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Synthesis of 5,5-Bicyclic Amidines as Ligands for Thermally Stable Vapor Deposition Precursors

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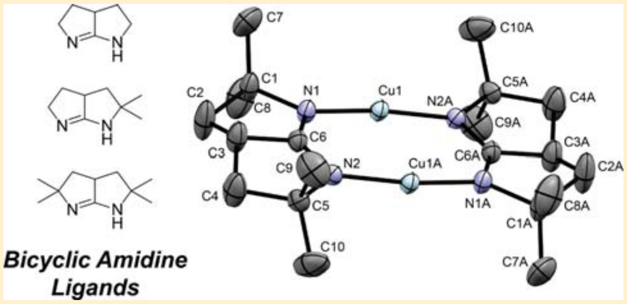
Supporting Information

ABSTRACT: We describe the syntheses of three fully aliphatic 5,5-bicyclic amidines. The syntheses are facile and scalable and can be easily modified to produce other 5,5-bicyclic amidine ligands with other substitution patterns. Treatment of one of the ligands with KHMDS and subsequent transmetalation with CuCl resulted in a dimeric copper(I) bicyclic amidinate complex in 55% yield after recrystallization. This modestly air stable complex exhibits good volatility and thermal decomposition rates 1 order of magnitude lower than those of a similar, but acyclic, copper(I) amidinate. Together, the ligands enable a general method for producing a library of thermally stable metal amidinate precursors with a wide variety of metals for use in vapor deposition.



Chemical vapor deposition (CVD) and atomic layer deposition (ALD) are vapor deposition processes that are capable of depositing highly conformal thin films while affording a great degree of control over film thickness.[1−4] They have found many applications in areas such as microelectronic devices, machine tools, and window coatings.[5] The precursors must possess high volatility, high thermal stability, and high reactivity with other precursors, with volatile and noncorrosive reaction byproducts.[6]

Metal amidinates, as exemplified by *N*,*N*′-diisopropylacetamidinatocopper(I) (**1a**), have been popular choices as precursors for the vapor deposition of films containing transition metals or rare-earth metals.[7−11] However, they can decompose at elevated temperatures, which may limit their usefulness as precursor ligands when a higher deposition temperature is desired.

It has been hypothesized that such thermal decomposition takes place via a β-hydride migration from one of the ligand side chains to the metal center, followed by M−N bond cleavage. DFT calculations on the mechanism and the transition state through which this takes place revealed that, in the transition state, the transferred H atom, the metal atom, and the N−C−N functional group of the ligand all lie in the same plane.[12,13]

Barry et al. have come partway to solving the problem with their careful study of *tert*-butylimino-2,2-dimethylpyrrolidine as the ligand.[14] A copper(I) complex with this ligand, which can be thought of as a monocyclic amidine, showed improved thermal stability in comparison to *N*′,*N*″-diisopropyl-*N*-dimethyl-guanidinatocopper(I). However, this monocyclic amidine still has one exocyclic alkyl group that could potentially undergo β-methyl migration to the metal.

As a result, we were motivated to design the 5,5-bicyclic amidines **2a**−**c** (Figure 1), in which the H atom cannot reach the planar transition state without twisting the ring system into a much higher energy state. Thus, the β-hydride (or β-methyl) migration to the metal is expected to be much slower in a metal bicyclic amidinate than in the corresponding acyclic amidinate.

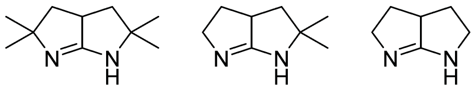

2a **2b** **2c**

Figure 1. 5,5-Bicyclic amidines synthesized in this work.

Although some 6,6- and 6,5-bicyclic amidines have been reported,[15−17] the syntheses are generally either tedious or are not easily modifiable to produce other amidine ligands with other substitution patterns. Regardless, in order to maximize precursor volatility, the lowest possible ligand molecular weight is generally desirable; moreover, a 5,5-bicyclic system would most effectively restrict β-hydrogen or β-methyl migration to the metal.

The fused five-membered-ring system has so far remained elusive, apart from one instance that proceeds via a radical cyclization.[18] Unfortunately, this method requires an intermediate that results in a product with an unwanted −CN group on the bicyclic core; furthermore, derivatives of **2a** would be inaccessible, as a highly improbable S_N2 reaction at a tertiary carbon would be required.

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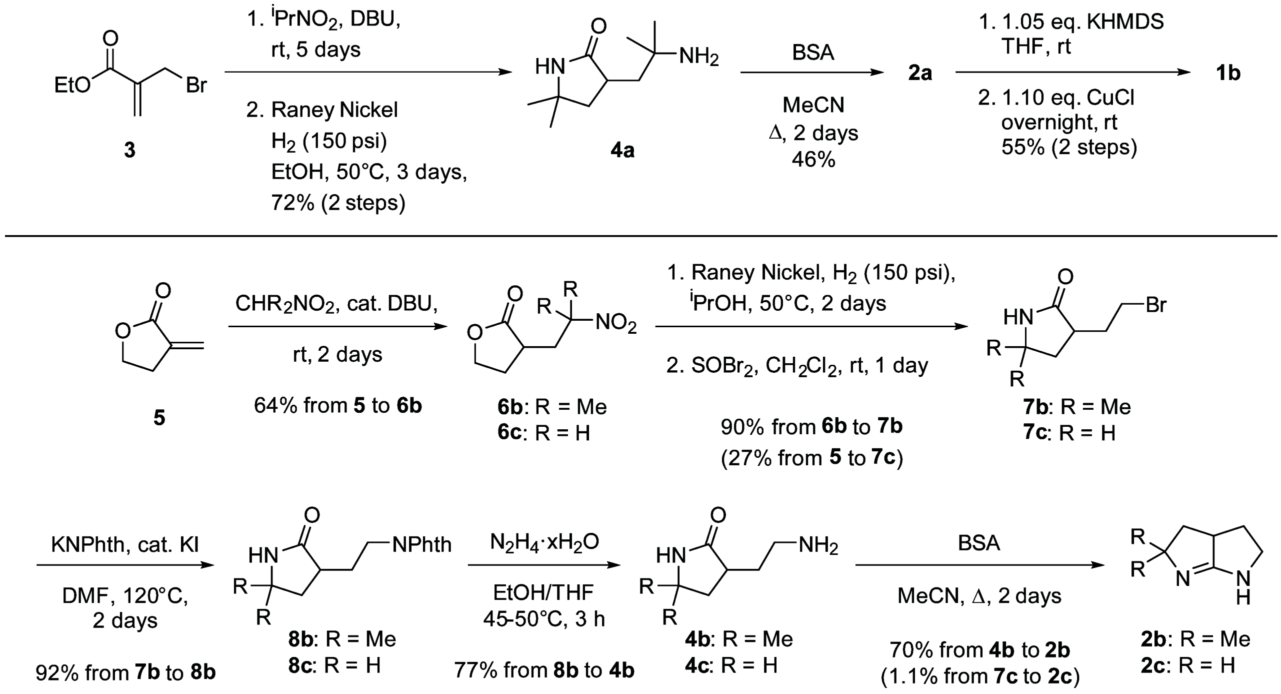
Scheme 1. Synthetic Routes to 5,5-Bicyclic Amidines 2a−c and Complex 1b[a]



[a]Yields in parentheses are for reactions where R = H.

As ALD is utilized in many commercial and industrial processes, a further challenge lies in the need for a synthesis that is relatively inexpensive and easily scalable while avoiding the use of laborious purification techniques such as column chromatography.

Herein, we report such a synthesis for **2a**, as well as a second synthesis for **2b**,**c** via a separate route (Scheme 1; see the Supporting Information). The intermediates leading to **2c** generally had significant water solubility, which contributed to lower yields. In all cases, the crucial step is the final cyclization to form the bicyclic core.

Several methods were unsuccessfully attempted: refluxing in toluene with catalytic TsOH under a Dean−Stark trap,[19] and BOP was tried as well.[20] After some experimentation, *N*,*O*-bis(trimethylsilyl)acetamide (BSA) was found to react cleanly to give the product amidines.[21]

Treatment of a solution of **2a** in THF with KHMDS, followed by transmetalation with CuCl, gave **1b**, a Cu(I) complex of **2a**. **1b** was isolated in 55% yield as white crystals after recrystallization from pentane. Unlike **1a**, **1b** is modestly air stable and can be handled safely in air for several hours without obvious decomposition. Even though **1b** has a melting point of 306−307 °C (sealed capillary), thermogravimetric analysis (TGA) of **1b** under 1 atm of N_2 and a linear temperature ramp of 10 °C/min shows that it sublimes cleanly, starting at a temperature of ~170 °C and completing at ~290 °C with <0.2% of residue (Figure 2). A previously reported TGA of **1a** under identical conditions[22] also showed clean sublimation beginning at ~150 °C and completing at ~260 °C. As such, the volatility of **1b** is slightly lower than that of **1a**, which is to be expected because of its higher molecular weight (457.61 vs 409.57 g/mol). Using isothermal step TGA, the enthalpy of sublimation of **1b** was found to be 109 kJ/mol, in comparison to 82.4 kJ/mol for **1a**[23] (see Figure S21 in the Supporting Information).

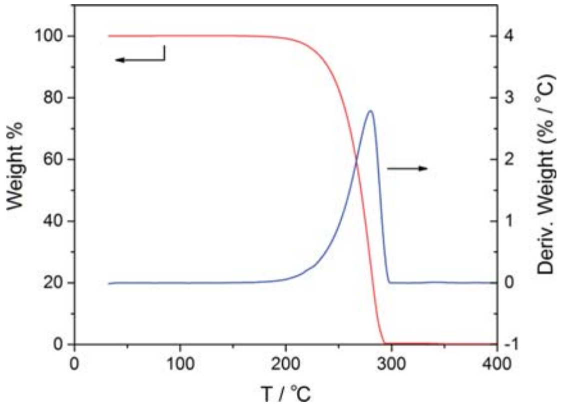


Figure 2. Thermogravimetric analysis of **1b**, performed on a TGO Q50 instrument (TA Instruments, Inc.) operating inside a nitrogen-filled glovebox at 1 atm.

Single-crystal X-ray diffraction (Figure 3) reveals that **1b** exists in the solid state as a dimer, as is the case with acyclic Cu(I) amidinates.[7] This new amidinate exhibits C_{2h} symmetry with identical N−Cu bond lengths of 1.85 Å and a N−C−N bond angle of 130.9°, which is larger than the previously reported value of 119.62° for complex **1a** because of the constraints of the bicyclic system. However, the ^{1}H and ^{13}C NMR spectra of **1b** (see the Supporting Information) suggest that another diastereomer, which has almost identical chemical shifts and we speculate has C_{2v} symmetry, is also produced from the same reaction.

In order to study the thermal stability of **1b**, solutions of **1a**[7,8] and **1b** in deuterated mesitylene (degassed by freeze−pump−thaw and dried over 4 Å molecular sieves) were flame-sealed

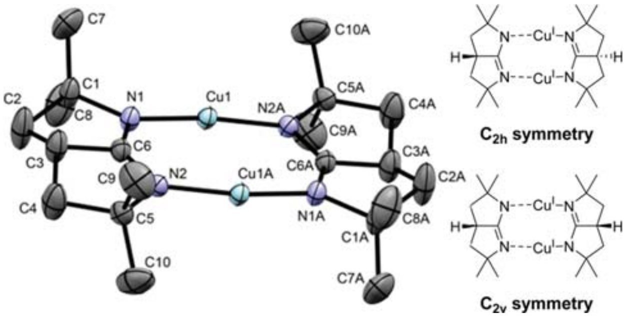


Figure 3. X-ray crystal structure of **1b**, showing 50% probability ellipsoids and partial atom-labeling schemes. Atoms labeled A are related to other atoms by an inversion center. The crystal structure has C_{2h} symmetry, but NMR suggests the presence of an additional diastereomer in solution, perhaps with C_{2v} symmetry.

inside separate heavy-walled NMR tubes and incubated at 200 °C (Figure 4). The fraction of **1a** remaining was determined by comparing the integrated β-proton signals in the ^{1}H NMR spectrum with the residual $-CHD_2$ signals from the solvent. In the case of **1b**, its low solubility in mesitylene meant that the stronger signal at 2.10 ppm was used instead to reduce error. For convenience, the aromatic solvent signals were set at 7.00 ppm.

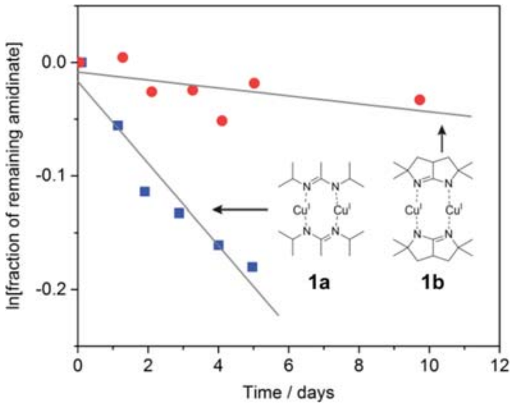


Figure 4. NMR decomposition study of **1a** (blue squares, lower data set) and **1b** (red circles, upper data set) performed in sealed tubes of degassed anhydrous mesitylene-d_{12} at 200 °C. The lines represent the best fits to a first-order decomposition rate law.

From the study, bicyclic complex **1b** was found to decompose 1 order of magnitude more slowly than acyclic **1a** at 200 °C. Assuming that the decompositions of **1a**,**b** both obey first-order kinetics, the decomposition rates are 4.2×10^{-7} and 4.1×10^{-8} s^{-1} respectively, corresponding to respective solution half-lives of 19 and 200 days. **1b** not only has no hydrogen atoms β to the metal but also features a rigid 5,5-bicyclic framework that constrains the conformational freedom of the methyl groups that are in their place to ensure that any decomposition via β-methyl migration has to proceed through a highly strained intermediate. These two factors have likely contributed to a dramatic increase in thermal stability. It is also worth noting that the diastereomeric ratio of **1b** did not change appreciably during the course of heating at 200 °C.

In summary, we have developed two facile, scalable synthetic routes to 5,5-bicyclic amidines **2a**−**c** for use as ligands in CVD or ALD precursors. Meanwhile, preliminary studies with **1b** show that such compounds are likely to show very high thermal stability while retaining good volatility, properties that will enable the high-temperature deposition of high-quality thin films. This series of ligands enables a general strategy for producing thermally stable metal amidinate precursors for use in the vapor deposition of many metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00954.

Crystallographic data for **1b** (CIF)

Experimental procedures and characterization of products and isolated intermediates and crystallographic data for **1b** (PDF)

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Notes

The authors declare no competing financial interest.

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