Appendices – DFT calculations

**Computational Details**

The geometry of the molecules was optimized using Gaussian 03.[[1]](#footnote-2) Exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed, utilising the 6-31g\* basis set.[[2]](#footnote-3) The resultant optimised geometries were subject to a frequency analysis and the refined by further density functional theory (DFT) calculations[[3]](#footnote-4) using the B3LYP functionals[[4]](#footnote-5),[[5]](#footnote-6) and the 6-311G\*\* basis set.[[6]](#footnote-7),[[7]](#footnote-8) The geometrical structural features from the DFT calculations are reported here while the total energy value from the DFT calculation is adjusted by including the zero-point energy abstracted from the HF calculation modified by the factor 0.91.

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| --- | --- | --- |
| **Bond distance** | **3** | **IIIA** |
| **Zn-C** | 1.967 | 1.969 |
| **Zn-ClA** | 2.3452, 2.3265 | 2.412, 2.432 |
| **Zn-ClB** | 2.509 | 2.738 |
| **Mg-ClA** | 2.4780, 2.512 | 2.511, 2.496 |
| **Mg-ClB** | 2.5632, 2.5761 | 2.570, 2.563 |
| **Mg-O** | 2.0589, 2.0559 | 2.119, 2.117 |

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**Table S1:** Comparison of the calculated bond distances (Å) for computed minimum energy theoretical structure of **III** (**IIIA)** with those from the X-ray crystallographic data of **38**

**Reactants – ZnCl2**

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**Reactants – EtMgCl**

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**Reaction of ZnCl2 with EtMgCl**

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**Reaction of ZnCl2 with EtMgCl in the presence of THF**

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**Dimerisations in the absence of THF**

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**Dimerisations in the presence of THF**

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