

Cite this: *Chem. Sci.*, 2020, **11**, 3516

All publication charges for this article have been paid for by the Royal Society of Chemistry

Sterically controlled reductive oligomerisations of CO by activated magnesium(I) compounds: deltate vs. ethenediolate formation†

K. Yuvaraj,^a Iskander Douair,^b Dafydd D. L. Jones,^a Laurent Maron^{*a} and Cameron Jones^{†a}

An extremely bulky, symmetrical three-coordinate magnesium(I) complex, $[(\text{TCHP}\text{Nacnac})\text{Mg}]_2$ ($\text{TCHP}\text{Nacnac} = [(\text{TCHP})\text{NCMe}]_2\text{CH}]^-$, $\text{TCHP} = 2,4,6\text{-tricyclohexylphenyl}$) has been prepared and shown to have an extremely long Mg–Mg bond (3.021(1) Å) for such a complex. It was shown not to react with either DMAP (4-dimethylaminopyridine) or CO. Three unsymmetrical 1 : 1 DMAP adducts of less bulky Mg–Mg bonded species have been prepared, viz. $[(\text{Ar}\text{Nacnac})\text{Mg}\text{--}\text{Mg}(\text{DMAP})(\text{Ar}\text{Nacnac})]$ ($\text{Ar}\text{Nacnac} = [(\text{Ar}\text{NCMe})_2\text{CH}]^-$, Ar = 2,6-xylyl (Xyl), mesityl (Mes) or 2,6-diethylphenyl (Dep)), and their reactivity toward CO explored. Like the previously reported bulkier complex, $[(\text{Dip}\text{Nacnac})\text{Mg}\text{--}\text{Mg}(\text{DMAP})(\text{Dip}\text{Nacnac})]$ (Dip = 2,6-diisopropylphenyl), $[(\text{Dep}\text{Nacnac})\text{Mg}\text{--}\text{Mg}(\text{DMAP})(\text{Dep}\text{Nacnac})]$ reductively trimerises CO to give a rare example of a deltate complex, $[(\text{Dep}\text{Nacnac})\text{Mg}(\mu\text{-C}_3\text{O}_3)\text{Mg}(\text{DMAP})(\text{Dep}\text{Nacnac})]_2$. In contrast, the two smaller adduct complexes react with only two CO molecules, ultimately giving unusual ethenediolate complexes $[(\text{Ar}\text{Nacnac})\text{Mg}(\mu\text{-OC(H)=C(DMAP-H)O})\text{Mg}(\text{Ar}\text{Nacnac})]_2$ (Ar = Xyl or Mes). DFT calculations show the latter reactions to proceed via reductive dimerizations of CO, and subsequent intramolecular C–H activation of Mg-ligated DMAP by “zig-zag” $[\text{C}_2\text{O}_2]^{2-}$ fragments of reaction intermediates. Calculations also suggest that magnesium deltate complexes are kinetic products in these reactions, while the magnesium ethenediolates are thermodynamic products. This study shows that subtle changes to the bulk of the reacting 1 : 1 DMAP–magnesium(I) adduct complexes can lead to fine steric control over the products arising from their CO reductive oligomerisations. Furthermore, it is found that the more activated nature of the adduct complexes, relative to their symmetrical, three-coordinate counterparts, $[(\text{Ar}\text{Nacnac})\text{Mg}]_2$, likely derives more from the polarisation of the Mg–Mg bonds of the former, than the elongated nature of those bonds.

Received 12th February 2020
Accepted 3rd March 2020

DOI: 10.1039/d0sc00836b

rsc.li/chemical-science

Introduction

Carbon monoxide is a readily available C_1 feedstock gas, that is used in many industrial processes for the production of hundreds of millions of tonnes of commodity chemicals each year. One of the most important of these processes is Fischer–Tropsch (F–T), which typically utilises heterogeneous transition metal catalysts to transform synthesis gas (CO/H_2) into liquid hydrocarbons and oxygenates on a massive scale.¹ Considering the importance of F–T, a great deal of effort has focussed on

investigating the mechanisms by which it operates. These investigations have increasingly involved the use of low-valent organometallic complexes as soluble models to shed light on the fundamental steps, e.g. C–C bond formations, that are central to the process.² Such studies have the potential to enhance the selectivity and energy efficiency of F–T, and to aid the development of new homogeneous catalysts of commercial importance.

In the realm of homogeneous organometallic models for the F–T process, considerable recent interest has been directed towards the activation and reductive homologation of CO, a normally inert gas which possesses one of the strongest bonds known ($\text{BDE} = 257 \text{ kcal mol}^{-1}$ (ref. 3)). For example, this work has led to the discovery that low-valent metal and non-metal compounds, from across the periodic table, can reductively oligomerise CO to ethynediolate, $[\text{OC}\equiv\text{CO}]^{2-}$, aromatic oxo-carbon dianions, $[\text{C}_n\text{O}_n]^{2-}$ ($n = 2\text{--}6$), and related species, under mild conditions.^{4–6} From a historical perspective, it should be noted that alkali metals have been known to reductively

^aSchool of Chemistry, Monash University, PO Box 23, VIC, 3800, Australia. E-mail: cameron.jones@monash.edu; Web: <http://www.monash.edu/science/research-groups/chemistry/jonesgroup>

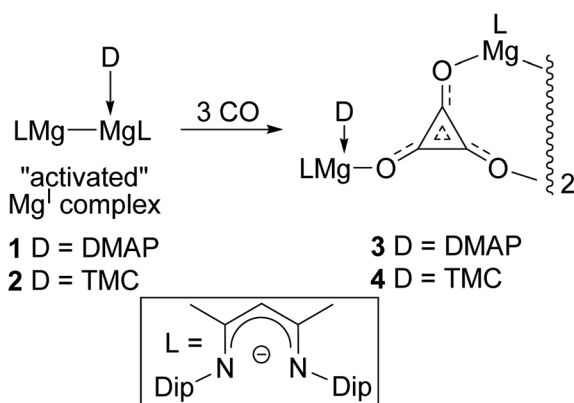
^bUniversité de Toulouse et CNRS, INSA, UPS, UMR 5215, LPCNO, 135 Avenue de Rangueil, F-31077 Toulouse, France. E-mail: laurent.maron@irsamc.ups-tlse.fr

† Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for all new compounds. Full details of computational studies. Crystal data, details of data collections and refinements. CCDC 1983483–1983492 For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc00836b

The solid-state molecular structures of the adducts (see Fig. 1b for the molecular structure of **8**) are also reminiscent of those for **1** and **2**, and show both to possess one trigonal planar, and one distorted tetrahedral, magnesium centre. Interestingly, their Mg–Mg bond lengths (**6**: 2.8925(9) Å; **8**: 2.9336(7) Å), while longer than those typically seen for symmetrical, three-coordinate magnesium(II) compounds (e.g. 2.875(1) Å for $\{[(^{\text{Dep}}\text{Nacnac})\text{Mg}]_2\}^{10}$), are not as long as the metal–metal interaction in **1** (*viz.* 3.0886(6) Å). Indeed, the Mg–Mg distances in this trio of compounds are loosely proportional to the size of their β -diketiminate ligands, and cover a range of more than 0.2 Å. This

Results and discussion

At the outset, a magnesium(I) adduct complex bearing substantially bulkier β -diketiminato ligands than the ^{DiP}Nacnac substituents in **1** and **2**, was targeted. The reasoning here stemmed from recent work by Harder and co-workers, who showed that the extremely bulky magnesium(I) compound,



Scheme 1 Previously reported syntheses of magnesium deltate complexes, **3** and **4** (Dip = 2,6-diisopropylphenyl, DMAP = 4-dimethylaminopyridine, TMC = :C((MeNCMe)₂)).⁸

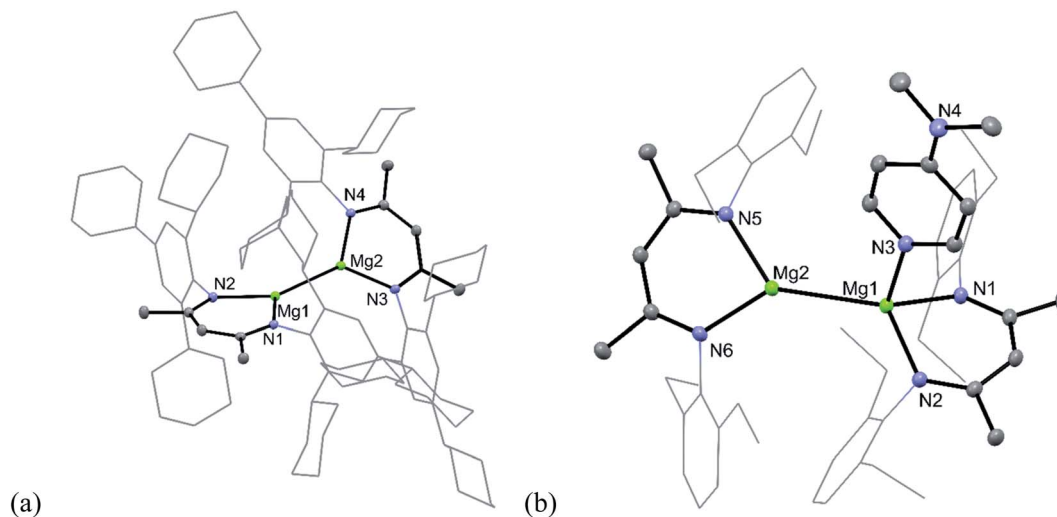


Fig. 1 Molecular structures of (a) **5** and (b) **8** (25% thermal ellipsoids are shown; hydrogen atoms omitted; aryl substituents shown as wireframe for clarity). Selected bond lengths (Å) and angles (°) for **5**: Mg(1)–Mg(2) 3.0208(9), N(1)–Mg(1)–N(2) 91.00(7), N(4)–Mg(2)–N(3) 90.86(7). Selected bond lengths (Å) and angles (°) for **8**: Mg(1)–N(1) 2.1037(14), Mg(1)–N(2) 2.1084(13), Mg(1)–N(3) 2.1790(14), Mg(1)–Mg(2) 2.9336(7), Mg(2)–N(6) 2.0894(13), Mg(2)–N(5) 2.1004(13), N(1)–Mg(1)–N(2) 89.18(5), N(1)–Mg(1)–N(3) 96.38(5), N(2)–Mg(1)–N(3) 101.97(5), N(6)–Mg(2)–N(5) 89.20(5).

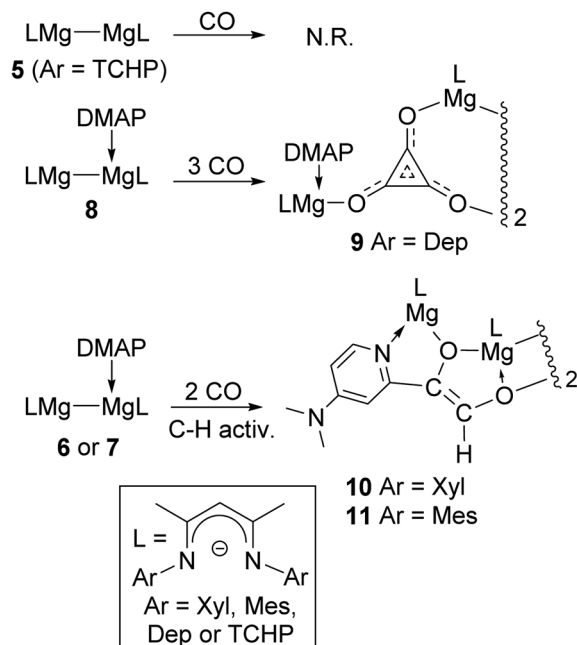
observation is fully consistent with the previously computed shallow potential energy surface for the elongation of Mg–Mg bonds in compounds such as $[(^{\text{Ar}}\text{Nacnac})\text{Mg}]_2$.^{13a}

With **6** and **8** in hand, toluene solutions of the compounds, and of *in situ* generated **7**, were stirred under atmospheres of CO, in order to investigate if their steric differences had an influence on the outcomes of these reactions. This seemed to be the case, as the most hindered adduct, **8**, behaved similarly to **1**, in that it reductively trimerised CO to give a low isolated yield of the magnesium deltate complex, **9**, as a colourless crystalline

solid (Scheme 2). In contrast, the two smaller adduct complexes, **6** and **7**, only consumed two equivalents of CO to give moderate isolated yields of the unusual, thermally stable ethenediolate complexes, **10** and **11**. These are presumably formed *via* an initial reductive dimerisation of CO, followed by activation of one of the *ortho*-C–H bonds of the coordinating DMAP molecule by the generated $[\text{C}_2\text{O}_2]^{2-}$ fragment (see below). It is noteworthy that, when the progress of all of these reactions was monitored by ^1H NMR spectroscopy, no intermediates in the formations of the CO coupled products were observed, and there was no evidence for mixtures of deltate or ethenediolate products in any case. Furthermore, treating the adduct complexes, **6**–**8**, with 1 : 1 mixtures of CO/ H_2 did not lead to involvement of dihydrogen in the reactions, which instead returned **9**–**11** in yields similar to those in its absence.¹⁴

Once crystallised, **9**–**11** are poorly soluble in most commonly used organic solvents. With that said, compounds **9** and **11** had sufficient solubility in d_8 -THF for their ^1H and ^{13}C NMR spectra to be recorded. The spectra for deltate complex, **9**, are consistent with its proposed formulation, and comparable to the spectra for **3**,⁸ in that they display two sets of signals for chemically inequivalent β -diketiminate ligands, and one set of DMAP resonances. The NMR spectra for **11** also exhibit two sets of β -diketiminate signals, while its ^1H NMR spectrum shows three chemically inequivalent aromatic proton signals for the DMAP ligand, and a singlet resonance at δ 6.27 ppm for the ethenediolate proton.

The molecular structures of **9** and **11** are depicted in Fig. 2, while that for **10** can be found in the ESI.† As compound **9** is essentially isostructural to **3**,⁸ little comment will be passed on it here, except to point out that its deltate dianions are close to planar, with nearly equivalent C–C and C–O bond lengths, that lie between those for localised single and double bonds.¹⁵ It is apparent, therefore, that there is a significant degree of



Scheme 2 Syntheses of compounds **9**–**11**.

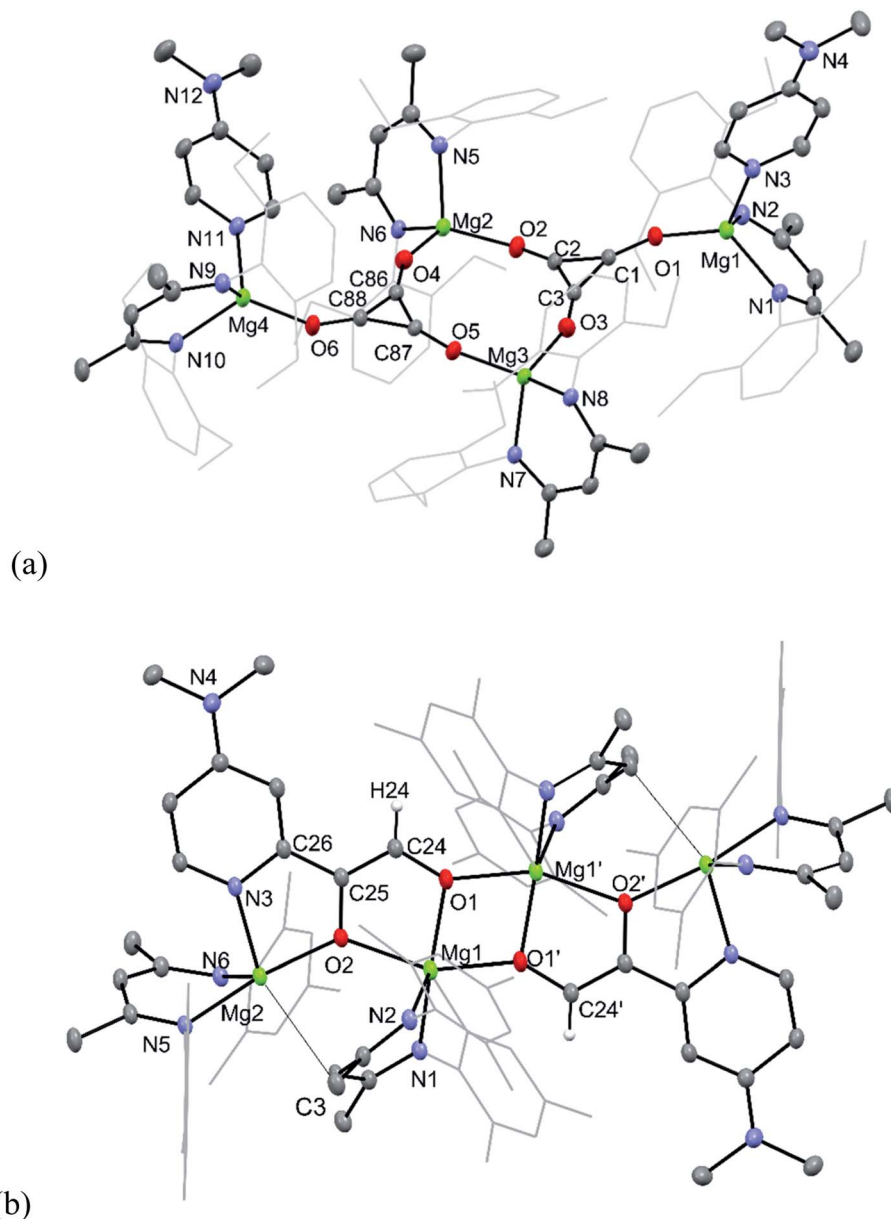


Fig. 2 Molecular structures of (a) **9** and (b) **11** (25% thermal ellipsoids are shown; hydrogen atoms, except alkenic protons omitted; aryl substituents shown as wireframe for clarity). Selected bond lengths (Å) and angles (°) for **9**: Mg(1)–O(1) 1.882(3), O(1)–C(1) 1.279(4), C(1)–C(3) 1.391(6), C(1)–C(2) 1.396(5), Mg(2)–O(4) 1.899(3), Mg(2)–O(2) 1.904(3), O(2)–C(2) 1.273(5), C(2)–C(3) 1.399(6), Mg(3)–O(3) 1.898(3), Mg(3)–O(5) 1.907(3), O(3)–C(3) 1.278(5), Mg(4)–O(6) 1.877(3), O(4)–C(86) 1.276(5), O(5)–C(87) 1.274(4), O(6)–C(88) 1.276(5), C(86)–C(88) 1.393(6), C(86)–C(87) 1.398(6), C(87)–C(88) 1.385(5), C(1)–O(1)–Mg(1) 157.5(3), O(4)–Mg(2)–O(2) 116.28(14), O(3)–Mg(3)–O(5) 113.76(14), C(86)–O(4)–Mg(2) 156.0(3). Selected bond lengths (Å) and angles (°) for **11**: Mg(1)–O(1) 2.0035(14), Mg(1)–O(1') 2.0238(16), Mg(1)–O(2) 2.0963(15), Mg(2)–O(2) 1.9822(14), Mg(2)–N(3) 2.1512(18), Mg(2)–C(3) 2.838(2), O(1)–C(24) 1.334(2), O(2)–C(25) 1.365(2), N(3)–C(26) 1.359(2), C(24)–C(25) 1.352(3), C(25)–C(26) 1.453(3), O(1)–Mg(1)–O(1') 75.14(7), O(1')–Mg(1)–O(2) 152.99(7), O(1)–Mg(1)–O(2) 80.11(6), O(2)–Mg(2)–N(3) 79.49(6).

electronic delocalisation over the compound's aromatic deltate dianions.¹⁶ In contrast, the only other previously structurally characterised deltate complex of a non s-block metal, [$\{U(COT^+)(Cp^*)\}_2(\mu-C_3O_3)$] ($COT^+ = [C_8H_6Pr_2-1,4]^-$; $Cp^* = [C_5Me_5]^-$), exhibits differing C–C and C–O interactions, and partial electronic delocalisation over the dianion.^{6a}

Compound **11** is isostructural to **10**, and its molecular structure reveals it to be a centrosymmetric dimer. The ethenediolate units possess localised C(24)–C(25) bonds, which are

substituted in *cis*-positions by a proton and C(26) of the C–H activated DMAP unit. One magnesium centre Mg(1) of each monomeric unit is chelated by both O-centres of the ethenediolate, while Mg(2) is *N,O*-chelated by that dianion. Oxygen atoms O(1) coordinate Mg atoms on the opposing monomeric units, giving rise to a central four-membered Mg_2O_2 ring. The bond lengths within the N_2C_3 backbone of each chelating β -diketiminato suggest electronic delocalisation over those ligands. Magnesium atoms Mg(1) have distorted trigonal



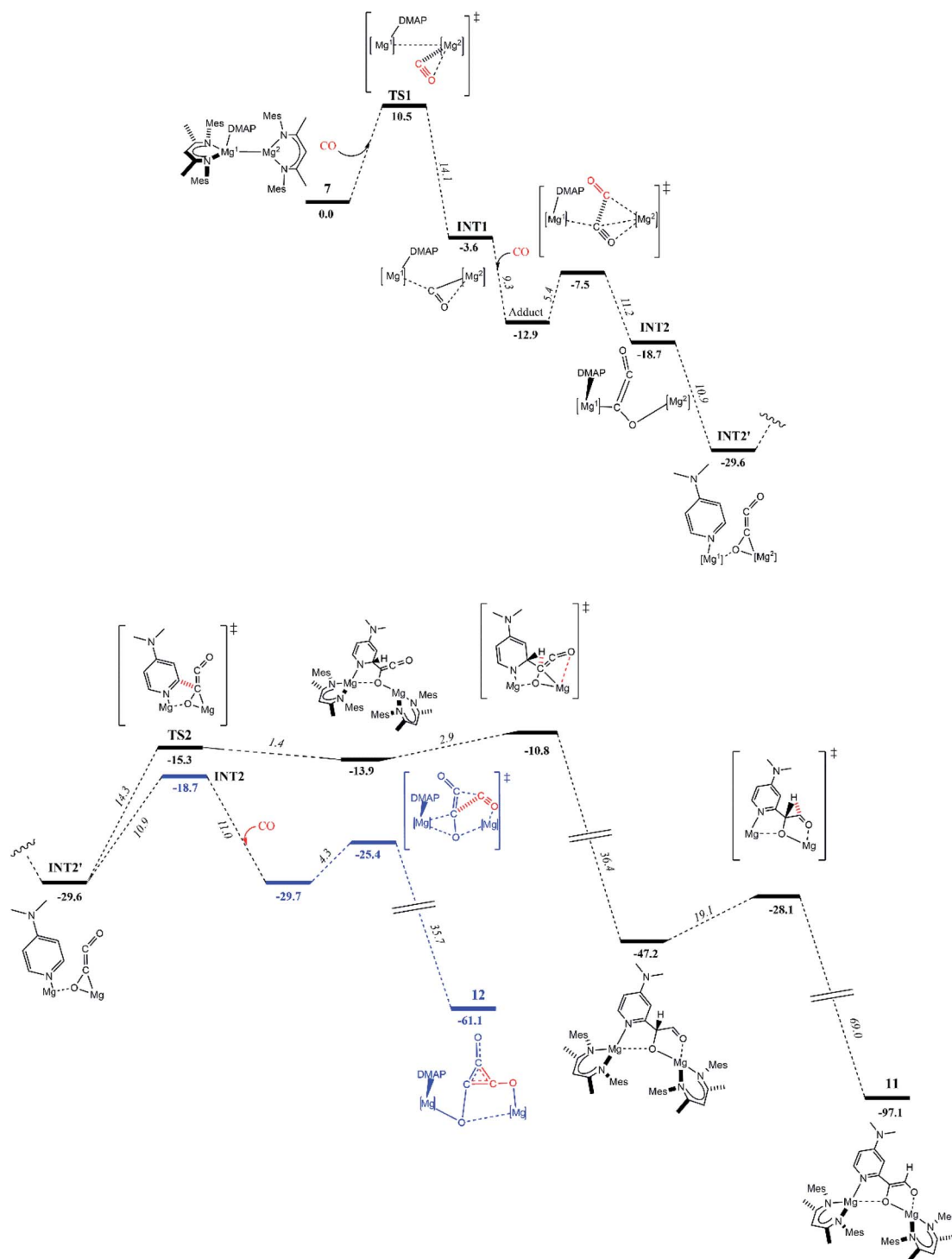


Fig. 3 Computed (B3PW91) enthalpy profile at 298 K for the formation of ethenediolate complex **11**, or deltate complex **12**, from magnesium(i)-adduct complex **7**, and two or three molecules of CO, respectively.

bipyramidal geometries, which is also the case for $\text{Mg}(2)$, when the long interaction between that atom and C(3) of one of the β -diketiminate ligands ($2.838(2)$ Å, cf. Σ van der Waals radii for $\text{Mg}/\text{C} = 3.43$ Å (ref. 17)) is taken into account.

It seems likely that the mechanism of formation of **9** is similar to that previously calculated for the closely related NHC

coordinated deltate complex, **4**.⁸ In that case, there were two sequential insertions of CO into the $\text{Mg}-\text{Mg}$ bond of the magnesium(i) starting material, yielding an intermediate with a *trans*-bent (“zig-zag”) $[\text{C}_2\text{O}_2]^{2-}$ dianion, bridging two $[(\text{Dip}^-\text{Nacnac})(\text{DMAP})_0 \text{ or } 1 \text{Mg}]^+$ fragments. This reacts with a third CO molecule, ultimately leading to deltate complex **4**. Interestingly,



a very similar mechanism, *via* a “zig-zag” intermediate, was computed by Cloke and co-workers for the formation of $[\{U(COT^+)(Cp^*)\}_2(\mu-C_3O_3)]$.^{6f,18} They also showed that controlling the stoichiometry of the reaction between $[U(COT^+)(Cp^*)(THF)]$ and CO led to the linear ethynediolate system, $[\{U(COT^+)(Cp^*)\}_2(\mu-OC\equiv CO)]$, which did not react with CO to give $[\{U(COT^+)(Cp^*)\}_2(\mu-C_3O_3)]$.^{6f} This result gave credence to the importance of the “zig-zag” intermediate in the formation of the latter complex. That is not to say that uranium ethynediolate complexes are unreactive, as Arnold and co-workers showed when they heated solutions of $[\{[(Me_3Si)_2N]_2U\}_2(\mu-OC\equiv CO)]$. This led to an intramolecular C–H activation of one of its methyl substituents, yielding an ethenediolate species, related to **10** and **11**.^{6g} This raised the question as to whether the mechanism of formation of **10** and **11** proceeds *via* reactive ethynediolate intermediates, $[\{({}^ArNacnac)Mg\}_2(\mu-OC\equiv CO)]$, or by another process.

To explore these possibilities, DFT calculations (B3PW91) were carried out to determine the reaction profile that led to **11** (Fig. 3). The initial stages of the reaction were found to be similar to that calculated for the formation of **4**.⁸ That is, the first step involves nucleophilic attack of the three-coordinate Mg^2 centre of polarized **7** (Natural Bond Orbitals, NBO, charges: Mg^1 0.45; Mg^2 0.19) at one of the π^* -orbitals of CO (see ESI† for further details), giving adduct **TS1** (10.5 kcal mol^{−1}). The coordinated CO then inserts into the Mg–Mg bond affording stable intermediate **INT1** (−3.6 kcal mol^{−1}). From **INT1**, a second CO insertion leads to a “zig-zag” intermediate **INT2** (−18.7 kcal mol^{−1}) *via* a low kinetic barrier (5.4 kcal mol^{−1}). It is of note that an alternative pathway was explored, whereby the DMAP C–H activation process occurred from **INT1**, but this was found not to be kinetically viable (barrier = 21.4 kcal mol^{−1}). Instead, the favoured intermediate **INT2** readily isomerised to the more stable (by 10.9 kcal mol^{−1}) “zig-zag” intermediate **INT2'**. Interestingly, this isomer appears more amenable to DMAP C–H activation, as one DMAP *ortho*-proton is pointing in the direction of the $[C_2O_2]^{2-}$ moiety. From **INT2'**, two kinetically reasonable pathways were examined. Firstly, isomerization back to **INT2** and reaction with a third molecule of CO led to the deltate complex **12** (−61.1 kcal mol^{−1}) *via* a pathway similar to that calculated for the formation of **4** (blue pathway). Secondly, **INT2'** undergoes an intramolecular DMAP C–H activation *via* a number of kinetically accessible steps, ultimately giving the experimentally observed product, **11** (black pathway). While compound **11** is significantly more stable (by 31.4 kcal mol^{−1}) than the alternative deltate product, **12**, the overall kinetic barrier to its formation is higher.

Taken as a whole, the experimental and computational studies indicate that **11** is the thermodynamic product of the reaction of **7** with excess CO, while deltate complex **12**, is the kinetic product. Despite this, in the experimental situation, compound **11** is formed in preference to the deltate complex, **12**, even when the reaction that afforded it is carried out at low temperature. Moreover, it is clear that **11** is not formed *via* an ethynediolate intermediate, $[\{({}^{Mes}Nacnac)Mg\}_2(\mu-OC\equiv CO)]$ (which was never experimentally observed), in contrast to Arnold's aforementioned report on intramolecular C–H

activation of a uranium ethynediolate complex.^{6g} It can additionally be speculated from the results of these and prior calculations, that ethenediolate complexes, **10** and **11**, result when less hindered activated magnesium(i) adduct complexes, **6** and **7**, are treated with CO, because an *ortho*-C–H bond of the ligating DMAP molecule can approach the $[C_2O_2]^{2-}$ fragment in the “zig-zag” transition state **TS2**, more readily than in reactions of **1** and **8** with CO. If so, in those latter cases, the kinetic barrier to ethenediolate formation should be raised sufficiently to favour formation of the experimentally observed deltate complexes, **3** and **9**. In the case of the extremely bulky magnesium(i) compound **5**, no DMAP adduct can be formed, but its Mg–Mg bond is very long, yet it does not react with CO under ambient conditions. This suggests that the enhanced reactivity of 1 : 1 adduct complexes **1** and **2**, and **6–8**, towards CO arises more from the polarised nature of their Mg–Mg bonds, than the elongation of those bonds.

Conclusions

In summary, an extremely bulky, symmetrical three-coordinate magnesium(i) complex has been prepared and shown to have a very long Mg–Mg bond for a such a species. This does not react with either DMAP or CO. Three 1 : 1 DMAP adducts of less bulky Mg–Mg bonded species have been prepared (one *in situ*), and their enhanced reactivity toward CO explored. It was found that when the compounds incorporate bulkier β -diketiminato ligands, they reductively trimerise CO to give magnesium deltate complexes. When substituted with smaller β -diketiminates, the magnesium(i) adducts react with only two CO molecules, ultimately giving unusual ethenediolate complexes. DFT calculations show that these reactions proceed *via* reductive dimerization of CO, and subsequent intramolecular C–H activation of Mg-ligated DMAP by “zig-zag” $[C_2O_2]^{2-}$ fragments of reaction intermediates. It is apparent that magnesium deltate complexes are kinetic products in these reactions, while magnesium ethenediolates are thermodynamic products. As a result, subtle changes to the bulk of the 1 : 1 DMAP–magnesium(i) adducts can lead to fine steric control over the products arising from their CO reductive oligomerisations. We continue to investigate the reactivity of activated magnesium(i) compounds towards CO and other small molecules, and how selectivity in the products of those reactions can be achieved.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

CJ and LM thank the Australian Research Council for funding. CJ acknowledges support from the US Air Force Asian Office of Aerospace Research and Development (grant FA2386-18-1-0125). KY acknowledges the Science and Engineering Research Board of India for a postdoctoral fellowship (SB/OS/PDF-098/2016-17). Part of this research was undertaken on the MX2 beamline at the Australian Synchrotron, part of ANSTO.



LM is a senior member of the Institut Universitaire de France. CalMip is also acknowledged for a generous grant of computing time.

References

- See for example: (a) *Advances in Fischer–Tropsch Synthesis Catalysts and Catalysis*, ed. B. H. Davis and M. L. Occelli, CRC, Boca Raton, FL, 2009; (b) A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692; (c) C. K. Rofer-DePoorter, *Chem. Rev.*, 1981, **81**, 447; (d) C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61.
- See for example: (a) L. D. Durfee and I. P. Rothwell, *Chem. Rev.*, 1988, **88**, 1059; (b) G. Erker, *Acc. Chem. Res.*, 1984, **17**, 103; (c) J. A. Gladysz, *Adv. Organomet. Chem.*, 1982, **20**, 1; (d) P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, 1980, **13**, 121.
- R. Kalescky, E. Kraka and D. Cremer, *J. Phys. Chem. A*, 2013, **117**, 8981.
- For examples of p-block element reductive oligomerizations of CO see: (a) H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan and A. Vargas, *Nat. Chem.*, 2013, **5**, 1025; (b) J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer and J. Mies, *Angew. Chem., Int. Ed.*, 2015, **54**, 13801; (c) B. Wang, G. Luo, M. Nishiura, Y. Luo and Z. Hou, *J. Am. Chem. Soc.*, 2017, **139**, 16967; (d) R. Y. Kong and M. R. Crimmin, *J. Am. Chem. Soc.*, 2018, **140**, 13614; (e) A. V. Protchenko, P. Vasko, D. C. H. Do, J. Hicks, M. A. Fuentes, C. Jones and S. Aldridge, *Angew. Chem., Int. Ed.*, 2019, **58**, 1808; (f) Y. Wang, A. Kostenko, T. J. Hadlington, M.-P. Luecke, S. Yao and M. Driess, *J. Am. Chem. Soc.*, 2019, **141**, 626; (g) A. Heilmann, J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Angew. Chem., Int. Ed.*, 2020, DOI: 10.1002/anie.201916073.
- For examples of d-block reductive oligomerizations of CO see: (a) P. A. Bianconi, I. D. Williams, M. P. Engeler and S. J. Lippard, *J. Am. Chem. Soc.*, 1986, **108**, 311; (b) P. A. Bianconi, R. N. Vrtis, Ch. Pulla Rao, I. D. Williams, M. P. Engeler and S. J. Lippard, *Organometallics*, 1987, **6**, 1968; (c) J. D. Protasiewicz and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 6564; (d) T. Watanabe, Y. Ishida, T. Matsuo and H. Kawaguchi, *J. Am. Chem. Soc.*, 2009, **131**, 3474; (e) H. R. Sharpe, A. M. Geer, L. J. Taylor, B. M. Gridley, T. J. Blundell, A. J. Blake, E. S. Davies, W. Lewis, J. McMaster, D. Robinson and D. L. Kays, *Nat. Commun.*, 2018, **9**, 3757.
- For examples of f-block reductive oligomerizations of CO see: (a) O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *Science*, 2006, **311**, 829; (b) B. Wayland and X. Fu, *Science*, 2006, **311**, 790; (c) W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang and J. L. Atwood, *J. Am. Chem. Soc.*, 1985, **107**, 3728; (d) O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *J. Am. Chem. Soc.*, 2006, **128**, 9602; (e) W. J. Evans, D. S. Lee, J. W. Ziller and N. Kaltsoyannis, *J. Am. Chem. Soc.*, 2006, **128**, 14176; (f) A. S. Frey, F. G. N. Cloke, P. B. Hitchcock, I. J. Day, J. C. Green and G. Aitkin, *J. Am. Chem. Soc.*, 2008, **130**, 13816; (g) P. L. Arnold, Z. R. Turner, R. M. Bellabarba and R. P. Tooze, *Chem. Sci.*, 2011, **2**, 77; (h) S. M. Mansell, N. Kaltsoyannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2011, **133**, 9036; (i) B. M. Gardner, J. C. Stewart, A. L. Davis, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, **109**, 9265; (j) N. Tsoureas, O. T. Summerscales, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2013, **32**, 1353; (k) I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242; (l) A. J. Ryan, J. W. Ziller and W. J. Evans, *Chem. Sci.*, 2020, **11**, 2006.
- For examples of s-block reductive oligomerizations of CO see: (a) L. Gmelin, *Ann. Phys.*, 1825, **4**, 31; (b) J. Liebig, *Ann. Pharm.*, 1834, **11**, 182; (c) W. Büchner, *Helv. Chim. Acta*, 1963, **46**, 2111; (d) P. W. Lednor and P. C. Versloot, *J. Chem. Soc., Chem. Commun.*, 1983, 284.
- K. Yuvaraj, I. Douair, A. Paparo, L. Maron and C. Jones, *J. Am. Chem. Soc.*, 2019, **141**, 8764.
- (a) C. Jones, *Nat. Rev. Chem.*, 2017, **1**, 0059; (b) A. Stasch and C. Jones, *Dalton Trans.*, 2011, **40**, 5659.
- R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch and C. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 8944.
- T. X. Gentner, B. Rosch, G. Ballmann, J. Langer, H. Elsen and S. Harder, *Angew. Chem., Int. Ed.*, 2019, **58**, 607.
- For synthetic routes to magnesium(I) compounds, see: (a) J. Hicks, M. Juckel, A. Paparo, D. Dange and C. Jones, *Organometallics*, 2018, **37**, 4810; (b) R. Peloso, I. Resa, A. Rodríguez, E. Carmona, K. Freitag, C. Jones, A. Stasch, A. J. Boutland and F. Lips, *Inorg. Synth.*, 2018, **37**, 33.
- Related 2 : 1 complexes, $[(\text{ArNacnac})(\text{DMAP})\text{Mg}]_2$ (Ar = Xyl or Dep), were also prepared and fully characterised. See ESI† for full details. For related 2 : 1 adducts, see (a) S. P. Green, C. Jones and A. Stasch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9079; (b) A. J. Boutland, D. Dange, A. Stasch, L. Maron and C. Jones, *Angew. Chem., Int. Ed.*, 2016, **55**, 9239.
- β -Diketiminato group 2 metal hydride complexes are known to couple CO to give ethenediolate and cyclopropanetriolate complexes. See, for example, ref. 10 and M. D. Anker, C. E. Kefalidis, Y. Yang, J. Fang, M. S. Hill, M. F. Mahon and L. Maron, *J. Am. Chem. Soc.*, 2017, **139**, 10036.
- As determined from a survey of the Cambridge Crystallographic Database, February, 2020.
- L. Franel, L. Radom and M. A. Vincent, *J. Mol. Struct.*, 1981, **76**, 1.
- M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. J. Truhlar, *J. Phys. Chem. A*, 2009, **113**, 5806.
- D. McKay, A. S. P. Frey, J. C. Green, F. G. N. Cloke and L. Maron, *Chem. Commun.*, 2012, **48**, 4118.

