

# Synthesis and Structures of Vinamidine $\text{Mn}^{\text{II}}$ , $\text{Zn}^{\text{II}}$ , and $\text{Cd}^{\text{II}}$ Iodine Derivatives

Jörg Prust,<sup>[a]</sup> Kerstin Most,<sup>[a]</sup> Ilka Müller,<sup>[a]</sup> Andreas Stasch,<sup>[a]</sup> Herbert W. Roesky,<sup>\*[a]</sup> and Isabel Usón<sup>[a]</sup>

*Dedicated to Professor Glen B. Deacon on the occasion of his 65th birthday*

**Keywords:** Cadmium / Manganese / N ligands / Zinc

We have focused on the synthesis of monomeric, functionalized starting materials containing manganese(II), zinc(II), and cadmium(II) by taking advantage of the sterically demanding and chelating property of the substituted vinamidine ligand 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene (NacNacH). Metal iodine derivatives containing vinamidines as the bulky ligand can be regarded as interesting precursors for preparing complexes with low-valent metal centers by reduction as

long as they are free of coordinated ether. The vinamidine complexes  $\text{NacNacM}(\mu\text{-I})_2\text{Li}(\text{OEt}_2)_2$  [ $\text{M} = \text{Mn}$  (**3**),  $\text{Zn}$  (**4**),  $\text{Cd}$  (**5**)] are obtained from the corresponding vinamidine lithium complex and  $\text{MI}_2$  ( $\text{M} = \text{Mn}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ) in good yields. A crystal structure analysis of **3**, **4**, and **5** shows them to be isostructural. All three structures have the vinamidine backbone in a boat conformation with the tetrahedrally coordinated metal center at the prow and the opposing carbon atom at the stern.

## Introduction

Vinamidines were first used in inorganic synthesis by Holm et al. and McGeachin et al. to synthesize moisture-stable  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  complexes.<sup>[1]</sup> In further research the surprising catalytic activity of vinamidine derivatives of various transition and main group metals was analyzed. Feldman et al. synthesized catalytically active aryl-substituted vinamidine complexes of  $\text{Pd}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$ , and Theopold et al. and Gibson et al. tested vinamidine complexes of  $\text{Ti}^{\text{III}}$ ,  $\text{V}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$  for olefin polymerization.<sup>[2,3]</sup>

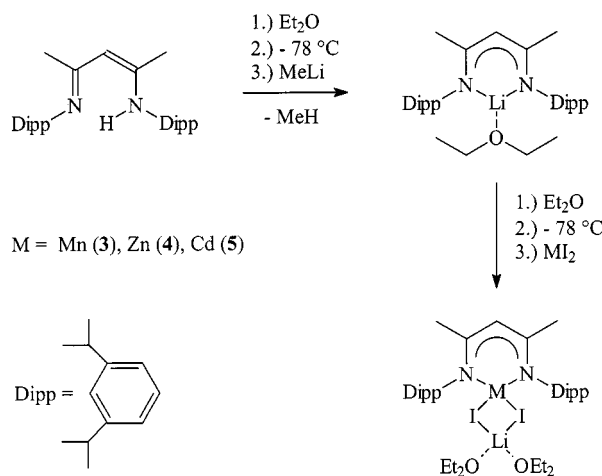
In the last few years the interest in the synthesis of monomeric and coordinatively unsaturated metal complexes with bulky vinamidine ligands has increased. In this research field several new compounds have been reported.<sup>[4]</sup> The vinamidine 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene (**1**) (NacNacH) is suitable for the synthesis of derivatives with unusually low coordinate main group elements. Recently we synthesized a monomeric  $\text{Al}^{\text{I}}$  compound using **1** as a stable carbene analogue, and Gibson et al. have prepared a mono-alkylmagnesium complex stabilized by **1**.<sup>[5,6]</sup> Our research focused on the synthesis of complexes with low coordinate Mn, Zn and Cd atoms.

Preparing the iodine-containing metal complexes of **1** has two functions: the size of the ligand should have a shielding effect on the metal center and therefore the nucleophilic attack should be minimized; these systems should also be interesting precursors for the preparation of complexes with low-valent metal atoms by reduction of the iodine complexes using alkali metals.

We have focused on the synthesis of  $\text{NacNacMI}$  ( $\text{M} = \text{Mn}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ) as monomeric, functionalized starting materials due to the sterically demanding and chelating properties of **1**.

## Results and Discussion

The reaction of  $\text{MeLi}$  with  $\text{NacNacH}$  (**1**) gives the pale yellow compound  $\text{NacNacLi}\cdot\text{OEt}_2$  (**2**) in good yield (> 95%). This ether-soluble lithium compound is a useful reagent for metathesis reactions with metal halides. Thus, the reaction of **2** with  $\text{MI}_2$  affords the iodide complexes  $\text{NacNacM}(\mu\text{-I})_2\text{Li}(\text{OEt}_2)_2$  ( $\text{M} = \text{Mn}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ) in reasonable yields (77–85%) (Scheme 1).



Scheme 1

Unfortunately compounds **3**, **4**, and **5** are moisture sensitive and give **1** as the primary hydrolysis product.  $^1\text{H}$  NMR

<sup>[a]</sup> Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany  
Fax: (internat.) +49-551/39-3373  
E-mail: hroesky@gwdg.de

spectroscopic data and the elemental analysis of **4** and **5** are consistent with the solid state structures, whereas the mass spectra of **3**, **4**, and **5** show several fragments assignable to the species free of  $\text{LiI}(\text{Et}_2\text{O})_2$ .<sup>[7]</sup>

The X-ray structure analysis of **3**, **4** (shown in Figure 1), and **5** shows that these compounds are isostructural. The crystallographic data are summarized in Table 1. Selected bond lengths and angles for **3**, **4**, and **5** are given in Table 2.

Figure 2 shows a superposition of **3**, **4**, and **5**. The only differences between the three structures are those derived from the different bond lengths in the coordination of the various metals. Therefore, we discuss the overall structure.

The central structural element is a  $\text{NacNacM}(\mu\text{-I})_2\text{Li}$  unit. The vinamidine ligand NacNac acts as a chelating ligand through its two N atoms, forming a six-membered ring with the metal. The central metal (**3**: Mn, **4**: Zn, **5**: Cd) and the lithium cation are bridged by the two iodine atoms. The N–M–N-angle is about  $95^\circ$  (**3**:  $94.2^\circ$ , **4**:  $98.6^\circ$ , **5**:  $91.5^\circ$ ) and the I–M–I-angle is  $101^\circ$  (**3**:  $101^\circ$ , **4**:  $101^\circ$ , **5**:  $101^\circ$ ). The tetrahedral coordination of the metal is distorted due to the strain imposed by the six-membered ring of the chelate, and the four-membered ring of the bridging halides.

The  $\text{M}-\text{N}-\text{C}(\text{CH}_3)-\text{CH}-\text{C}(\text{CH}_3)-\text{N}$  unit is not planar. The six-membered ring displays a boat conformation with the metal at the prow and C(2) at the stern. This deviation from planarity is imposed by the metal, as the planar situation implies more distortion in the tetrahedral

environment of the metal. Thus, deviation from planarity increases with the metal radius. The metal is about  $0.30 \text{ \AA}$  (**3**:  $0.33 \text{ \AA}$ , **4**:  $0.29 \text{ \AA}$ , **5**:  $0.34 \text{ \AA}$ ) out of the plane defined by

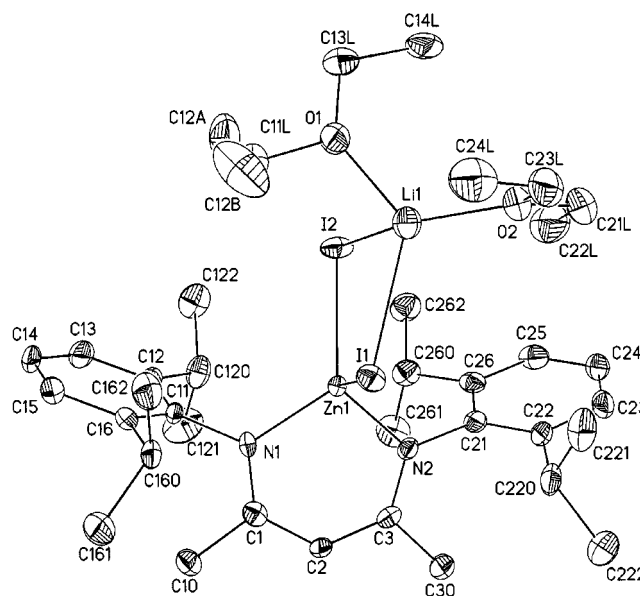


Figure 1. Molecular structure of **4** (hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°] are given in Table 2

Table 1. Crystallographic data for **3**, **4** and **5**

|                                                               | <b>3</b>                                                                                                                                   | <b>4</b>                                                                                                                                     | <b>5</b>                                                                                                                                   |
|---------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| Empirical formula                                             | $\text{C}_{37}\text{H}_{61}\text{I}_2\text{LiMnN}_2\text{O}_2$                                                                             | $\text{C}_{37}\text{H}_{61}\text{I}_2\text{LiN}_2\text{O}_2\text{Zn}$                                                                        | $\text{C}_{37}\text{H}_{61}\text{CdLiI}_2\text{N}_2\text{O}_2$                                                                             |
| Molecular weight                                              | 881.56                                                                                                                                     | 891.99                                                                                                                                       | 939.02                                                                                                                                     |
| Temperature [K]                                               | 133(2)                                                                                                                                     | 133(2)                                                                                                                                       | 133(2)                                                                                                                                     |
| Wavelength [Å]                                                | 0.71073                                                                                                                                    | 0.71073                                                                                                                                      | 0.71073                                                                                                                                    |
| Crystal system                                                | triclinic                                                                                                                                  | triclinic                                                                                                                                    | triclinic                                                                                                                                  |
| Space group                                                   | $P\bar{1}$                                                                                                                                 | $P\bar{1}$                                                                                                                                   | $P\bar{1}$                                                                                                                                 |
| Unit cell dimensions [Å]                                      | $a = 9.773(2)$<br>$b = 10.413(2)$<br>$c = 20.699(4)$<br>$\alpha = 86.39(3)^\circ$<br>$\beta = 85.01(3)^\circ$<br>$\gamma = 78.89(3)^\circ$ | $a = 9.6715(19)$<br>$b = 10.374(2)$<br>$c = 20.688(4)$<br>$\alpha = 86.17(3)^\circ$<br>$\beta = 84.64(3)^\circ$<br>$\gamma = 78.50(3)^\circ$ | $a = 9.780(2)$<br>$b = 10.410(2)$<br>$c = 20.658(4)$<br>$\alpha = 86.70(3)^\circ$<br>$\beta = 85.19(3)^\circ$<br>$\gamma = 79.86(3)^\circ$ |
| Volume [Å <sup>3</sup> ]                                      | 2056.9(7)                                                                                                                                  | 2022.7(7)                                                                                                                                    | 2060.9(7)                                                                                                                                  |
| Z                                                             | 2                                                                                                                                          | 2                                                                                                                                            | 2                                                                                                                                          |
| Density (calcd.) [Mg/m <sup>3</sup> ]                         | 1.423                                                                                                                                      | 1.465                                                                                                                                        | 1.513                                                                                                                                      |
| Absorption coefficient [mm <sup>−1</sup> ]                    | 1.852                                                                                                                                      | 2.164                                                                                                                                        | 2.058                                                                                                                                      |
| $F(000)$                                                      | 894                                                                                                                                        | 904                                                                                                                                          | 940                                                                                                                                        |
| Crystal size [mm <sup>3</sup> ]                               | $0.30 \times 0.30 \times 0.20$                                                                                                             | $0.40 \times 0.40 \times 0.30$                                                                                                               | $0.40 \times 0.30 \times 0.20$                                                                                                             |
| $\theta$ range for data collection                            | $1.98$ to $26.34^\circ$                                                                                                                    | $2.01$ to $23.25^\circ$                                                                                                                      | $1.98$ to $26.37^\circ$                                                                                                                    |
| Reflections collected                                         | 55863                                                                                                                                      | 27007                                                                                                                                        | 59137                                                                                                                                      |
| Independent reflections                                       | 8319 [ $R_{\text{int}} = 0.0495$ ]                                                                                                         | 5766 [ $R_{\text{int}} = 0.0531$ ]                                                                                                           | 8429 [ $R_{\text{int}} = 0.0417$ ]                                                                                                         |
| Data/restraints/parameters                                    | 8319/69/429                                                                                                                                | 5766/69/431                                                                                                                                  | 8429/69/431                                                                                                                                |
| Goodness-of-fit on $F^2$                                      | 1.161                                                                                                                                      | 1.144                                                                                                                                        | 1.152                                                                                                                                      |
| Final $R$ indices [ $I > 2\sigma(I)$ ]                        | $R1 = 0.0461$<br>$wR2 = 0.1180$                                                                                                            | $R1 = 0.0363$<br>$wR2 = 0.0911$                                                                                                              | $R1 = 0.0308$<br>$wR2 = 0.0728$                                                                                                            |
| $R$ indices (all data)                                        | $R1 = 0.0524$<br>$wR2 = 0.1217$                                                                                                            | $R1 = 0.0403$<br>$wR2 = 0.0941$                                                                                                              | $R1 = 0.0339$<br>$wR2 = 0.0741$                                                                                                            |
| Largest diff. peak and hole [e <sup>−</sup> Å <sup>−3</sup> ] | 1.718 and $-1.615$                                                                                                                         | 1.175 and $-1.013$                                                                                                                           | 1.408 and $-1.031$                                                                                                                         |

Table 2. Comparison of bond length [ $\text{\AA}$ ] and angles [ $^\circ$ ] of **3**, **4**, **5**

|                 | <b>3</b> (M = Mn) | <b>4</b> (M = Zn) | <b>5</b> (M = Cd) |
|-----------------|-------------------|-------------------|-------------------|
| M–N(1)          | 2.067(4)          | 1.984 (3)         | 2.188(2)          |
| M–N(2)          | 2.090(4)          | 1.991(4)          | 2.196(2)          |
| M–I(2)          | 2.7230(9)         | 2.6142(8)         | 2.7518(7)         |
| M–I(1)          | 2.7354(9)         | 2.6648(8)         | 2.7920(7)         |
| I(1)Li(1)       | 2.817(8)          | 2.784(8)          | 2.816(6)          |
| I(2)–Li(1)      | 2.920(9)          | 2.919(8)          | 2.975(6)          |
| N(1)–C(1)       | 1.347(5)          | 1.318(6)          | 1.322(4)          |
| N(1)–C(11)      | 1.447(5)          | 1.453(6)          | 1.440(4)          |
| N(2)–C(3)       | 1.336(5)          | 1.332(6)          | 1.332(4)          |
| N(2)–C(21)      | 1.445(5)          | 1.436(6)          | 1.439(3)          |
| C(1)–C(2)       | 1.411(6)          | 1.399(6)          | 1.407(4)          |
| C(1)–C(10)      | 1.511(6)          | 1.515(6)          | 1.519(4)          |
| C(2)–C(3)       | 1.407(6)          | 1.398(6)          | 1.410(4)          |
| C(3)–C(30)      | 1.523(6)          | 1.520(6)          | 1.512(4)          |
| Li(1)–O(1)      | 1.912(10)         | 1.930(9)          | 1.899(6)          |
| Li(1)–O(2)      | 1.982(10)         | 1.956(9)          | 1.962(6)          |
| N(1)–M–N(2)     | 94.38(14)         | 98.78(15)         | 91.46(9)          |
| N(1)–M–I(2)     | 119.67(10)        | 118.13(11)        | 121.77(7)         |
| N(2)–M–I(2)     | 117.28(10)        | 116.92(11)        | 116.92(7)         |
| N(1)–M–I(1)     | 113.04(10)        | 111.76(11)        | 113.31(7)         |
| N(2)–M–I(1)     | 112.05(11)        | 110.38(11)        | 112.92(7)         |
| I(2)–M–I(1)     | 101.07(4)         | 101.22(3)         | 101.13(3)         |
| M–I(1)–Li(1)    | 82.13(18)         | 83.38(17)         | 82.10(12)         |
| M–I(2)–Li(1)    | 80.45(16)         | 81.67(16)         | 79.95(12)         |
| C(1)–N(1)–M     | 120.3(3)          | 118.8(3)          | 120.13(19)        |
| C(3)–N(2)–M     | 120.3(3)          | 117.9(3)          | 120.23(19)        |
| N(1)–C(1)–C(2)  | 124.5(4)          | 124.6(4)          | 125.7(3)          |
| C(3)–C(2)–C(1)  | 131.1(4)          | 130.4(4)          | 132.7(3)          |
| N(2)–C(3)–C(2)  | 124.4(4)          | 124.9(4)          | 124.9(3)          |
| O(1)–Li(1)–O(2) | 114.9(5)          | 114.2(4)          | 116.2(3)          |
| O(1)–Li(1)–I(1) | 118.4(4)          | 118.3(4)          | 117.6(2)          |
| O(2)–Li(1)–I(1) | 102.9(4)          | 105.5(3)          | 102.7(2)          |
| O(1)–Li(1)–I(2) | 93.1(3)           | 93.2(3)           | 92.1(2)           |
| O(2)–Li(1)–I(2) | 133.1(4)          | 133.8(4)          | 132.6(3)          |
| I(1)–Li(1)–I(2) | 94.5(3)           | 91.3(2)           | 95.33(15)         |

N(1)–C(1)C(10)–C(3)C(30)–N(2) and C(2) is about 0.19  $\text{\AA}$  (**3**: 0.18  $\text{\AA}$ , **4**: 0.19  $\text{\AA}$ , **5**: 0.19  $\text{\AA}$ ) out of this plane.

Nevertheless, the  $\pi$ -electrons of the vinamidine are delocalized since the C(1)–C(2) and the C(2)–C(3) as well as the C(1)–N(1) and the C(3)–N(2) bond lengths are equal within the experimental error and correspond to C–C and C–N distances in aromatic systems. Both N–M bond lengths are equal.

Although the bond lengths of the metal center to I(1) and I(2) are equal within the experimental error (**3**: 2.73/2.72  $\text{\AA}$ , **4**: 2.66/2.61  $\text{\AA}$ , **5**: 2.79/2.75  $\text{\AA}$ ), the bond lengths of Li to I(1) and I(2) are significantly different (**3**: 2.81/2.92  $\text{\AA}$ , **4**: 2.78/2.92  $\text{\AA}$ , **5**: 2.82/2.98  $\text{\AA}$ ). We suggest packing effects to be responsible for these differences. The M–I–Li–I ring is not planar (dihedral angle, **3**: 15.5°, **4**: 17.7°, **5**: 14.1°).

The coordination sphere of the Li cation is completed by two diethyl ether molecules.

## Conclusion

Unfortunately, the synthesis of low coordinate monomeric metal iodides has so far not been successful as  $\text{LiI}$ –

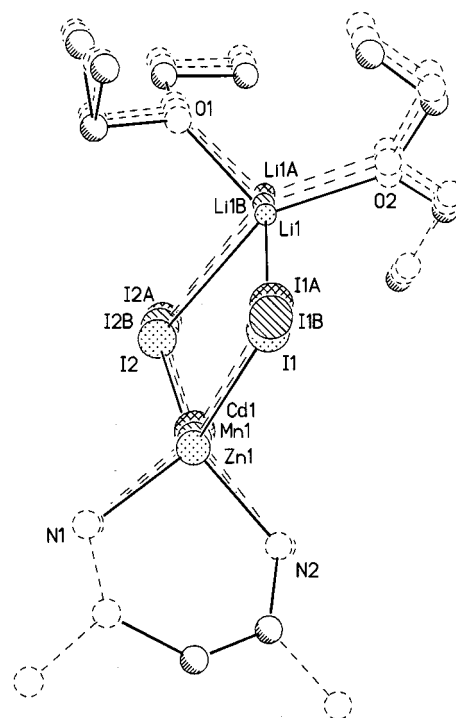


Figure 2. Comparison of the molecular structures of **3**, **4**, and **5**. (organic substituents have been omitted for clarity)

$(\text{Et}_2\text{O})_2$  is always found coordinated to the metal centers. Moreover, the reduction of iodides with sodium or potassium was also not successful. Consequently further research is directed toward the synthesis of metal complexes free of  $\text{LiI}(\text{Et}_2\text{O})_2$  using hydrocarbons as solvent.

## Experimental Section

**General:** All reactions were performed using standard Schlenk and dry box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. All NMR spectra were obtained in 5 mm tubes using dry degassed  $[\text{D}_6]\text{benzene}$  as a solvent, referenced to external  $\text{SiMe}_4$ . Elemental analyses were performed by the Analytisch-Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen.

Compound **1** was prepared according to the literature method.<sup>[3]</sup>

**Preparation of 2:**  $\text{MeLi}$  (22.9 mL, 36.6 mmol, 1.6 M in  $\text{Et}_2\text{O}$ ) was added dropwise with a syringe over 10 min. to a stirred solution of **1** (15.3 g, 36.6 mmol) in  $\text{Et}_2\text{O}$  (200 mL) at  $-78^\circ\text{C}$ . The mixture was stirred at  $-78^\circ\text{C}$  for an additional 10 min. and allowed to warm to room temperature, stirred overnight, and reduced in volume to approximately 30 mL. Pale yellow solid **2** was isolated by filtration, washed with pentane ( $3 \times 10$  mL), and dried in vacuo. (16.2 g, 89% yield). M.p.: 142–144  $^\circ\text{C}$ . –  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.03 (t,  $J$  = 6.8 Hz, 12 H,  $\text{OCH}_2\text{CH}_3$ ), 1.19 [d,  $J$  = 6.8 Hz, 12 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.22 [d,  $J$  = 6.8 Hz, 12 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.93 (s, 6 H,  $\text{CH}_3$ ), 3.33 (q,  $J$  = 6.8 Hz, 8 H,  $\text{OCH}_2\text{CH}_3$ ), 3.40 [sept.,  $J$  = 6.8 Hz, 4 H,  $\text{CH}(\text{CH}_3)_2$ ], 5.00 (s, 1 H, CH), 7.17 (m, 6 H, ArH). –  $^7\text{Li}$  NMR [155 MHz,  $\text{C}_6\text{D}_6$ , ( $\text{LiCl}/\text{D}_2\text{O}$ )]:  $\delta$  = 1.61 (s). –  $\text{C}_{33}\text{H}_{51}\text{LiN}_2\text{O}$  (498.45): C 79.48, H 10.31, N 5.62; found C 80.26, H 10.21, N 5.63.

**Preparation of 3:** Compound **2** (2.50 g, 5.01 mmol) in Et<sub>2</sub>O (20 mL) was added to a suspension of MnI<sub>2</sub> (1.54 g, 5.01 mmol) in Et<sub>2</sub>O (20 mL) at –78 °C. The reaction mixture was stirred at –78 °C for an additional 10 min. and allowed to warm to room temperature. After stirring the pink solution overnight the color changed to yellow. The yellow solution was filtered and the solvent removed under reduced pressure to a volume of 10 mL. Yellow crystals were obtained after 1 day at –24 °C. (3.75 g, 85% yield).<sup>[8]</sup> – MS (EI): *m/z* (%) = 202 (47) [DippNCCH<sub>3</sub>], 599 (100) [NacNacMnI]. – IR (Nujol):  $\tilde{\nu}$  = 1655 (m), 1625 (m), 1262 (m), 1079 (s), 793 (s), 290 (m) cm<sup>–1</sup>. – C<sub>37</sub>H<sub>61</sub>I<sub>2</sub>LiMnN<sub>2</sub>O<sub>2</sub> (881.58): C 50.41, H 6.97, N 3.18; found C 50.43, H 6.89, N 3.23.<sup>[7]</sup>

**Preparation of 4:** Compound **2** (1.26 g, 2.54 mmol) in Et<sub>2</sub>O (20 mL) was added to a suspension of ZnI<sub>2</sub> (811 mg, 2.54 mmol) in Et<sub>2</sub>O (20 mL) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 24 h. The solution was filtered and the solvent removed under reduced pressure to a volume of 5 mL. Colorless crystals were obtained after 4 days at 2 °C. (1.79 g, 79% yield).<sup>[8]</sup> – <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.05 (t, *J* = 6.8 Hz, 12 H, CH<sub>3</sub>CH<sub>2</sub>O), 1.14 [d, *J* = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.36 [d, *J* = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.68 (s, 6 H, CH<sub>3</sub>), 3.20 (t, *J* = 6.8 Hz, 12 H, CH<sub>3</sub>CH<sub>2</sub>O), 3.51 [sept., *J* = 6.8 Hz, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>], 4.86 (s, 1 H, CH), 7.13 (m, 6 H, ArH). – <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 23.3 (s), 24.3 (s), 24.5 (s), 27.8 (s), 28.9 (s), 97.0 (s), 123.6 (s), 123.7 (s), 124.7 (s), 125.3 (s), 125.9 (s), 126.9 (s), 143.9 (s), 171.2 (s). – MS (EI): *m/z* (%) = 202 (100) [DippNCCH<sub>3</sub>], 608 (47) [NacNacZnI]. – IR (Nujol):  $\tilde{\nu}$  = 1701 (m), 1615 (s), 1465 (m), 1412 (m), 1255 (s), 1054 (s), 763 (m), 243 (m) cm<sup>–1</sup>. – C<sub>37</sub>H<sub>61</sub>I<sub>2</sub>LiN<sub>2</sub>O<sub>2</sub>Zn (892.03): C 49.82, H 6.89, N 3.14; found C 49.60, H 6.61, N 3.59.

**Preparation of 5:** Compound **2** (1.00 g, 2.01 mmol) in Et<sub>2</sub>O (20 mL) was added to a suspension of CdI<sub>2</sub> (733 mg, 2.01 mmol) in Et<sub>2</sub>O (20 mL) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 36 h. After filtration from the residue the solvent was removed under reduced pressure to a volume of 10 mL. Colorless crystals were obtained after 6 days at 2 °C. (1.45 g, 77% yield).<sup>[8]</sup> – <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.02 (t, *J* = 6.8 Hz, 12 H, CH<sub>3</sub>CH<sub>2</sub>O), 1.12 [d, *J* = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.33 [d, *J* = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.63 (s, 6 H, CH<sub>3</sub>), 3.21 (t, *J* = 6.8 Hz, 12 H, CH<sub>3</sub>CH<sub>2</sub>O), 3.44 [sept., *J* = 6.8 Hz, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>], 4.81 (s, 1 H, CH), 7.11 (m, 6 H, ArH). – <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 23.4 (s), 24.1 (s), 24.4 (s), 27.9 (s), 28.6 (s), 28.9 (s), 96.8 (s), 123.5 (s), 123.7 (s), 124.8 (s), 125.2 (s), 125.8 (s), 127.1 (s), 145.4 (s), 170.0 (s). – MS (EI): *m/z* (%) = 202 (100) [DippNCCH<sub>3</sub>], 417 (52) [NacNac], 658 (58) [NacNacCdI]. – IR (Nujol):  $\tilde{\nu}$  = 1732 (m), 1440 (m), 1406 (s), 1268 (s), 1021 (m), 759 (s), 435 (m) cm<sup>–1</sup>. – C<sub>37</sub>H<sub>61</sub>CdI<sub>2</sub>LiN<sub>2</sub>O<sub>2</sub> (939.05): C 47.32, H 6.55, N 2.98; found C 46.89, H 6.32, N 2.77.

**X-ray Crystallography:** Crystals of **3** (mol. wt. 881.58), **4** (892.03), and **5** (939.05) were grown from a concentrated Et<sub>2</sub>O solution cooled to –24 °C (**3**) or 2 °C (**4**, **5**). They crystallized in the triclinic crystal system with space group *P* $\bar{1}$ . Relevant details and data statistics are summarized in Table 1. The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.<sup>[9]</sup> Diffraction data were collected on a Stoe–Siemens–Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K, with graphite-monochromated Mo-*K*<sub>α</sub> radiation ( $\lambda$  = 0.71073 Å).

The structures were solved by direct methods using SHELXS-97<sup>[10]</sup> and refined against *F*<sup>2</sup> on all data by full-matrix least-squares with SHELXL-97.<sup>[11]</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atoms on C(10) in the structures of **4** and **5**, however, were refined as an idealized disordered methyl group with two half-occupied positions related to one another by a rotation of 60°. These hydrogen atoms were allowed to ride on the carbon atom and rotate about the C(10)–C(1) bond. In all three structures the disordered methyl group of one of the diethyl ether molecules was modeled with the help of similarity restraints for 1–2 and 1–3 distances and displacement parameters. In all three structures there are residual electron density maxima near the iodine atoms and Li(1), presumably due to disorder which could not be modeled. This unmodeled disorder could play a role in the apparently distorted geometry at Li(1).

Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 154416 (**3**), CCDC 154417 (**4**), CCDC 154418 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

## Acknowledgments

The financial support of the Deutsche Forschungsgemeinschaft and Göttinger Akademie der Wissenschaften is gratefully acknowledged.

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Received December 14, 2000  
[100472]