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# Neutral zinc(II) and molybdenum(0) complexes with chiral guanidine ligands: synthesis, characterisation and applications

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**Abstract**—The synthesis and properties of three bidentate zinc(II) complexes with several chiral bidentate and one molybdenum(0) with analogous tridendate neutral chiral guanidine ligands are reported. *N*′,*N*″-Diisopropyl-(*S*)-2-(*N*,*N*-dialkylaminomethyl) pyrrolidine-1-carboximid-amides **1**–**3** reacted with anhydrous zinc(II) chloride to form mono-ligand complexes **4**–**6**, which exist as chain structures in solid state with an NH···Cl interaction between the monomer units. The X-ray crystal structures of **4**–**6** show the zinc(II) ion in a tetrahedral environment in which the C2 side chain nitrogen atom and the imine group coordinate with the metal centre. Chiral guanidine **2** was treated with (nbd)$Mo(CO)_4$ to yield the corresponding molybdenum complex **7**. The molecular structure of **7** has been determined by X-ray crystallography. In contrast to **5**, guanidine **2** acts as a tridentate ligand in **7** and the Mo(0) centre is in an octahedral coordination environment. NMR spectroscopy was performed to determine solution structures which were further supported by X-ray analysis. The chiral zinc guanidine complexes **4**–**6** were prepared in an effort to design chiral guanidine catalysts for asymmetric synthesis.


## 1. Introduction

Guanidines are a class of compounds of great biological and chemical importance.[1] Due to their hydrophilic nature, they also play an important role in the stabilisation of protein conformations through hydrogen bonding and in the mediation of solubility of natural products.[2] In some cases, due to their strong basic character, guanidines can be considered superbases, which readily undergo protonation to generate resonance-stabilised guanidinium cations.[3] Chiral guanidines are expected to have a potential as asymmetric reagents, but their limited use as chiral auxiliaries in asymmetric synthesis obviously is the result of a lack of convenient preparation methods.[4] Previously, we reported the simple preparation of chiral guanidines containing a (*S*)-2-(*N*,*N*-dialkylaminomethyl)pyrrolidine unit as potential chiral superbases.[5] Guanidines are encountered in coordination chemistry as guanidinium counter cations, as chelate guanidinate and as neutral guanidine ligands with different metals, partly due to their interesting electronic properties and capacity for simple modification.[6] Zinc complexes containing coordinated guanidines are of recent origin and, to date, are restricted to a relatively small number of examples.[7]

Our investigation of the coordinating behaviour of the chiral guanidines **1**–**3** at the bivalent zinc(II) centre is based on the development of zinc guanidine complexes for asymmetric syntheses. Herein, we report on the synthesis and crystal structures of three zinc guanidine complexes in which the zinc centres are bis-coordinated by the neutral chiral guanidine units and one molybdenum complex in which the chiral guanidines act as a tridentate ligand. Furthermore, we report the first attempts to test the applicability of **4**–**6** as chiral auxiliaries in asymmetric nitroaldol (Henry) reaction.

## 2. Results and discussion

Complexes **4**–**6** were synthesised in good yields by combining dehydrated $ZnCl_2$ with 1 equiv of **1**–**3** in dry acetonitrile. This led to the formation of a white precipitate,

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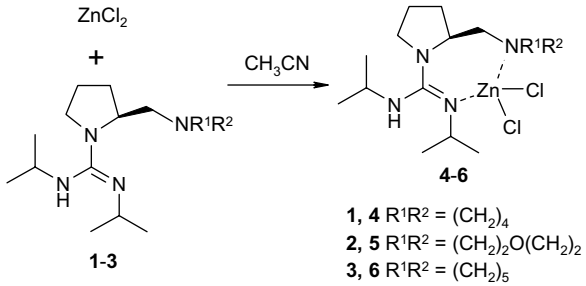
which could be crystallised from an acetonitrile solution by concentration and cooling (Scheme 1). The zinc guanidine complexes **4–6** were found to be sensitive to moisture.




**Scheme 1.** Synthesis of **4–6**.

X-ray crystal structure determinations were performed in order to establish the configurations of **4–6** and gain information concerning the coordination and structure of the chiral guanidine ligands. The molecular structure of **4** is shown in Figure 1 with selected bond lengths and angles of **4–6** given in Table 1.

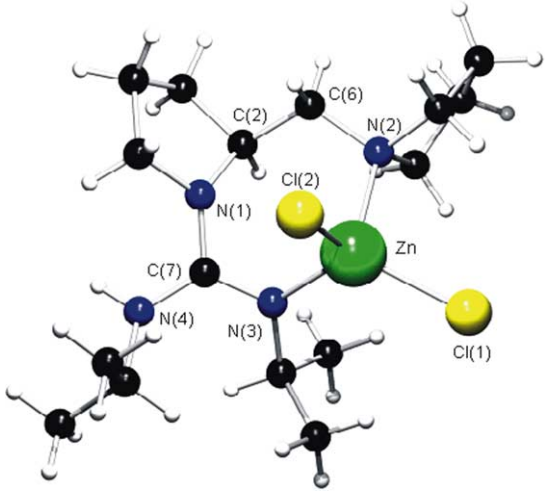



**Figure 1.** Molecular structure of **4**.

In the structures of **4–6**, the zinc(II) centre is tetracoordinated with one imine (N3) and one amine nitrogen (N2) of the guanidine ligand and two chlorides, generating a slightly distorted tetrahedral geometry at the zinc(II) cation. A seven-membered chelate ring was formed in **4–6** and its conformation is defined by the atoms N(3), C(7), N(1); C(2), C(6) and N(2). The angles around the central carbon (C7) of the guanidine ligand amount to 360° and thus establish the planarity of the $N_2CN$ skeleton (Table 1). In addition, the longer distance of the C=N-bond, compared with the non-coordinated guanidines, also reveal some electronic consequences of the metal coordination to the imine nitrogen.[8]

The three NCN angles around the central carbon (C6) in **4–6** show significant variations, which may presumably

**Table 1.** Selected bond lengths (Å) and angles (°) for the zinc(II) complexes **4–6**

| | **4** | **5** | **6** |
|---|---|---|---|
| N(1)–C(7) | 1.378(4) | 1.352(5) | 1.366(4) |
| N(3)–C(7) | 1.320(4) | 1.329(4) | 1.320(4) |
| N(4)–C(7) | 1.346(4) | 1.359(5) | 1.359(5) |
| Zn–N(3) | 1.990(3) | 1.999(3) | 1.980(2) |
| Zn–N(2) | 2.080(3) | 2.116(3) | 2.090(3) |
| Zn–Cl(1) | 2.2433(10) | 2.2543(10) | 2.2422(9) |
| Zn–Cl(2) | 2.2779(8) | 2.2810(9) | 2.2768(10) |
| N(1)–C(7)–N(3) | 117.5(3) | 118.9(3) | 118.3(3) |
| N(1)–C(7)–N(4) | 117.7(3) | 117.6(3) | 117.6(3) |
| N(4)–C(7)–N(3) | 124.8(3) | 123.5(3) | 124.1(3) |
| Cl(1)–Zn–Cl(2) | 112.20(4) | 109.55(4) | 112.34(4) |
| N(3)–Zn–N(2) | 106.61(12) | 108.53(12) | 107.18(11) |
| N(2)–Zn–Cl(1) | 104.55(9) | 112.77(9) | 105.40(8) |
| N(2)–Zn–Cl(2) | 103.66(8) | 100.48(9) | 102.96(8) |
| N(3)–Zn–Cl(1) | 120.00(8) | 116.34(9) | 119.17(8) |
| N(2)–Zn–Cl(2) | 108.35(8) | 107.89(10) | 108.38(9) |

be attributed to intramolecular crowding within the monomeric guanidine unit, due to the steric ambitious isopropyl groups (Table 1). As expected, the crystals of **4–6** are chiral. Compound **4** has the space group $P2_1$, **5** and **6** both have the space group $P2_12_12_1$. The absolute configuration of the stereogenic C(2) carbon in **4–6** were determined to be an (*S*)-configuration.

Another interesting feature of the X-ray crystal structures of **4–6** is the intermolecular N–H···Cl hydrogen bonding. The zinc-bound chloride [Cl(2)] interacts with the N(4)–H groups of another molecule, generating a chain structure (Fig. 2). The N(4)–Cl(2) length of 3.287 Å is very similar to those reported for dichloro-

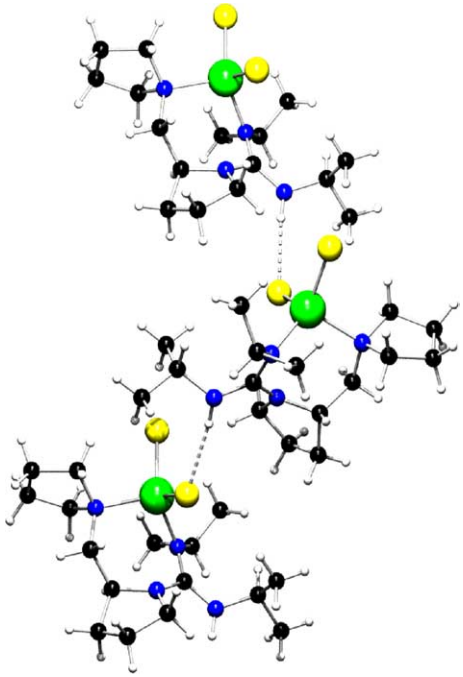


**Figure 2.** Stereoview showing the association to a chain of molecules of **4** via intermolecular N–H···Cl hydrogen bonds.

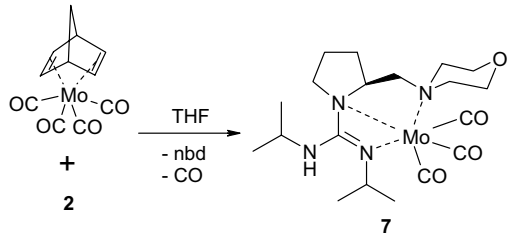
zinc(II) complexes, and is consistent with a weak intermolecular hydrogen bond in a solid state.[9a] The $^{13}C$ NMR studies of the isolated zinc complexes **4**–**6** in acetonitrile reveal a downfield shift of the characteristic guanidine carbon resonances at $\delta$ 156–162 ppm relative to **1**–**3**, which is consistent with a C=N···Zn interaction for the molecules in solution (Table 2). The magnitude of the downfield shift experienced by the guanidine resonance is 7.6 ppm for **4** relative to the free ligand **1**, 4.7 ppm for **6** relative to **3** and 3.6 ppm for **5** relative **2**. This reinforces the idea that the strength of the guanidine nitrogen binding to the zinc(II) centre follows the order **4** > **6** > **5**. It is also noteworthy, that only in the $^{13}C$ NMR spectra of **4** were well-separated signals for C(2′) and C(5′) observed. This fact indicates a stronger interaction between the zinc(II) centre and the second ring nitrogen N(2) in complex **4** in comparison to **5** and **6**.

**Table 2.** Comparison of the guanidine carbon $^{13}C$ chemical shift data for **1**–**3**[5] and **4**–**6**

| | $^{13}C$ (ppm) | | $^{13}C$ (ppm) |
|---|---|---|---|
| **1** | 153.1 | **4** | 160.7 |
| **2** | 152.8 | **5** | 156.4 |
| **3** | 152.7 | **6** | 157.3 |
| | | **7** | 155.6 |

In addition, we were interested in investigating the potential of **1**–**3** as neutral chelating ligands for different transition metals. Initial attempts to recrystallise the obtained complexes of **1**–**3** with CuI, $CuCl_2$ and $MnCl_2$ were not successful. Therefore, we decided to use a tetracarbonyl molybdenum adduct to obtain a chiral guanidine molybdenum complex.

Treatment of guanidine **2** with tetracarbonyl(2,5-norbornadiene)molybdenum led to the formation of the stable complex **7** by substitution of one carbonyl group and elimination of the norbornadiene unit (Scheme 2).




**Scheme 2.** Preparation of **7**.

Single crystals suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile solution of **7**. The structure of **7** is shown in Figure 3 and selected distances and angles are given in Table 3.

The Mo(0) centre is in a slightly distorted trigonal antiprismatic environment and coordinated to the three nitrogen atoms N(1), N(2) and N(3) in a trigonal plane. The three carbonyl units describe the second plane. The structure of the $Mo(CO)_3$ group can be described as a

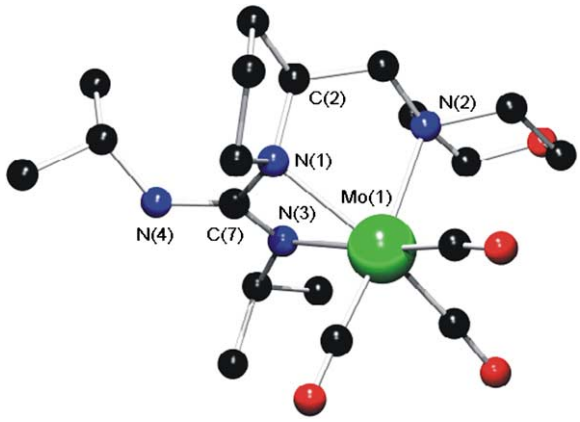



**Figure 3.** Molecular structure of **7**.

**Table 3.** Selected bond lengths (Å) and angles (°) for the molybdenum(0) complex **7**

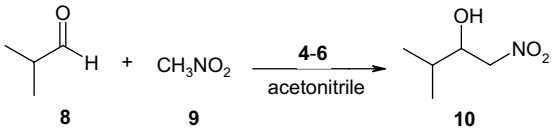
| | |
|---|---|
| N(1)–C(7) | 1.449(3) |
| N(4)–C(7) | 1.356(3) |
| N(3)–C(7) | 1.283(3) |
| Mo(1)–N(1) | 2.382(2) |
| Mo(1)–N(2) | 2.417(2) |
| Mo(1)–N(3) | 2.262(2) |
| N(1)–C(7)–N(4) | 121.1(2) |
| N(1)–C(7)–N(3) | 110.97(19) |
| N(3)–C(7)–N(4) | 127.8(2) |
| N(1)–Mo(1)–N(2) | 75.23(7) |
| N(2)–Mo(1)–N(3) | 88.02(7) |
| N(1)–Mo(1)–N(3) | 57.99(7) |

half-sandwich 'piano-stool'. Furthermore, the molybdenum tricarbonyl fragment in **7** is coordinated in a seven-membered chelate ring, which is defined by the atoms Mo(1), N(3), C(7), N(1), C(2), C(6) and N(2). In contrast to **4**–**6**, guanidine **2** exists as a tridentate ligand and coordinates with nitrogen atoms N(1), N(2) and N(3). In this case, the angles around the central carbon C(7) of the guanidine ligand add up to 360°, indicating the strict planarity of the $CN_3$ unit. The stereogenic centre C(2) was determined to have an (*S*)-configuration.

The MS spectrum of **7** showed the presence of a $Mo(CO)_3$ group, which confirmed the results of the X-ray crystallographic analysis. The IR consisted of two bands in the carbonyl stretching region, a singlet at approximately 1896 $cm^{-1}$, and a very strong singlet at 1746 $cm^{-1}$ (two CO ligands). Compared to the free CO molecule, the strong donor influence of **2** led to a downfield shift of the CO groups in complex **7**. These patterns are expected for a fac-octahedral tricarbonyl metal complex with asymmetric CO ligands. Further information about the nitrogen coordination could be gathered from IR data in the C=N region. In the free ligand **2**[5], the imine band was observed at 1623 $cm^{-1}$. In **7**, this peak were found, essentially unchanged, at 1628 $cm^{-1}$. Previous studies of transition metal guanidine complexes have shown a similar reduction in the

imine stretching frequency.[10] A $^{13}C$ NMR study of **7** in acetonitrile revealed a downfield shift of the $CN_3$ carbon relative to the free guanidine **2** (Table 2), which is consistent with a Mo···N=C interaction.

Gao and Martell recently reported a new type of asymmetric catalyst which involves a trinuclear zinc centre with chiral macrocyclic ligands.[11] Trost et al. have developed a novel type of dinuclear zinc catalyst which has successfully been utilised in asymmetric Henry and aldol reactions.[12,13] Inspired by Trost et al. work,[12] we tested by using the neutral zinc(II) complexes **4–6** to catalyse the asymmetric nitroaldol reaction. The reaction between 2-methylpropanal **8** and nitromethane **9** was selected as a representative Henry reaction (Scheme 3).




**Scheme 3.** Henry reaction.

The first nitroaldol reactions were carried out at room temperature using a 1:10 stoichiometry of zinc catalysts **4–6** to aldehyde. The results obtained are not reported herein since all the observed yields were very poor (<5%). Subsequently, we examined the Henry reaction with molar ratios of **4–8** under the same conditions. As shown in Table 4, using molar ratios of 1:1 afforded excellent yields of the desired nitro alcohol **10** in the case of using **4**. Surprisingly, the Henry reaction with **5** and **6** led to the desired nitro alcohol **10** only with very poor yields. Disappointingly the application of **4** in the Henry reaction only had a small effect on the stereochemistry of the product **10**, as shown in Table 4. Presumably the ring size of the bridge bonded ring had much more influence on the mechanism than expected.

**Table 4.** Various zinc complex bases **4–6** for the asymmetric nitro aldol reaction

| Zinc complex | Product | Yield[a] (%) | ee[b] (%) |
|---|---|---|---|
| **4** | **10** | 90 | 2 |
| **5** | **10** | <5 | — |
| **6** | **10** | <5 | — |

[a] Isolated yield.
[b] Determined by chiral HPLC analysis using Daicel Chiralcel OD–H.

## 3. Conclusion

Examination of the literature reveals that the coordination chemistry of (*S*)-2-(*N*,*N*-dialkylaminomethyl)pyrrolidine derived guanidines is unexplored. Herein we have reported on the formation of the first zinc(II) and molybdenum(0) complexes with chiral *N*′,*N*″-diisopropyl-(*S*)-2-(*N*,*N*-dialkylaminomethyl)-pyrrolidine-1-carboximid-amide ligands **1–3**. Thorough spectroscopic and structural examinations of **4–6** reveal the coordination of the ligand via its imine and second ring nitrogens. In contrast, the chiral guanidine **2** acts as tridentate ligand in **7**, the first example of a monomeric $Mo(CO)_3$ complex supported by a chiral nitrogen-based ligand. Furthermore, intermolecular N–H···Cl–Zn-bonds were found in the solid structures of **4–6**. Additionally, only the synthesised complexes **4** worked very well as a neutral zinc guanidine base in the Henry reaction and gave nitro alcohol **10** in excellent yields. Further investigations to improve the enantioselectivity with related guanidines are under way in our laboratories.

## 4. Experimental

### 4.1. General

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques and all solvents were dried using appropriate drying agents. Melting points are uncorrected. NMR spectra were recorded on a Bruker AC 250 MHz and AC 400 MHz using the residual solvent resonance as an internal standard. $CD_3CN$ (H $\delta$ = 1.94, C $\delta$ = 118.3) was used as solvents. Optical rotations were recorded on a Polartronic E and are reported as $[\alpha]_D^{rt}$ (*c* in grams per 100 mL, solvent). Elemental analyses were conducted by the microanalytical service of our department. IR spectra were recorded on an ATR–BIORAD FTS-25. All compounds were fully characterised and given microanalytical data (±0.4%). Chiral HPLC was performed on a Jasco model. Starting chiral guanidines **1–3** were prepared according to our previously published procedure.[5] Zinc chloride and $(nbd)Mo(CO)_4$ (nbd = 2,5-norbornadiene) were purchased from commercial sources and were used as received.

### 4.2. Synthesis of zinc guanidine complexes 4–6

A solution of **1–3** (1.4 mmol) in 5 mL of dry acetonitrile was added to a suspension of dehydrated $ZnCl_2$ (1.5 mmol) in 5 mL dry acetonitrile under argon. The resulting mixture was refluxed for 20 min, filtered warm through Celite and concentrated to a volume of approximately 1 mL. Zinc complexes **4–6** precipitated upon addition of dry diethyl ether (5 mL). The suspension was filtered, washed with absolute diethyl ether (10 mL) and dried in vacuo to afford solid **4–6**. Single crystals suitable for X-ray analysis were obtained from acetonitrile by concentration and cooling.

**4.2.1. Dichloro{*N*,*N*′-diisopropyl-(*S*)-2-(pyrrolidin-1-ylmethyl)-pyrrolidine-1-carboximid-amide}zinc(II) 4.** Yield 80%. (Found: C, 45.56; H, 7.72; N, 13.34. $C_{16}H_{32}N_4Cl_2Zn$ requires C, 46.11; H, 7.74; N, 13.44). $^1H$ NMR ($CD_3CN$): $\delta$ 3.96 (m, 1H, CH), 3.79 (s, NH), 3.65 (m, 1H, *i*-Pr-CH), 3.63 (m, 1H, *i*-Pr-CH), 3.61/3.49 (m, 2H, $CH_2$), 3.55/2.56 (m, 2H, $CH_2$), 3.50/2.59 (m, 2H, $CH_2$), 3.06/2.33 (m, 2H, $CH_2$), 2.11/1.81 (m, 4H, $2 \times CH_2$), 1.92 (m, 2H, $CH_2$), 1.95/1.57 (m, 2H, $CH_2$), 1.44 (d, $J$ = 6.6 Hz, 3H, $CH_3$), 1.32 (d, $J$ = 6.4 Hz, 3H, $CH_3$), 1.23 (d, $J$ = 6.5 Hz, 3H, $CH_3$), 1.15 (d, $J$ = 6.3 Hz, 3H, $CH_3$). $^{13}C$ NMR ($CD_3CN$): $\delta$ 160.7 ($CN_3$), 61.5 ($CH_2$), 59.4 (CH), 57.4 ($CH_2$), 54.4

($CH_2$), 50.3 (CH), 47.5 (CH), 46.3 ($CH_2$), 31.3 ($CH_2$), 25.2 ($CH_3$), 25.1 ($CH_3$), 23.6 ($CH_3$), 22.8 ($CH_3$), 22.6 ($2\times CH_2$), 22.4 ($CH_2$). IR (ATR, $\nu$/cm$^{-1}$): 3293 ($\nu_{NH}$), 2966–2877 ($\nu_{CH}$), 1648 ($\nu_{CN}$). DEI-MS, *m/z* 378 $(M-HCl)^+$. $[\alpha]_D^{20} = -121.1$ (*c* 2.8, $CH_3CN$).

**4.2.2. Dichloro{*N*,*N*′-diisopropyl-(*S*)-2-(morpholin-4-yl-methyl)-pyrrolidine-1-carboximid-amide}zinc(II) 5.** Yield 71%. (Found: C, 42.69; H, 7.14; N, 12.18. $C_{16}H_{32}N_4Cl_2Zn\times 2H_2O$ requires C, 42.42; H, 8.01; N, 12.37). $^1$H NMR ($CD_3CN$): $\delta$ 3.95 (m, 1H, CH), 3.66 (m, 6H, $2\times$*i*-Pr-CH + $2\times OCH_2$), 3.61/3.42 (m, 2H, $CH_2$), 2.66/2.45 (m, 4H, $2\times CH_2$), 2.62/2.35 (m, 2H, $CH_2$), 2.08/1.71 (m, 2H, $CH_2$), 1.95/1.85 (m, 2H, $CH_2$), 1.33 (d, $J$ = 6.6 Hz, 6H, $2\times CH_3$), 1.23 (d, $J$ = 6.4 Hz, 6H, $2\times CH_3$), NH at room temperature not detected. $^{13}$C NMR ($CD_3CN$): $\delta$ 156.4 ($CN_3$), 67.1 ($2\times CH_2$), 65.7 ($CH_2$), 60.1 (CH), 54.8 ($2\times CH_2$), 49.6 ($CH_2$), 49.0 ($2\times CH$), 31.3 ($CH_2$), 24.8 ($2\times CH_3$), 23.9 ($CH_2$), 23.1 ($2\times CH_3$). IR (ATR, $\nu$/cm$^{-1}$): 3307 ($\nu_{NH}$), 2970–2877 ($\nu_{CH}$), 1623 ($\nu_{CN}$), 1114 ($\nu_{COC}$). DEI-MS, *m/z* 394 $(M-HCl)^+$. $[\alpha]_D^{20} = -83.5$ (*c* 2.3, $CH_3CN$).

**4.2.3. Dichloro{*N*,*N*′-diisopropyl-(*S*)-2-(piperidin-1-yl-methyl)-pyrrolidine-1-carboximid-amide}zinc(II) 6.** Yield 76%. (Found: C, 39.46; H, 6.89; N, 10.74. $C_{17}H_{34}N_4Cl_2Zn\times ZnO$ requires C, 39.87; H, 6.69; N, 10.94). $^1$H NMR ($CD_3CN$): $\delta$ 3.95 (m, 1H, CH), 3.67/3.43 (m, 2H, $CH_2$), 3.67 (m, 2H, $2\times$*i*-Pr-CH), 2.62/2.43 (m, 4H, $2\times CH_2$), 2.56/2.32 (m, 2H, $CH_2$), 2.08 (m, 2H, $CH_2$), 1.76–1.40 (m, 8H, $4\times CH_2$), 1.33 (d, $J$ = 6.6 Hz, 6H, $2\times CH_3$), 1.25 (d, $J$ = 6.3 Hz, 6H, $2\times CH_3$), NH at room temperature not detected. $^{13}$C NMR ($CD_3CN$): $\delta$ 157.3 ($CN_3$), 65.5 ($CH_2$), 60.4 (CH), 55.2 ($2\times CH_2$), 49.1 ($CH_2$), 48.7 ($2\times CH$), 31.0 ($CH_2$), 24.4 ($2\times CH_3$), 23.8 ($CH_2$), 23.4 ($CH_2$), 23.5 ($2\times CH_3$). IR (ATR, $\nu$/cm$^{-1}$): 3290 ($\nu_{NH}$), 2967–2876 ($\nu_{CH}$), 1603 ($\nu_{CN}$). DEI-MS, *m/z* 392 $(M-HCl)^+$. $[\alpha]_D^{20} = -90.6$ (*c* 1.7, $CH_3CN$).

### 4.3. Preparation of [*N*,*N*′-Diisopropyl-(*S*)-2-(morpholin-4-yl-methyl)-pyrrolidine-1-carboximid-amide]Mo(CO)$_3$ 7

Two hundred milligrams (0.67 mmol) of (nbd)Mo(CO)$_4$ was dissolved in 5 mL dry tetrahydrofuran under argon. 218 mg (0.74 mmol) of **2** was added and the solution stirred for 2 h at room temperature. The yellow precipitate which thus formed was collected by filtration, washed with dry *n*-pentane and dried under vacuum (187 mg, 59%). Crystals suitable for X-ray analysis was obtained by slow evaporation of **7** in acetonitrile. (Found: C, 48.61; H, 6.67; N, 13.21. $C_{19}H_{32}MoN_4O_4 + CH_3CN$ requires C, 48.74; H, 6.82; N, 13.53). $^1$H NMR ($CD_3CN$): $\delta$ 4.08 (m, 1H, CH), 3.74–3.23 (m, 8H, $2\times$*i*-Pr-CH + $2\times OCH_2$ + $CH_2$), 2.55/2.19 (m, 2H, $CH_2$), 2.47 (m, 4H, $2\times CH_2$), 2.02/1.65 (m, 2H, $CH_2$), 1.82 (m, 2H, $CH_2$), 1.17 (d, $J$ = 6.4 Hz, 6H, $2\times CH_3$), 1.12 (d, $J$ = 6.4 Hz, 6H, $2\times CH_3$), NH at room temperature not detected. $^{13}$C NMR ($CD_3CN$): $\delta$ 206.5 (CO), 205.2 (CO), 203.0 (CO), 155.6 ($CN_3$), 67.5 ($2\times CH_2$), 64.8 ($CH_2$), 57.3 (CH), 55.2 ($2\times CH_2$), 50.1 ($CH_2$), 47.9 ($2\times CH$), 31.4 ($CH_2$), 24.8 ($CH_2$), 24.5 ($2\times CH_3$), 24.4 ($2\times CH_3$). IR (ATR, $\nu$/cm$^{-1}$): 3324 ($\nu_{NH}$), 2967–2873 ($\nu_{CH}$), 1896, 1748 ($\nu_{CO}$), 1627 ($\nu_{CN}$). DEI-MS, *m/z* 476 ($M^+$). $[\alpha]_D^{20} = -50.5$ (*c* 1.6, $CH_3CN$).

### 4.4. X-ray crystallography

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz and polarisation effects, but not for absorption.[14,15] The structures were solved by direct methods (SHELXS[16]) and refined by full-matrix least squares techniques against $F_0^2$ (SHELXL-97[17]). The hydrogen atoms for the amine groups N3 for the three compounds were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[17] XP (SIEMENS analytical X-ray instruments, Inc.) was used for structure representations.

**4.4.1. Crystal data for 4.**[18] $C_{16}H_{32}Cl_2N_4Zn$, Mr = 416.73 g mol$^{-1}$, colourless prism, size $0.03\times 0.03\times 0.02$ mm$^3$, monoclinic, space group $P2_1$, $a$ = 8.8741(2), $b$ = 13.0475(4), $c$ = 9.2741(3) Å, $\beta$ = 106.240(1)°, $V$ = 1030.95(5) Å$^3$, $T$ = −90 °C, $Z$ = 2, $\rho_{calcd}$ = 1.342 g cm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 14.55 cm$^{-1}$, $F$(000) = 440, 6293 reflections in $h$(−10/11), $k$(−15/16), $l$(−10/12), measured in the range $2.29° \leqslant \Theta \leqslant 27.62°$, completeness $\Theta_{max}$ = 98.2%, 4044 independent reflections, $R_{int}$ = 0.033, 3491 reflections with $F_0 > 4\sigma(F_0)$, 212 parameters, 1 restraints, $R1_{obs}$ = 0.037, $wR^2_{obs}$ = 0.075, $R1_{all}$ = 0.049, $wR^2_{all}$ = 0.080, GOOF = 1.010, Flack-parameter 0.003(12), largest difference peak and hole: 0.326/−0.380 e Å$^{-3}$.

**4.4.2. Crystal data for 5.**[18] $C_{16}H_{31}Cl_2N_4OZn$, Mr = 431.72 g mol$^{-1}$, colourless prism, size $0.03\times 0.03\times 0.02$ mm$^3$, orthorhombic, space group $P2_12_12_1$, $a$ = 9.1221(3), $b$ = 13.2793(4), $c$ = 16.6507(8) Å, $V$ = 2016.9(1) Å$^3$, $T$ = −90 °C, $Z$ = 4, $\rho_{calcd}$ = 1.422 g cm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 14.93 cm$^{-1}$, $F$(000) = 908, 10640 reflections in $h$(−10/11), $k$(−14/17), $l$(−21/18), measured in the range $2.55° \leqslant \Theta \leqslant 27.48°$, completeness $\Theta_{max}$ = 99.4%, 4539 independent reflections, $R_{int}$ = 0.047, 3833 reflections with $F_0 > 4\sigma(F_0)$, 221 parameters, 0 restraints, $R1_{obs}$ = 0.042, $wR^2_{obs}$ = 0.095, $R1_{all}$ = 0.057, $wR^2_{all}$ = 0.103, GOOF = 0.999, Flack-parameter −0.011(15), largest difference peak and hole: 0.626/−0.515 e Å$^{-3}$.

**4.4.3. Crystal data for 6.**[18] $C_{17}H_{34}Cl_2N_4Zn$, Mr = 430.75 g mol$^{-1}$, colourless prism, size $0.03\times 0.03\times 0.03$ mm$^3$, orthorhombic, space group $P2_12_12_1$, $a$ = 9.2851(5), $b$ = 12.9826(4), $c$ = 17.5008(7) Å, $V$ = 2109.6(1) Å$^3$, $T$ = −90 °C, $Z$ = 4, $\rho_{calcd}$ = 1.356 g cm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 14.24 cm$^{-1}$, $F$(000) = 912, 12334 reflections in $h$(−12/10), $k$(−16/16), $l$(−22/22), measured in the range $1.95° \leqslant \Theta \leqslant 27.48°$, completeness $\Theta_{max}$ = 99.9%, 4813 independent reflections, $R_{int}$ = 0.062, 3462 reflections with $F_0 > 4\sigma(F_0)$, 221 parameters, 0 restraints, $R1_{obs}$ = 0.042, $wR^2_{obs}$ = 0.077, $R1_{all}$ = 0.079, $wR^2_{all}$ = 0.087, GOOF = 0.992, Flack-parameter

−0.001(16), largest difference peak and hole: 0.335/−0.397 e Å$^{-3}$.

**4.4.4. Crystal data for 7.**[18] $C_{19}H_{32}MoN_4O_4{\cdot}0.5C_2H_3N$, Mr = 496.95 g mol$^{-1}$, colourless prism, size 0.03 × 0.03 × 0.02 mm$^3$, orthorhombic, space group $P2_12_12$, $a$ = 13.4437(3), $b$ = 17.1211(3), $c$ = 10.2054(2) Å, $V$ = 2348.99(8) Å$^3$, $T$ = −90 °C, $Z$ = 4, $\rho_{calcd}$ = 1.405 g cm$^{-3}$, $\mu$ (Mo-K$_\alpha$) = 5.91 cm$^{-1}$, $F(000)$ = 1036, 16723 reflections in $h$(−17/17), $k$(−22/22), $l$(−11/13), measured in the range 1.93° ⩽ $\Theta$ ⩽ 27.47°, completeness $\Theta_{max}$ = 99.4%, 5321 independent reflections, $R_{int}$ = 0.025, 5102 reflections with $F_0 > 4\sigma(F_0)$, 261 parameters, 0 restraints, $R1_{obs}$ = 0.027, $wR^2_{obs}$ = 0.071, $R1_{all}$ = 0.030, $wR^2_{all}$ = 0.073, GOOF = 1.031, Flack-parameter −0.03(3), largest difference peak and hole: 1.120/−1.131 e Å$^{-3}$.

**4.4.5. Typical procedure for the asymmetric Henry reaction of nitromethane and 2-methylpropanal to 10.** Under an argon atmosphere, nitromethane **8** (3.8 mmol) and 2-methylpropanal **9** (3.8 mmol) was added to a solution of **4**–**6** (3.8 mmol) in 60 mL anhydrous acetonitrile at room temperature. The resulting mixture was stirred for 24 h at room temperature, reduced in vacuum and quenched by aqueous HCl (29.7 mol/L) until the solution showed pH 1. After extraction with diethyl ether, the organic layer was dried over anhydrous $MgSO_4$. The solvent and any remaining unreacted aldehyde and nitromethane were removed under reduced pressure. Purification by bulb-to-bulb distillation ($10^{-1}$ Torr, 70 °C) afforded the desired nitro alcohol **10**. The product was identified by $^1$H NMR spectroscopy.

**4.4.6. 3-Methyl-1-nitrobutan-2-ol 10.** Yield see Table 4. (Found: C, 45.27; H, 8.00; N, 10.60. $C_{13}H_{27}N_3O$ requires C, 45.10; H, 8.33; N, 10.52). $^1$H NMR ($CDCl_3$): $\delta$ 0.96–1.00 (m, 2H, $CH_2$), 1.73–1.86 (m, 1H, CH), 2.54 (s, 1H, OH), 4.06–4.13 (m, 1H, CH), 4.35–4.51 (m, 6H, $CH_3$). IR (ATR): 3431 ($\nu_{OH}$), 2969–2881 ($\nu_{CH}$), 1549 ($\nu_{NO2}$) cm$^{-1}$. MS $m/z$ (%): 134 (M + 1)$^+$ (64).

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