31] J. Alcazar, I. Almena, M. Begtrup, A. de la Hoz, 'Synthesis of 4-Hydroxylamino-1-azabuta-1,3-dienes and their Cyclization to 2-Substituted Pyrazole 1-oxides', *J. Chem. Soc. Perkin Trans. 1* **1995**, 2773–2781.
[32] F. Wille, W. Schwab, J. Kroner, '1-Substituierte 1,4-Dihydro-3,5-pyridindicarbaldehyde', *Monatsh. Chem.* **1979**, *110*, 613–638.
[33] J. Burkhard, Z. Arnold, 'Reactions of Triformylmethane with Adamantane Derivatives Containing Primary Amino Group', *Collect. Czech. Chem. Commun.* **1992**, *57*, 1947–1950.
[34] K. J. Fisher, '*N*-lithio Derivatives of α,β Unsaturated Amino Imines', *Tetrahedron Lett.* **1970**, *11*, 2613–2616.
[35] F. S. Mair, D. Scully, A. J. Edwards, P. R. Raithby, R. Snaith, 'Synthetic, Structural, Spectroscopic and Calculational Studies of a Lithium β-Diketiminate Complex', *Polyhedron* **1995**, *14*, 2397–2401.
[36] D. J. E. Spencer, A. M. Reynolds, P. L. Holland, B. A. Jazdzewski, C. Duboc-Toia, L. Le Pape, S. Yokota, Y. Tachi, S. Itoh, W. B. Tolman, 'Copper Chemistry of β-Diketiminate Ligands: Monomer/Dimer Equilibria and a New Class of Bis(μ-oxo)dicopper Compounds', *Inorg. Chem.* **2002**, *41*, 6307–6321.
[37] Y. Cheng, D. J. Doyle, P. B. Hitchcock, M. F. Lappert, 'The β-Dialdiminato Ligand $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]^-$: the Conjugate Acid and Li, Al, Ga and In Derivatives', *Dalton Trans.* **2006**, 4449–4460.
[38] P. B. Hitchcock, M. F. Lappert, G. Li, A. V. Protchenko, 'β-Diiminato Ligand (L) Transformations in Reactions of KL with PI_3 and I_2 $[L=\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]$', *Chem. Commun.* **2007**, 846–848.
[39] V. P. Kurbatov, S. V. Serbina, O. A. Osipov, 'Synthesis and Structure of Chelates of Cobalt(II) and Zinc(II) with β-Iminopropenylamines', *Russ. J. Gen. Chem.* **1973**, *43*, 702–705.
[40] V. P. Kurbatov, S. V. Serbina, O. A. Osipov, 'Preparation and Properties of Inner Complexes of Copper, Nickel, and Palladium with β-Aminovinylimines [Malondiidene(diamines)]', *Russ. J. Inorg. Chem.* **1973**, *18*, 1414–1416.
[41] A. F. Ghiron, R. K. Murmann, E. O. Schlemper, 'Condensation of a Pseudoaromatic Planar Nickel(II) Complex: Structural and Kinetic Studies', *Inorg. Chem.* **1985**, *24*, 3271–3278.
[42] R. K. Murmann, J. Chipley, P. Droege, 'Structural Comparisons between Cu(II) and Ni(II) Diaza-coupled Quasi-aromatic α-Amineoxime Complexes', *J. Chem. Crystallogr.* **1998**, *28*, 465–473.
[43] V. Sinha, B. Pribanic, B. de Bruin, M. Trincado, H. Grützmacher, 'Ligand- and Metal-Based Reactivity of a Neutral Ruthenium Diolefin Diazadiene Complex: The Innocent, the Guilty and the Suspicious', *Chem. Eur. J.* **2018**, *24*, 5513–5521.
[44] F. Casas Cancela, 'Synthesis, Structure, and Reactivity of Low Valent Metal Complexes Bearing Amino-Olefin Chelating Ligands', Ph.D. thesis, ETH Zürich, 2021.
[45] L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, Ithaca, 1960, p. 260.
[46] R. F. Childs, B. D. Dickie, 'The Photoisomerizations of Protonated Schiff Base Derivatives of Some Enals', *J. Chem. Soc. Chem. Commun.* **1981**, 1268–1269.
[47] R. F. Childs, B. D. Dickie, 'Photochemical and Thermal Stereomutations of 3-Aryl-2-propenylideniminium Salts', *J. Am. Chem. Soc.* **1983**, *105*, 5041–5046.
[48] I. M. Kolthoff, M. K. Chantooni Jr., S. Bhowmik, 'Dissociation Constants of Uncharged and Monovalent Cation Acids in Dimethyl Sulfoxide', *J. Am. Chem. Soc.* **1968**, *90*, 23–28.
[49] F. G. Bordwell, 'Equilibrium Acidities in Dimethyl Sulfoxide Solution', *Acc. Chem. Res.* **1988**, *21*, 456–463.
[50] F. Kapteijn, A. J. van der Steen, J. C. Mol, 'Thermodynamics of the Geometrical Isomerization of 2-Butene and 2-Pentene', *J. Chem. Thermodyn.* **1983**, *15*, 137–146.
[51] A. Liberles, A. Greenberg, J. E. Eilers, 'Attractive Steric Effects', *J. Chem. Educ.* **1973**, *50*, 676–678.
[52] D. M. Pawar, A. A. Khalil, D. R. Hooks, K. Collins, T. Elliott, J. Stafford, L. Smith, E. A. Noe, '*E* and *Z* Conformations of Esters, Thiol Esters, and Amides', *J. Am. Chem. Soc.* **1998**, *120*, 2108–2112.
[53] J. P. Terhorst, W. L. Jorgensen, '*E/Z* Energetics for Molecular Modeling and Design', *J. Chem. Theory Comput.* **2010**, *6*, 2762–2769.
[54] C. Dugave, L. Demange, '*Cis–Trans* Isomerization of Organic Molecules and Biomolecules: Implications and Applications', *Chem. Rev.* **2003**, *103*, 2475–2532.
[55] A. G. Martínez, E. T. Vilar, A. G. Fraile, P. Martínez-Ruiz, 'A Computational and Experimental Study on the Relative

Stabilities of *Cis* and *Trans* Isomers of *N*-Alkylamides in Gas Phase and in Solution', *J. Phys. Chem. A* **2002**, *106*, 4942–4950.
[56] S. Chizu, T. Yoshimitsu, N. Nagatoshi, A. Masahiro, I. Shinobu, 'Structural Characterization of Copper(I) Complexes Supported by β-Diketiminate Ligands with Different Substitution Patterns', *Bull. Chem. Soc. Jpn.* **2006**, *79*, 118–125.
[57] D. D. L. Jones, S. Watts, C. Jones, 'Synthesis and Characterization of Super Bulky β-Diketiminato Group 1 Metal Complexes', *Inorganics* **2021**, *9*, 72.
[58] C. Zovko, S. Bestgen, C. Schoo, A. Görner, J. M. Goicoechea, P. W. Roesky, 'A Phosphine Functionalized β-Diketimine Ligand for the Synthesis of Manifold Metal Complexes', *Chem. Eur. J.* **2020**, *26*, 13191–13202.
[59] R. E. Cowley, P. L. Holland, 'Ligand Effects on Hydrogen Atom Transfer from Hydrocarbons to Three-Coordinate Iron Imides', *Inorg. Chem.* **2012**, *51*, 8352–8361.
[60] R. S. Rojas, A. R. Cabrera, B. C. Peoples, K. Spannhoff, M. Valderrama, R. Fröhlich, G. Kehr, G. Erker, 'Synthesis of [(π-cyano-P-nacnac)Cp] and [(π-cyano-nacnac)Cp]-zirconium Complexes, and their Remote Activation for Ethylene Polymerization', *Dalton Trans.* **2012**, *41*, 1243–1251.
[61] J. Liu, L. Vieille-Petit, A. Linden, X. Luan, R. Dorta, 'Synthesis and Structural Characterization of Li^{I}, Zn^{II}, Cd^{II}, and Hg^{II} Complexes containing a Fluorinated β-Diketiminate Ligand', *J. Organomet. Chem.* **2012**, *719*, 80–86.
[62] R. E. Marsh, 'Space Groups *P*1 and *Cc*: How Are They Doing?', *Acta Crystallogr. Sect. B* **2009**, *65*, 782–783.
[63] N. B. Morozova, P. A. Stabnikov, I. A. Baidina, P. P. Semyannikov, S. V. Trubin, I. K. Igumenov, 'Structure and Thermal Properties of Volatile Copper(II) Complexes with β-Diimine Derivatives of Acetylacetone and the Structure of 2-(Methylamino)-4-(methylimino)-pentene-2 Crystals', *J. Struct. Chem.* **2007**, *48*, 889–898.
[64] S. Kulpe, B. Schulz, 'The Crystal Structure of 1-Anilino-3-phenylimino Propene-(1), $C_{15}H_{14}N_2$', *Krist. Tech.* **1981**, *16*, 39–47.
[65] D. Vidovic, J. N. Jones, J. A. Moore, A. H. Cowley, 'Lithium, Aluminum, and Gallium Complexes of the C_6F_5-Substituted β-Diketiminate Ligand $[HC(CMe)_2(NC_6F_5)_2]^-$', *Z. Anorg. Allg. Chem.* **2005**, *631*, 2888–2892.
[66] J. R. Lynch, A. R. Kennedy, J. Barker, J. Reid, R. E. Mulvey, 'Crystallographic Characterisation of Organolithium and Organomagnesium Intermediates in Reactions of Aldehydes and Ketones', *Helv. Chim. Acta* **2022**, *105*, e202200082.

Received November 4, 2022
Accepted February 28, 2023