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**SUPPLEMENTARY MATERIAL**

# Towards the synthesis of guanidinate- and amidinate-bridged dimers of Mn and Ni

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***Synthesis and Characterization of $Mn\{\mu\text{-}NC(NMe_2)_2\}_4Li_2\cdot 3THF$ 6***

1,1,3,3-Tetramethylguanidine (0.48 mL, 4.5 mmol) was stirred in THF (5 mL). *t*-BuLi (2.7 mL, 1.7 M in hexanes, 4.5 mmol) was syringed into this solution dropwise under Ar at –78 °C, and the resulting yellow suspension allowed to warm to room temperature to give a white suspension. This was then cooled again to –78 °C and a suspension of $Cp_2Mn$ (278 mg, 1.5 mmol) in THF (5 mL) was syringed in dropwise by cannula. The resulting solution was allowed to warm to room temperature before being stirred overnight and then filtered *in vacuo* and stored at –30 °C. This afforded brown crystals of **6** in low yield (50 mg, 5% wrt guanidine), m. p. >360 ºC. $\delta_H$ (500 MHz, $d_8$-THF) 2.63 (s, 3H, NMe). $\delta_C$ (125 MHz, $d_8$-THF) 103.4 ($CN_2$), 37.5 (Me). Satisfactory elemental analysis could not be obtained after multiple attempts. X-ray crystal data: $C_{32}H_{72}Li_2MnN_{12}O_3$, $M$ = 741.84, tetragonal, space group $P4_2bc$, $a = b$ = 25.5067(2), $c$ = 13.2394(2) Å, $V$ = 8613.44(16) Å$^3$, $Z$ = 8, $\rho_{calcd}$ = 1.144 g cm$^{-3}$, Mo-K$_\alpha$ radiation, $\lambda$ = 0.71073 Å, $\mu$ = 0.350 mm$^{-1}$, $T$ = 150(2)K. 104719 data (12577 unique, $R_{int}$ = 0.0440, θ < 30.84 °) were collected. $wR2$ = 0.1175, conventional $R$ = 0.0475 on $F$ values of 9680 reflections with $F^2 > 2\sigma(F^2)$, $S$ = 1.029, 467 parameters. Residual electron density extrema ±0.554 eÅ$^{-3}$.

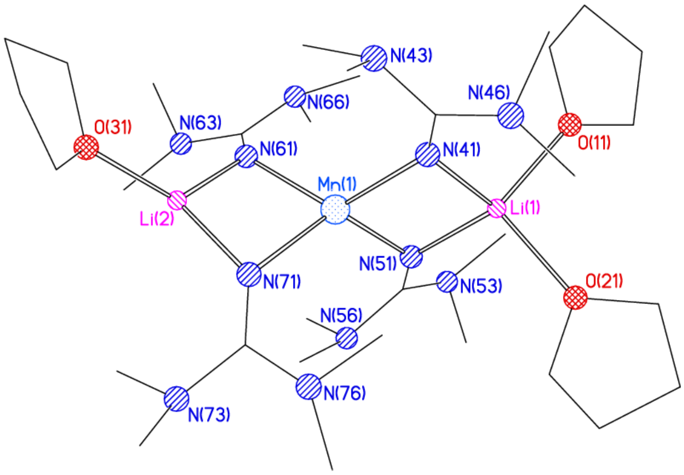


**Figure S1** Molecular structure of guanidinate-ligated spirocycle **6**. Selected bond lengths (Å) and angles (°):N–Mn(1) 2.0943(18)-2.1189(18), N–Li(1) 2.019(4)-2.036(5), N–Li(2) 1.927(5)-1.941(5), O–Li(1) 2.046(4)-2.056(4), O–Li(2) 1.942(5), C┈NMn 1.253(3)-1.260(3), N(41)/(61)–Mn(1)–N(51)/(71) 88.75(7)-91.83(7), N–Li–N 95.8(2)-99.9(2), Mn–N–Li 84.28(15)-86.35(13).

***Theoretical Modelling of 5***

$Ni_2$(MeN┈CH┈NMe) **5** was investigated by quantum chemical methods at Hartree-Fock (HF), density-functional (BLYP) and hybrid density-functional (B3PW91, B3LYP) levels using the Gaussian09 program package and the Natural Bond Order module implemented in the package.[S1] Carbon, hydrogen and nitrogen were represented by 6-311G basis sets including an additional diffuse and a polarizing function, and nickel by an effective-core potential basis set of MDF10-type with an (8s7p6d1f)/[6s5p3d1f] valence space.[S2,S3] Cartesian coordinates of the geometrically optimized structure of **5** at B3LYP level are as follows:

| **Element** | **x/Å** | **y/Å** | **z/Å** |
|---|---|---|---|
| Ni | 0.000000 | 0.000000 | 1.255812 |
| Ni | 0.000000 | 0.000000 | -1.255812 |
| N | -0.000042 | 1.931671 | 1.171236 |

| | | | |
|---|---|---|---|
| N | 0.000042 | 1.931671 | -1.171236 |
| C | 0.000000 | 2.533327 | 0.000000 |
| H | 0.000000 | 3.632540 | 0.000000 |
| C | -0.000372 | 2.768005 | 2.364575 |
| H | -0.889639 | 3.410080 | 2.426675 |
| H | 0.888309 | 3.410899 | 2.426572 |
| H | -0.000029 | 2.133853 | 3.252699 |
| C | 0.000372 | 2.768005 | -2.364575 |
| H | 0.889639 | 3.410080 | -2.426675 |
| H | 0.000029 | 2.133853 | -3.252699 |
| H | -0.888309 | 3.410899 | -2.426572 |
| N | 0.000042 | -1.931671 | 1.171236 |
| N | -0.000042 | -1.931671 | -1.171236 |
| C | 0.000000 | -2.533327 | 0.000000 |
| H | 0.000000 | -3.632540 | 0.000000 |
| C | 0.000372 | -2.768005 | 2.364575 |
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| H | -0.000029 | -2.133853 | -3.252699 |
| N | -1.931671 | -0.000042 | 1.171236 |
| N | -1.931671 | 0.000042 | -1.171236 |
| C | -2.533327 | 0.000000 | 0.000000 |
| H | -3.632540 | 0.000000 | 0.000000 |
| C | -2.768005 | -0.000372 | 2.364575 |
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| C | 2.533327 | 0.000000 | 0.000000 |
| H | 3.632540 | 0.000000 | 0.000000 |
| C | 2.768005 | 0.000372 | 2.364575 |
| H | 3.410080 | 0.889639 | 2.426675 |
| H | 2.133853 | 0.000029 | 3.252699 |
| H | 3.410899 | -0.888309 | 2.426572 |
| C | 2.768005 | -0.000372 | -2.364575 |
| H | 3.410080 | -0.889639 | -2.426675 |
| H | 3.410899 | 0.888309 | -2.426572 |
| H | 2.133853 | -0.000029 | -3.252699 |

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