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

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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 $[(\text{Ar}\text{Nacnac})\text{Mg}(\mu\text{-OC(H)=C}(\text{DMAP}^-\text{H})\text{O})\text{Mg}(\text{Ar}\text{Nacnac})]_2$ (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.

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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

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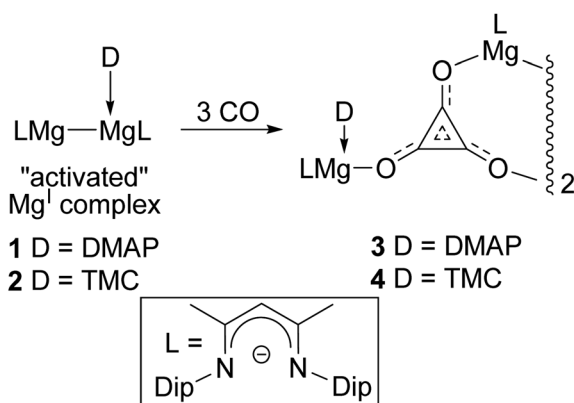
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The solid-state molecular structures of the adducts (see Fig. 1b for the molecular structure of **8**) are also reminiscent of those for **1** and **2**, and show both to possess one trigonal planar, and one distorted tetrahedral, magnesium centre. 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).

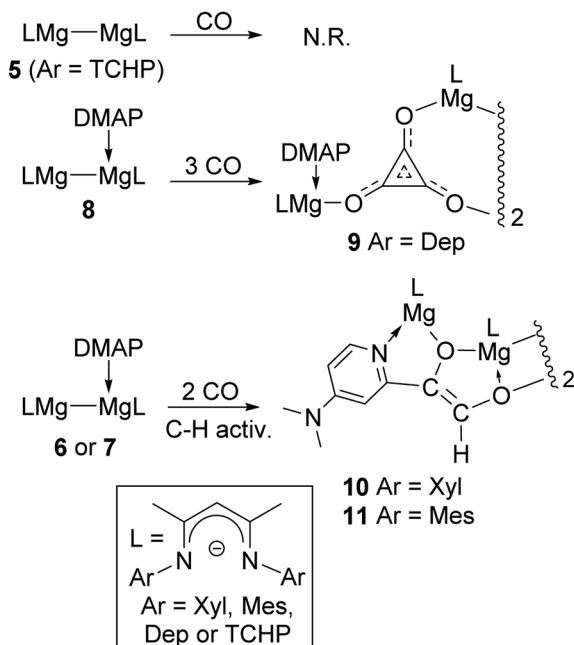
observation is fully consistent with the previously computed shallow potential energy surface for the elongation of Mg–Mg bonds in compounds such as $[(^{\text{Ar}}\text{Nacnac})\text{Mg}]_2$.^{13a}

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**.

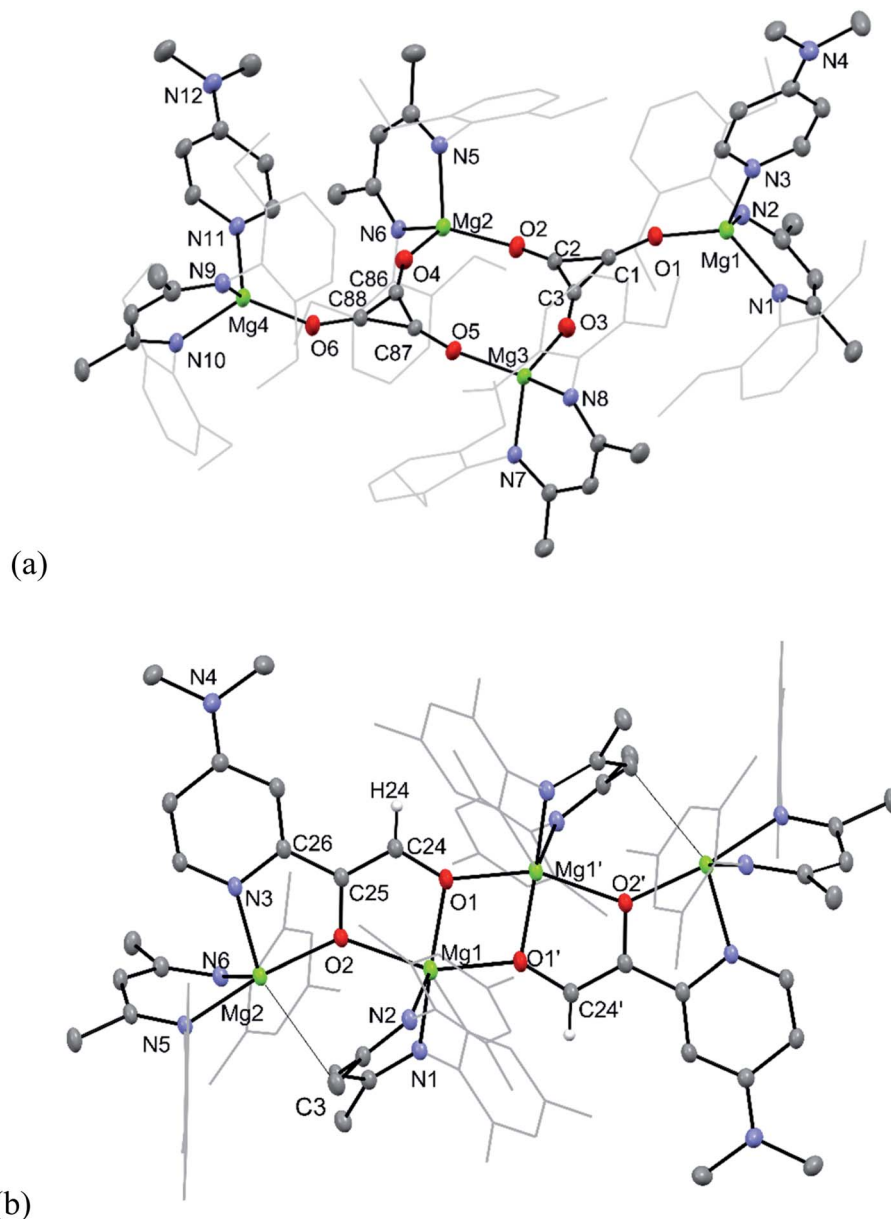


Fig. 2 Molecular structures of (a) **9** and (b) **11** (25% thermal ellipsoids are shown; hydrogen atoms, except alkenic protons omitted; aryl substituents shown as wireframe for clarity). Selected bond lengths (Å) and angles (°) for **9**: Mg(1)–O(1) 1.882(3), O(1)–C(1) 1.279(4), C(1)–C(3) 1.391(6), 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 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 Mg/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 Mg–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,



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, $[(^{\text{Mes}}\text{Nacnac})\text{Mg}]_2(\mu\text{-OC}\equiv\text{CO})$ (which was never experimentally observed), in contrast to Arnold's aforementioned report on intramolecular C-H

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