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Complexes: Formation of Magnesium Enediolates**

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Reductive Coupling of CO with Magnesium Anthracene Complexes: Formation of Magnesium Enediolates

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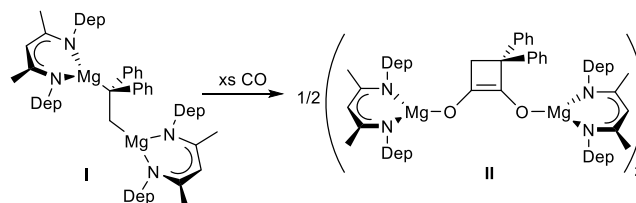
Two β -diketiminato-magnesium anthracene complexes, $[(ArNacnac)Mg]_2(\mu-C_{14}H_{10})$ ($ArNacnac = [HC(MeCNAr)_2]$, $Ar =$ mesityl (Mes) or 2,6-diethylphenyl (Dep)) react with 1 atm. CO at room temperature to give tetra-magnesium enediolate complexes $[(ArNacnac)Mg]_4(O_2C_{16}H_{10})_2$ *via* coupling of two molecules of CO with the anthracenediyl fragment. Similarly, reaction of magnesium anthracene, $[Mg(THF)_3(C_{14}H_{10})]$, with CO afforded a low isolated yield of a tetra-magnesium complex bearing both dianthraceneylenediolate and dibenzocyclohepteneolateyl ligands. The presented reactions represent very rare examples of magnesium alkyl carbonylations that occur under mild conditions, and in the absence of catalysts.

The carbonylation of organic molecules and fragments is central to many important chemical processes, including hydroformylation,¹ Fischer-Tropsch² and the Pauson-Khand reaction.³ Such synthetic transformations typically require stoichiometric or catalytic amounts of mid to late transition metal complexes or materials to proceed, and often involve the facile insertion of CO into M–C bonds at some stage of the process.⁴ While similar carbon monoxide activation reactions are known for early d-block and f-block organometallic compounds, they are not as widespread.⁵ Rarer still are activations of CO with main group organometallic compounds, though limited, sometimes synthetically useful, examples have been reported for both s- and p-block metal alkyls.⁶

In recent years, we and others have become interested in the reductive activation of CO (as a C_1 building block) using dimagnesium(I) compounds or magnesium(II) hydrides, in order to generate value added products through Fischer-Tropsch like processes. To this end, magnesium(I) compounds have been shown to reductively homologate CO to give a range of magnesium complexes of oxocarbon anions, $[C_nO_n]^{2-}$ ($n = 2$ or 3) or $[C_6O_6]^{6-}$,^{7–9} while insertions of CO into Mg–H bonds, followed by C–C bond forming processes, yield ethylenediolate,

$[H(O)C=C(O)H]^{2-}$, or cyclopropanetriolate, $[C_3H_3O_3]^{3-}$, complexes.^{10,11} In related work, Hill and co-workers have demonstrated that insertion of CO into Mg–N bonds ultimately affords magnesium amidate complexes; while Stephan and co-workers showed reaction of $LiNCy_2$ ($Cy =$ cyclohexyl) with syngas (CO/H_2) gives a range of Fischer-Tropsch like products.¹¹

Despite the recent success had with the activation of CO using reactive magnesium compounds, there were no well-defined examples of CO insertion or coupling reactions involving organomagnesium species, save for sporadic reports on multiple product carbonylations of Grignard reagents carried out under high pressures of CO, typically in the presence of catalysts.^{6(a),12,13} This paucity was reversed in 2017 when it was shown that the highly reactive 1,2-dimagnesioethane **I** (formed by the reversible reduction of 1,1-diphenylethylene with a magnesium(I) compound) reacts with excess CO under ambient conditions to give the cyclobutenediolate complex, **II** (Scheme 1).¹⁴ Computational studies suggested that the reaction proceeds *via* an initial insertion of CO into an Mg–C bond of **I**, followed by coupling to a second molecule of CO, and several intramolecular rearrangements to give **II**. We were keen to extend the scope of magnesium alkyl induced CO coupling reactions, and saw strained and very reactive magnesium anthracene complexes as ideal for this purpose. Here we show



that magnesium anthracenes can indeed reductively couple CO to give enediolate complexes under mild conditions.

Scheme 1. Previously reported enediolate formation *via* a magnesium alkyl induced CO coupling reaction (Dep = 2,6-diethylphenyl).

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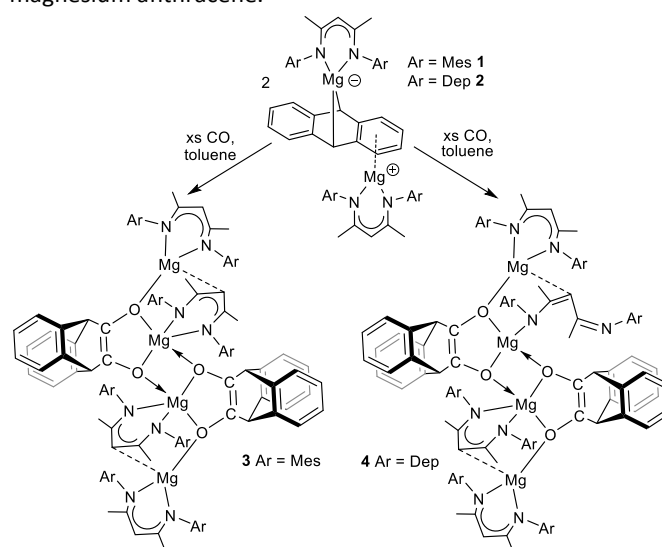
Electronic Supplementary Information (ESI) available: Experimental procedures and characterisation data for all new compounds. Crystal data, details of data collections and refinements. CCDC numbers: 2097136–2097139 See DOI: 10.1039/x0xx00000x

While highly reactive magnesium anthracene, $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$, has been widely exploited, for example as a reducing agent in inorganic and organic synthesis,¹⁵ and as a source of activated magnesium for the reversible Mg/MgH₂ hydrogen storage couple,¹⁶ the very low solubility of the compound in organic solvents (even THF) has limited its applications to some extent. In a prior study we have shown that the dimagnesium(I) compound $[\{(\text{Mes}^{\text{s}}\text{Nacnac})\text{Mg}\}_2]$ ($\text{Mes}^{\text{s}}\text{Nacnac} = [\text{HC}(\text{MeCNMe})_2]$; Mes = mesityl)¹⁷ doubly reduces anthracene to give the closely related contact ion pair complex **1** (Scheme 2).¹⁸ As this has good solubility in coordinating and non-coordinating solvents, we saw it as a viable substitute for $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$ in the current study. Moreover, for the purpose of reactivity comparisons, the 2,6-diethylphenyl (Dep) substituted analogue, **2**, was prepared in good yield as a dark red crystalline solid from reaction of anthracene with $[\{(\text{Dep}^{\text{s}}\text{Nacnac})\text{Mg}\}_2]$.¹⁷ Compound **2** is isostructural to **1** in the solid state, and like that compound, displays fluxional behaviour in solution, consistent with rapid inversion of the saturated anthracenediyl carbon centres, and concomitant migration of both $\text{Mg}(\text{Dep}^{\text{s}}\text{Nacnac})$ fragments between the three anthracene rings at room temperature (see ESI for variable temperature NMR spectra).¹⁸

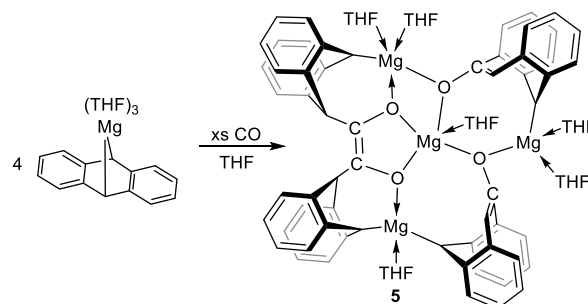
With **1** and **2** in hand, they were dissolved in toluene and the resultant solutions placed under 1 atmosphere of dry CO, then left at ambient temperature overnight. Subsequent work-up of the mixtures led to the isolation of the unusual enediolate magnesium complexes **3** and **4** as colourless crystalline solids in yields of 52 % and 27 % respectively (Scheme 2). Following the reaction that gave the more soluble complex **4** by ¹H NMR spectroscopy, revealed that it is formed in much higher yields (> 70 %) than obtained for the isolated crystalline solid. In the absence of meaningful computational results, it cannot be sure what the mechanisms of formation of **3** and **4** entail, but similar to the situation for **II**, it can be speculated that insertion of CO molecules into the Mg–C sigma bonds of **1** and **2** with concomitant rearrangements and C–C bond couplings lead to the enediolate fragment. It is worthy of mention that a somewhat related, reversible insertion of CO into one Al–C bond of a strained [2.2.1] aluminabicyclic, $[(\text{Dip}^{\text{s}}\text{Nacnac})\text{Al}(\kappa^2\text{-}1,4\text{-C}_6\text{H}_8)]$, has recently been reported by Crimmin and co-workers, but in that case the product was unreactive toward a second molecule of CO.^{6(c)}

For sake of comparison with the reactions that gave **3** and **4**, and despite the very low solubility of $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$, a THF slurry of this compound was placed under 1 atmosphere of CO at room temperature. This yielded an orange precipitate which settled below a pale orange solution. After filtration, a very low yield (< 5 %) of the orange complex **5** deposited (Scheme 3).¹⁹ Once crystallised, this compound, and the initial orange precipitate from the reaction, showed essentially no solubility in THF. Accordingly, it cannot be sure if **5** is the only product of the reaction, or if all the orange magnesium anthracene reactant was consumed. Notwithstanding this, the novelty of **5** is worth discussing here. It apparently arises from the reaction and assembly of four molecules of $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$ with four CO molecules to give a tetrametallic system. This incorporates

one tetraanionic enediolatediyl ligand, which can be envisaged as arising from initial insertion of CO into Mg–C bonds of two molecules of $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$ to give carbenic intermediates, $\{(\text{C}_{14}\text{H}_{10})\{\text{C}(\text{-})\text{-OMg}\}\}$, which couple to give the enediolatediyl ligand (cf. the formation of **II**). In addition, the complex incorporates two dianionic dibenzocyclohepteneolateyl ligands which seemingly derive from net insertion of CO into a C_{sp2}–C_{sp3} bond of $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$, perhaps *via* initial insertion of CO into an Mg–C bond of the magnesium reactant. We are not aware of any similar ring expansion reactions involving magnesium anthracene.



Scheme 2. Synthesis of enediolate complexes **3** and **4**.



Scheme 3. Synthesis of compound **5**.

We have previously shown that the highly activated 1,2-dimagnesiumethane species **I** can react with CO, H₂ and ethylene under mild conditions and in the absence of catalysts.¹⁴ Similarly, $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$ is known to react with H₂ to give MgH₂ and 9,10-dihydroanthracene;¹⁵ and inserts ethylene into one of its Mg–C bonds.²⁰ In light of these results, we investigated reactions of **1–4** with ethylene or H₂ (separately or as a mixture), in order to explore the possibility of net couplings of two or three of the small molecule substrates, initiated by the magnesium reactant. Although coupling reactions did not eventuate, it is noteworthy that the hydrogenation (1 atm.) of **2** at 80 °C for 14h cleanly led to a mixture of 9,10-dihydroanthracene and $[\{(\text{Dep}^{\text{s}}\text{Nacnac})\text{Mg}(\mu\text{-H})\}_2]$ ^{10(a)} (cf. the hydrogenation of $[\text{Mg}(\text{THF})_3(\text{C}_{14}\text{H}_{10})]$ ¹⁵).

Compounds **3** and **4** are moisture sensitive, but stable at room temperature for months when stored under dinitrogen. Meaningful solution state NMR data could not be obtained for **3**, as it shows negligible solubility in non-coordinating and coordinating deuterated solvents, including d_8 -THF. In contrast, its Dep substituted analogue **4** displays some solubility in d_6 -benzene before it crystallises. Its NMR spectra are less complicated than its unsymmetrical solid-state structure would suggest (see below). That is, although the solid-state structures of **3** and **4** are very similar, the symmetry of **4** is broken by one of its β -diketiminato ligands acting as a partially delocalised imino-eneamide, bridging two Mg centres *via* an amide centre and a close interaction with its γ -carbon. The imine fragment remains uncoordinated, as opposed to the other κ^3 - N,N,C -bridging β -diketiminato in the complex. It is possible that in solution the more symmetrical structure of **4** arises from a rapid change in coordination mode of the unique β -diketiminato ligand from κ^2 - N,C - to κ^3 - N,N,C - at room temperature. The low solubility of **4** in non-coordinating solvents at reduced temperatures prevented a variable temperature NMR spectroscopic analysis of this possibility.

As mentioned above, the solid-state structures of **3** and **4** are similar, so only that of the more symmetric compound **3** is depicted in Figure 1 (see ESI for the molecular structure of **4**). This shows it to be a centrosymmetric dimer, with each monomeric unit comprising a bicyclic enediolate unit coordinated by two (Mes Nacnac)Mg units. The enediolate fragment is very similar to that in the chromium complex [(DIP Nacnac)Cr(THF)(κ^2 - O,O -C₁₆H₁₀O₂)], but that complex was prepared by a chromium(I) reduction of ethanoanthracenedione,²¹ and not the reductive coupling of CO with anthracene. One [Mes Nacnac]⁻ anion of each monomeric unit of **3** acts as a delocalised κ^2 - N,N -ligand, while the γ -carbon of the other has a significant interaction with Mg(2), leading to it acting as what is best described as a less delocalised κ^3 - N,N,C -bis(imino)alkyl. This unusual coordination mode has precedent in a complex derived from the reductive coupling of benzonitrile using $\{[(^{Mes})Nacnac]Mg\}_2$.²²

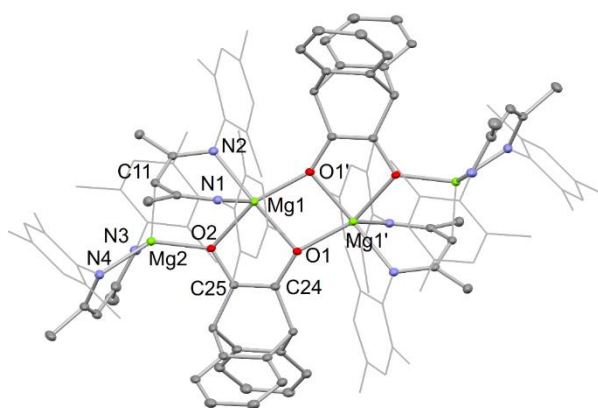


Figure 1. Molecular structure of **3** (20% ellipsoids; mesityl substituents shown as wire frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)-O(1) 2.0018(17), Mg(1)-O(1') 2.0959(17), Mg(1)-O(2) 2.1413(17), Mg(1)-N(1) 2.144(2), Mg(1)-N(2) 2.168(2), Mg(2)-O(2) 1.9187(17), Mg(2)-N(4) 2.058(2), Mg(2)-N(3) 2.067(3), Mg(2)-C(11) 2.359(2), O(1)-C(24) 1.363(3), O(2)-C(25) 1.365(3), C(24)-C(25) 1.319(3), O(1)-Mg(1)-O(2) 81.05(7), O(2)-Mg(2)-C(11) 88.61(8), O(1)-Mg(1)-O(1') 77.77(7).

The molecular structure of tetrametallic **5** is shown in Figure 2. As mentioned above, it incorporates a tetraanionic *cis*-dianthraceneylenediolate ligand which chelates one magnesium centre, while at the same time coordinating in a κ^1 : κ^1 - O,O -fashion to two Mg atoms. The two dianionic dibenzocyclohepteneolateyl ligands are each coordinated to one Mg centre through their sp^3 -hybridised carbon, while their anionic O -centres bridge two magnesiums. As far as we are aware, both anionic ligand types in **5** are without precedent in the literature.

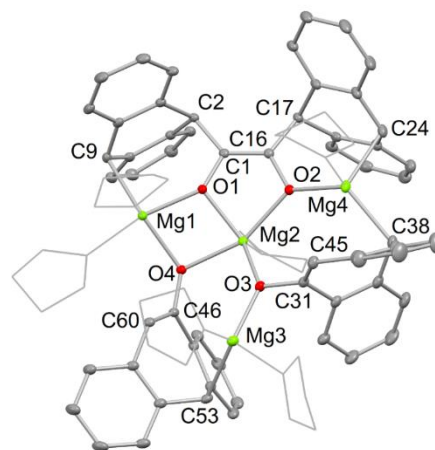


Figure 2. Molecular structure of **5** (20% ellipsoids; THF ligands shown as wire frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)-O(1) 1.9733(13), Mg(1)-C(9) 2.2709(19), O(1)-Mg(2) 1.9849(12), Mg(2)-O(2) 2.0891(13), Mg(3)-O(3) 2.0134(15), Mg(3)-C(53) 2.206(2), Mg(4)-C(38) 2.218(2), Mg(4)-C(24) 2.230(3), C(1)-C(16) 1.350(2), C(31)-C(45) 1.347(3), C(46)-C(60) 1.349(3), O(1)-Mg(1)-C(9) 95.95(6), O(1)-Mg(2)-O(2) 80.31(5), O(3)-Mg(3)-C(53) 126.24(7), C(38)-Mg(4)-C(24) 108.59(9).

In summary, the reaction of three magnesium anthracene complexes with carbon monoxide lead to the coupling of two molecules of CO with the anthracenediyl moiety, to give magnesium enediolate complexes. The net insertion of CO into a C–C bond of the anthracenediyl fragment has also generated magnesium coordinated dibenzocyclohepteneolateyl ligands in one complex. All of these reactions represent very rare examples of magnesium alkyl carbonylations that occur under mild conditions, and in the absence of catalysts. They demonstrate the potential to produce more complex organic molecules from coupling reactions between CO, or other normally inert small molecule substrates, with highly reactive organomagnesium compounds. We continue to explore this possibility in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 See, for example: (a) R. Franke, D. Selent, A. Börner, *Chem. Rev.*, 2012, **112**, 5675-5732; (b) J. Pospech, I. Fleischer, R. Franke, S. Buchholz, M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 2852-2872; (c) F. Hebrard, P. Kalck, *Chem. Rev.*, 2009, **109**, 4272-4282; (d) X. Wu, X. J. Fang, L. P. Wu, R. Jackstell, H. Neumann, M. Beller, *Acc. Chem. Res.*, 2014, **47**, 1041-1053.
- 2 See, for example: (a) *Advances in Fischer–Tropsch Synthesis Catalysts and Catalysis*, 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**, 1692-1744; (c) C. K. Rofer-DePoorter, *Chem. Rev.*, 1981, **81**, 447-474; (d) J. A. Gladysz, *Adv. Organomet. Chem.*, 1982, **20**, 1-38.
- 3 See, for example: (a) K. M. Brummond, J. L. Kent, *Tetrahedron*, 2000, **56**, 3263-3283; (b) S. E. Gibson, A. Stevenazzi, *Angew. Chem. Int. Ed.*, 2003, **42**, 1800-1810.
- 4 J. F. Hartwig, *Organotransition metal chemistry: from bonding to catalysis*, University Science Books, 2010, pp. 349–365.
- 5 See, for example: (a) J. M. Manriquez, D. R. McAlister, R. D. Sanner, J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 2716-2724; (b) T. Y. Meyer, L. R. Garner, N. C. Baenziger, L. Messerle, *Inorg. Chem.*, 1990, **29**, 4045-4050; (c) P. J. Fagan, J. M. Manriquez, T. J. Marks, V. W. Day, S. H. Vollmer, C. S. Day, *J. Am. Chem. Soc.*, 1980, **102**, 5393-5396; (d) J. M. Manriquez, P. J. Fagan, T. J. Marks, C. S. Day, V. W. Day, *J. Am. Chem. Soc.*, 1978, **100**, 7112-7114.
- 6 See, for example: (a) C. Narayana, M. Periasamy, *Synthesis*, 1985, **1985**, 253-268; (b) X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 6912-6913; (c) R. Y. Kong, M. R. Crimmin, *Chem. Commun.*, 2019, **55**, 6181-6184; (d) M. R. Mason, B. Song, K. Kirschbaum, *J. Am. Chem. Soc.*, 2004, **126**, 11812–11813; (e) R. Y. Kong, M. R. Crimmin, *J. Am. Chem. Soc.*, 2018, **140**, 13614-13617.
- 7 (a) K. Yuvaraj, I. Douair, D. D. L. Jones, L. Maron, C. Jones, *Chem. Sci.*, 2020, **11**, 3516-3522; (b) K. Yuvaraj, I. Douair, A. Paparo, L. Maron, C. Jones, *J. Am. Chem. Soc.*, 2019, **141**, 8764-8768.
- 8 A. Paparo, K. Yuvaraj, A. J. R. Matthews, I. Douair, L. Maron, C. Jones, *Angew. Chem. Int. Ed.*, 2021, **60**, 630-634.
- 9 For a recent review on reductive homologation of CO, see: R. Y. Kong, M. R. Crimmin, *Dalton Trans.*, 2020, **49**, 16587-16597.
- 10 (a) R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch, C. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 8944-8947; (b) M. D. Anker, M. S. Hill, J. Lowe, M. F. Mahon, *Angew. Chem. Int. Ed.*, 2015, **54**, 10009-10011.
- 11 (a) M. D. Anker, C. E. Kefalidis, Y. Yang, J. Fang, M. S. Hill, M. F. Mahon, L. Maron, *J. Am. Chem. Soc.*, 2017, **139**, 10036-10054; (b) M. Xu, Z.-W. Qu, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.*, 2021, **143**, 634-638.
- 12 W. J. J. M. Sprangers, R. Louw, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1895-1901.
- 13 N.B. There is one report on well-defined magnesium acyls, though not formed *via* insertion of CO into Mg–C bonds: A. J. Boutland, C. A. Lamsfus, B. Maitland, L. Maron, A. Stasch, C. Jones, *Chem. Eur. J.*, 2017, **23**, 14049-14055.
- 14 (a) A. J. Boutland, A. Carroll, C. A. Lamsfus, A. Stasch, L. Maron, C. Jones, *J. Am. Chem. Soc.*, 2017, **139**, 18190-18193; (b) D. Dange, A. R. Gair, D. D. L. Jones, M. Juckel, S. Aldridge, C. Jones, *Chem. Sci.*, 2019, **10**, 3208-3216.
- 15 See, for example: (a) B. Bogdanovic, *Acc. Chem. Res.*, 1988, **21**, 261-267; (b) S. Harvey, P. C. Junk, C. L. Raston, G. Salem, *J. Org. Chem.*, 1988, **53**, 3134-3140.
- 16 B. Bogdanovic, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 262-273.
- 17 J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics*, 2018, **37**, 4810-4813.
- 18 C. Jones, L. McDyre, D. M. Murphy, A. Stasch, *Chem. Commun.*, 2010, **46**, 1511-1513.
- 19 N.B. The reaction of magnesium anthracene with CO has previously been reported to return anthracene: K. Wei, L. Shijian, *Youji Huaxue*, 1986, **3**, 207-209.
- 20 B. Bogdanovic, N. Janke, C. Krüger, K. Schlichte, J. Treber, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 1025-1026.
- 21 W. H. Monillas, G. P. A. Yap, K. H. Theopold, *J. Chem. Crystallogr.*, 2011, **41**, 415-418.
- 22 M. Ma, A. Stasch, C. Jones, *Chem. Eur. J.*, 2012, **18**, 10669-10676.

Graphical Abstract

The carbonylation of magnesium anthracene complexes under ambient conditions, and in the absence of catalysts, leads to the reductive coupling of CO, and the formation of unusual magnesium enediolate complexes (see picture, Ar = bulky aryl).

