Low-coordinate first-row transition metal complexes in catalysis and small molecule activation

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Enforcing unusually low coordination numbers on transition metals with sterically demanding ligands has long been an area of interest for chemists. Historically, the synthesis of these challenging molecules has helped to elucidate fundamental principles of bonding and reactivity. More recently, there has been a move towards exploiting these highly reactive complexes to achieve a range of transformations using cheap, earth-abundant metals. In this Perspective, we will highlight selected examples of transition metal complexes with low coordination numbers that have been used in catalysis and the activation of small molecules featuring strong bonds (N₂, CO₂, and CO).

Introduction

The stabilisation of transition metal complexes featuring unusually low coordination numbers remains a challenging and active area of research for synthetic inorganic chemists. These species are typically stabilised by sterically demanding ligands, which shield the metal from oligomerisation or further coordination by Lewis basic ligands. To this end, a vast array of bulky ligands have been prepared and utilised for this purpose; including amides, alkyls, silyls, aryls, and carbenes. The development of such ligands has been instrumental in advancing the range of complexes featuring low-coordinate and highly reactive transition metal centres, and has facilitated the isolation of new classes of compounds, such as species featuring metal–metal multiple bonds.

As the chemistry of low-coordinate complexes has developed, there has been an increasing interest in the exploitation of their reactivity. With the 3d metals, which are cheap and

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earth-abundant,9–11 enforcing low-coordinate geometries can drastically alter the reactivity and properties of these elements.7 For example, two-coordinate 3d metal complexes have been shown to act as single molecule magnets,12–14 and have been employed in the synthesis of Zintl ions.15 In recent years, exciting examples of such species catalysing unusual reactions or promoting the activation of challenging substrates have started to appear in the literature. Our research group has become increasingly interested in this field, with some of our recent work looking at the use of m-terphenyl complexes in the stoichiometric activation of small molecules and the catalysis of chemical reactions.

The term “low-coordinate” can be a rather tricky one to define when applied to the transition metals. One can argue, for example, that coordination numbers of four could be considered low for high oxidation state iron or vanadium compounds. One could also discuss how to define formal coordination number, and therefore depending on your definition “low-coordinate complexes” could cover a very broad range of species indeed. Given that Perspective articles are meant to be brief, we have restricted ourselves to considering complexes with a formal coordination number of three or less where, for example, ligands such as alkyls, aryls, amides, carbenes, phosphines, alkenes, etc. are considered to occupy one coordination site, and $\eta^1$-C$_6$H$_6$ to occupy three. This is not meant to provide a rigorous definition of “low-coordinate” but has instead been chosen to keep this discussion focused.

Even with this restriction, there are still too many examples for this article to be an exhaustive account of the field. As such, this Perspective will cover selected examples of catalysis and small molecule activation by low-coordinate complexes as defined above.

Catalysis

Given the increasing importance of sustainability in catalysis, there has been a shift away from the use of platinum group metals (such as platinum, palladium, and rhodium) towards cheaper and more abundant first-row transition metals.9–11 In particular, the use of low coordination numbers for 3d transition metal complexes is affording catalysts for a wide range of reactions. A commonly employed ligand system used to support low-coordinate first-row transition metal catalysts is the $\beta$-diketiminate; bidentate monoanionic ligands that bind through nitrogen. This ligand has been complexed to numerous metals, and such species have been shown to catalyse a wide variety of transformations including polymerisation,16,17 catalytic hydrodeflourination,18,19 Z-selective alkene isomerisation,20 nitrene transfer reactions,21,22 the dehydrocoupling of phosphines,23 phosphine-boranes and amine-boranes,24 and the hydrophosphinination25 and hydroboration26 of alkenes and alkynes. One example of such a catalyst is shown in Scheme 1, with the three-coordinate iron(II) catalyst (1), and the proposed mechanism by which it catalyses the dehydrocoupling of dimethylamine-borane.24 The development of $\beta$-diketiminate 3d complexes as catalysts was covered in a recent Perspective article by Ruth Webster, and we recommend consulting this article for a more in-depth look at such species.27 Thus, this section will focus on low coordinate 3d metal catalysts that do not feature $\beta$-diketiminate ligands. The discussion will be subdivided by metal, to aid clarity.

Nickel

For the most part the metal complexes covered in this review are highly reactive species which have been forced into disfavoured low-coordinate geometries by sterically demanding ligands. However, nickel is something of an exception to this. Complexes of Ni(0) are found to readily adopt two- or three-coordinate geometries when combined with neutral donor ligands such as phosphines and N-heterocyclic carbenes (NHCs), and such species have proven competent catalysts for a broad range of organic transformations. In recent years, there have been examples of C–H activation with the alkenylation,28 alkylation,29–31 and stannylation32 of aromatic systems, C–O bond cleavage,33–35 and catalytic cycloaddition chemistry.36 The catalysts are typically generated in situ from bis(cyclooctadiene)nickel(0) and the required ligand, with some
examples from the groups of Hartwig and Nakao shown in Scheme 2.28,33,34 There are too many examples to cover in detail here, and we recommend that readers interested in the field consult some of the excellent in-depth reviews on this topic.37,38

Low-coordinate catalysts based on Ni(I) and Ni(II) are somewhat less common, although certainly not unheard of. For example, several low-coordinate Ni(i) complexes have been investigated as catalysts for Kumada cross-coupling reactions.12,39-42 The Ni(0) species 2a and 2b were reacted with chlorobenzene or bromobenzene to generate the Ni(i) NHC complexes 3a-c (with elimination of biphenyl),40,42 all of which catalyse the Kumada reaction (Scheme 3) between aryl magnesium bromides and aryl chlorides or bromides. Compounds 3b-c also catalyse the coupling of aryl boronic acids to aryl bromides (Suzuki coupling).42 These complexes are interesting as case studies for the reactivity of low coordinate metals, but more convenient and less sensitive nickel catalysts exist for such transformations.43

Matsubara and co-workers found that treatment of 3a with triphenylphosphine afforded the mixed NHC/phosphine complex 4, which catalysed the Buchwald–Hartwig amination of aryl halides (chlorides, bromides and iodides) by diphenylamine under mild conditions (40–70 °C), affording yields ranging between 41–98% dependent on substrate.44 The catalyst showed good tolerance of ketone, alkene, and nitro functional groups; providing the first example of a nickel catalyst capable of coupling diphenylamine to aryl halides to afford triphenylamine derivatives (Scheme 3).41

Following on from this work, the Matsubara group very recently published an improved Ni(i) amination catalyst (5a) which coupled a range of primary and secondary amines to 4-bromobenzophenone in yields ranging from 58–96%.44 The initial pre-catalyst 5a is four-coordinate, but the active species is believed to be the two-coordinate Ni(i) amide species 5b (Scheme 4). This species was also synthesised, isolated, and found to be catalytically active.44 An exchange reaction with 2,2′-biquinoline revealed that the 2,2′-bipyridine ligand on 5a is labile and readily exchanged, allowing for the generation of the active two-coordinate species.44 EPR spectroscopy of a stoichiometric mixture of 5b and 4-bromoanisole provided evidence of both Ni(i) and Ni(II) species in solution, providing direct support for the involvement of a Ni(II) intermediate in the catalytic cycle. Such Ni(i)/Ni(II) redox cycles have previously been proposed for a number of nickel catalysts,45-47 but this study provides some of the best direct evidence for the existence of a Ni(II) intermediate.44 The catalytic cycle proposed by Matsubara et al. is presented in Scheme 4.

Nickel(i) catalysts bearing NHCS of different ring sizes (Scheme 5) were investigated for their efficacy in Kumada cross-coupling reactions, with EPR spectroscopy revealing that the magnetic properties of the complexes were strongly affected by ring size. The NHCS with the smallest ring size gave the best catalysts, although no correlation was observed with the magnetic parameters. The combination of a six-membered ring and mesityl flanking groups was found to give the best catalytic performance, with biaryl yields of 51–83% obtained at room temperature.12,39

A two-coordinate Kumada cross-coupling catalyst is seen in the Ni(II) bis(silylamide) complex 6a reported by Lipschutz and Tilley (Scheme 6).48,49 This catalyst was more effective for electron-poor aryl halides and, notably, promoted couplings to pyridine-based heterocycles. Stoichiometric reaction of 6a with MeMgBr resulted in the rapid formation of an alkylated Ni(II) species, 6b.48 This compound was found to react over
45 minutes with 1-iodonaphthalene to afford the coupled product (1-methylnaphthalene) in low yield (13%) along with 1,1′-binaphthalene and Ni(III) methyl complex 6c. Reacting 1-iodonaphthalene with 2 equivalents of 6b, by contrast, gave clean and rapid conversion to 1-methylnaphthalene in 98% yield. It is believed that the formation of 1,1′-binaphthalene in the stoichiometric reaction is due to the formation of naphthyl radicals, and the second equivalent of 6b is required to trap these. The radical nature of this step is supported by a radical clock experiment coupling (iodomethyl)cyclopropane to PhMgBr, which resulted in 4-phenyl-1-butene, the expected product of a radical rearrangement. Finally, an anionic Ni(I) species (6e) can be obtained by chemical reduction of 6a, and the reaction of 6c and 6e results in a redox equilibrium affording 6b and 6a. Based on the results of these various stoichiometric transformations, Lipschutz and Tilley proposed the catalytic cycle shown in Scheme 6.48 Species 6a is also an effective catalyst for the hydrosilylation of 1-octene with diphenylsilane, a resulting (n-octyl)diphenylsilane as the sole product after 2 h at room temperature (5 mol% catalyst loading).50

Treatment of the Ni(II) chloride pincer complexes 7a–b with lithium triethylborohydride affords the four-coordinate Ni(II) hydrides 8a–b.51 These complexes can reversibly lose hydrogen, and under ambient pressure exist predominantly as the three coordinate Ni(i) species 9a–b (Scheme 7a, Fig. 1). The dehydrogenation reaction is second order with respect to 8b, and likely proceeds via a biomolecular elimination reaction.51 These compounds catalyse hydrodehalogenation reactions, such as the dehalogenation of geminal dihalogenides,51 and defluorination of geminal difluorocyclopropanes to fluoroalkenes.52 Such reactions are regarded as a promising route to partially halogenated compounds from readily available perhalogenated species.53 Both reactions are stereoselective, with moderate ee (enantiomeric excess) values for the monohalides of 20–74%,51 and high Z-selectivity in the formation of alkenes from cyclopropanes.52 Reactions with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) resulted in catalyst inhibition, suggesting that the mechanism is radical in nature.51,52 This was further supported by reactions with radical clock reagents.51 The proposed catalytic cycle for the dehalogenation of geminal dihalogenides is shown in Scheme 7b.51
The reaction between proligand $10$, $n$BuLi, and trans-$[\text{Ni(PPh}_3)_2(\text{Ph})\text{Cl}]$ resulted in the formation of Ni(I) complex $11$, with concomitant elimination of biphenyl (Scheme 8a). This spontaneous reduction of the nickel centre presumably occurs to reduce the steric demands arising from the bulky bidentate ligand. This three-coordinate species was found to be a remarkably active catalyst for the polymerisation of norbornene in the presence of a methylaluminoxane (MAO) co-catalyst (Scheme 8b), affording high molecular weight polynorbornene ($M_w$ ca. $10^6$ g mol$^{-1}$) with catalytic activities of up to $2.82 \times 10^7$ gPNP mol$^{-1}$Ni h$^{-1}$.

**Cobalt**

Several two- and three-coordinate cobalt catalysts bearing N-heterocyclic carbene (NHC) ligands have been published by Deng and co-workers. The three-coordinate Co(i) species $12$ was shown to catalyse the hydrosilylation of terminal alkynes, showing broad functional group tolerance and moderate to good selectivity for formation of the E-alkene (Scheme 9a). Subsequently, the Co(ii) amide species $13$, bearing an asymmetric NHC ligand, catalysed the hydrosilylation of terminal alkynes, showing broad functional group tolerance and moderate to good selectivity for formation of the E-alkene (Scheme 9a). Subsequently, the Co(ii) amide species $13$, bearing an asymmetric NHC ligand, catalysed the hydrosilylation of terminal alkynes, showing broad functional group tolerance and moderate to good selectivity for formation of the E-alkene (Scheme 9a).

Scheme 7 (a) Synthesis of the three-coordinate Ni(i) species $9a$ and $9b$. (b) Proposed mechanism for catalytic, stereoselective hydrodehalogenation of geminal dihalogenides by $9a$ and $9b$. LiBHEt$_3$ is used in excess as a reductant and hydride source.$^{54,52}$

Scheme 8 (a) Synthesis of three-coordinate Ni(i) complex $11$ with elimination of biphenyl from a Ni(ii) source. (b) Polymerisation of norbornene by $11$ in the presence of MAO co-catalyst.$^{54}$
The formation of terminal alkenes affording predominantly anti-Markovnikov products (Scheme 9b). This catalyst was most effective for reactions with triethoxysilane; reactions with other silanes, including triphenylsilane and triethylsilane, gave poor conversions and low yields.\textsuperscript{57} Following this investigation, a selection of two-, three-, and four-coordinate Co\textsubscript{(I)} NHC complexes were able to achieve different selectivity (Markovnikov, anti-Markovnikov, or hydrogenation) for the reaction of diphenylsilane with terminal alkenes, dependent on the choice of catalyst (Scheme 9c).\textsuperscript{58} While cobalt hydrosilylation catalysts are widely known, those displaying Markovnikov or hydrogenation selectivity are relatively rare,\textsuperscript{58,60,61} so these cobalt NHCs provide a valuable addition to the field.

More recently, the three-coordinate Co\textsubscript{(0)} complexes \textsuperscript{14} and \textsuperscript{15} were shown to catalyse the dehydrocoupling of primary arylphosphines to the corresponding diphosphanes (Scheme 10), an unusual example of a cobalt catalyst for such a transformation.\textsuperscript{59} The catalysts afforded the coupled products in moderate to good yields (47–73%), but were ineffective with the secondary phosphate Ph\textsubscript{2}PH and primary alkyl phosphine tBuPH\textsubscript{2} (7% and 8% yields, respectively).\textsuperscript{59}

\textbf{Manganese and iron}

In recent work by our research group, a series of Mn\textsubscript{II} and Fe\textsubscript{II} \textit{m}-terphenyl complexes were found to catalyse the cyclo-trimerisation of primary aliphatic isocyanates (Scheme 11).\textsuperscript{62} The reactions proceeded cleanly under mild conditions to isocyanurates, which find use as polymer additives to improve their physical properties,\textsuperscript{63,64} in addition to applications in microporous materials,\textsuperscript{65,66} selective ion bonding,\textsuperscript{67} and drug delivery.\textsuperscript{68–71} Two different flanking aryl groups were employed in the \textit{m}-terphenyl ligands; [2,6-Mes\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]\textsuperscript{-}, and the less sterically encumbering [2,6-Tmp\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]\textsuperscript{-} (Tmp = 2,4,5-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2}), giving catalytically active manganese and iron complexes (16–19, Scheme 11a). The Mes-substituted complexes are two-coordinate, while the less bulky Tmp-substituted ligands stabilise three-coordinate complexes, with metal-coordination by an additional THF ligand. While \textsuperscript{17} and \textsuperscript{19} showed no significant difference in reactivity, two-coordinate \textsuperscript{16} was found to give a faster reaction rate than \textsuperscript{18}. Catalyst poisoning and radical trap experiments showed no evidence for the formation of catalytic nanoparticles or the involvement of radical processes, and, as a result, the mechanism is postulated to proceed \textit{via} a homogeneous pathway. Kinetic experiments in the reaction of \textsuperscript{16} with ethyl isocyanate showed a first order

\begin{figure*}
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\includegraphics[width=\textwidth]{Scheme_9.png}
\caption{Cobalt NHC complexes in hydrosilylation reactions. (a) Complex \textsuperscript{12}, featuring an NHC and phosphine ligand, selectively gives \textit{E}-alkenes from the reaction of terminal alkynes with triphenylsilane. (b) Co\textsubscript{(II)} amide NHC complex \textsuperscript{13} gives anti-Markovnikov products in the reaction of triethoxysilane with terminal alkenes. (c) Different Co\textsubscript{(I)} NHC complexes afford different selectivities in the reaction of diphenylsilane with terminal alkenes. Ad = 1-Adamantyl.\textsuperscript{55–58}}
\end{figure*}
rate dependence in both 16 and substrate. Based on these observations, a mechanism was proposed involving Lewis acid catalysis (Scheme 9c).

The manganese complexes 17, 19 (Scheme 11a) and the xylyl-substituted analogue catalyse the dehydrocoupling of di-methylamine-borane (Scheme 12),72 which is of interest in the chemical storage and release of hydrogen.73–76 While the reaction was slow at room temperature, increasing the reaction temperature to 60 °C provided relatively clean conversion to the cyclic dimer [Me$_2$NBH$_2$]$_2$ in high yields and reasonable timeframes. The linear species Me$_2$NH–BH$_2$–NMe$_2$–BH$_3$ was also observed as a side product and intermediate in the reaction. While reactions with the two-coordinate catalyst 17 (and its xylyl analogue) showed no appreciable change upon addition of elemental mercury, reactions with the three-coordinate 19 showed a significant drop in activity. Furthermore, reaction of 19 with Me$_2$NH-BH$_3$ results in the rapid formation of a dark red suspension, while 17 remains a clear yellow solution. This evidence suggests that the reaction with 19 is heterogeneous in nature, involving the formation of catalytic nanoparticles, while reactions with 17 proceed via a homogeneous route. This was confirmed by isolation of the manganese nanoparticles from reactions between 19 and Me$_2$NH-BH$_3$, followed by characterisation by transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX).72 This reaction serves as an example of how small changes in the steric properties of the flanking aryl groups of $m$-terphenyl ligands can result in significant differences in reactivity.

The iron(II) m-terphenyl complexes 16 and 18 (Scheme 11a) are effective catalysts for the hydrophosphination of isocyanates.77 This reaction affords a mixture of phosphinocarboxamide and phosphinodicarboxamide products, corresponding to both mono- and diinsertion of the isocyanate into the P–H bond (Scheme 13a). Such diinsertion reactions are rare78 and the double insertion of an isocyanate into a P–H bond has led to a family of phosphinodicarboxamide compounds. By changing the reaction conditions, this reaction can be made selective to afford either the phosphinocarboxamide (reaction in THF solvent) or phosphinodicarboxamide (through the reaction in benzene or toluene solutions in the presence of Et$_3$N·HCl) (Scheme 13b).

Reaction monitoring through in situ $^1$H and $^{31}$P NMR spectroscopy reveals that the three-coordinate complex 18 shows significantly higher activity than 16, which may be due to the presence of a labile THF ligand. Interestingly, reactions with 16 show an induction period of ca. 2 h, while no such induction period was observed in reactions catalysed by 18. Monitoring of stoichiometric reactions by IR spectroscopy suggest that an iron amidate complex may be the active catalytic species in this reaction (Scheme 13c). Poisoning experiments have suggested that the reaction is homogeneous and does not involve radical processes; and a catalytic cycle where the transition metal acts as a Lewis acid was proposed to account for these observations (Scheme 13c).77
The two-coordinate Fe(II) amide 22 catalyses the hydrosilylation of ketones, affording the corresponding silyl ethers in good to quantitative yields (Scheme 14b)." The catalyst was effective for the reaction of diphenylsilane with a range of ketones, proceeding cleanly at room temperature with low catalyst loadings (0.01–2.7 mol%). However, the reaction failed with tertiary silanes or silanes with bulky substituents, presumably due to steric effects. Species 22 represents an early example of an iron catalyst for this industrially relevant transformation, although it has since been supplanted by more convenient systems.

Small molecule activation

The activation of small molecules such as N₂, CO₂, and CO poses significant but exciting challenges. Utilising these molecules generally involves overcoming large energy barriers.
owing to their high bond strengths and, in some cases, low polarity. However, the activation of such molecules is of significant industrial importance in reactions such as the Haber process and Fischer–Tropsch catalysis. The development of homogeneous systems for functionalising these relatively inert species is thus an area of considerable research interest. In this section, we will outline some examples of low-coordinate first-row transition metal complexes that are able to bind and activate these small molecules.

**Nitrogen activation**

An early example of a low-coordinate 3d metal binding and activating dinitrogen is the nickel phosphine complex 24a, which was first synthesised in 1968 and crystallographically characterised in 1971 (Fig. 2). In this structure, the N₂ unit is protected by a cage of cyclohexyl rings, and a related compound featuring PPr₃ ligands (24b) was reported in 2013. Another notable early example of N₂ binding is seen in the mixed Fe/Mo complex 25, which was the first complex to feature a three-coordinate iron centre coordinated entirely by N₂-derived ligands.
Some elegant examples of N\textsubscript{2} fixation and activation with low-coordinate 3d metals are seen in the series of iron and cobalt \(\beta\)-diketiminate complexes investigated by the Holland group. Reduction of the metal(II) chloride species (26a–c) using KC\textsubscript{8} under a nitrogen atmosphere affords the dinuclear N\textsubscript{2}-bridged complexes 27a–c (Scheme 15).\textsuperscript{91–95} Of these N\textsubscript{2}-bridged species, complex 27b was shown to be an effective pre-catalyst for the synthesis of asymmetric carbodiimides from organoazides and isocyanates.\textsuperscript{21} The reduction of a THF solution of 26c with Reike magnesium (Mg*) under a N\textsubscript{2} atmosphere affords the highly unusual complex 28c, which features a magnesium bridging between two N\textsubscript{2} ligands.\textsuperscript{96} This complex was sufficiently stable for isolation and characterisation by single crystal X-ray diffraction. The corresponding Mg* reductions with 26a and 26b afforded the metastable Fe complexes 28a and 28b, which could only be characterised in THF solution by infrared (\(\nu_{\text{NN}} = 1808\text{ cm}^{-1}\) for 28a; 1818 cm\(^{-1}\) for 28b) and Mössbauer spectroscopy.

Complexes 27a–c can also be reduced by potassium to afford the metal(0) species 29a–c, which features two K\textsuperscript{+} ions coordinated to the aromatic Dipp rings.\textsuperscript{91–95} The side-on coordination of K\textsuperscript{+} results in elongated N–N bonds [29a 1.233(6) Å; 29b 1.215(6) Å; 29c 1.220(2) Å],\textsuperscript{91–95} compared to those observed in 27a–c [27a 1.189(4) Å; 27b 1.186(7) Å; 27c 1.139(2) Å].\textsuperscript{91–95} Treatment of the reduced iron species 29b with 18-crown-6 affords a new four-coordinate complex 30, in which potassium is coordinated by an N\textsubscript{2} ligand.\textsuperscript{97} This species is active towards silylation, reacting with Me\textsubscript{3}SiI to afford the three-coordinate Fe(III) hydrazido species 31 along with Fe(II) iodide 32. It should be noted that reacting 29b with Me\textsubscript{3}SiI directly affords 31 in low yields (ca. 5%) with long reaction times.

Complexes 27a–c can be compared with the closely related chromium complex 34, prepared by Theopold and co-workers.\textsuperscript{98} Despite having a very similar ligand framework, in 34 the two nickel atoms bind dinitrogen side-on rather than end on as in 27a–c. Complex 34 was prepared by magnesium reduction of the Cr(II) iodide 33 in THF solution under a nitrogen atmosphere (Scheme 16). This side-on coordination results in greater lengthening of the N–N bond (1.249(5) Å in 34)\textsuperscript{98} compared with the end-on coordination of 27a–c.

While the binding and partial reduction of dinitrogen in this manner presents exciting possibilities, the full reduction of nitrogen to ammonia by a homogeneous catalyst remains a challenging prospect.\textsuperscript{99,100} One example of a low-coordinate complex which is capable of reducing N\textsubscript{2} in this manner is the Fe cyclic alkyl amino carbene (CAAC) complex 35, recently published by Peters, Ung and co-workers.\textsuperscript{101,102} This two-coordinate complex was capable of binding N\textsubscript{2} reversibly at low temperatures (ca. −78 °C) which resulted in significant changes in the UV/Vis spectra of a solution in pentane.\textsuperscript{102} The reaction between this complex and KC\textsubscript{8} at −95 °C in the presence of

**Fig. 3** Molecular structure of 36. Hydrogen atoms omitted and flanking groups of CAAC ligands are depicted as wireframe for clarity. Anisotropic displacement ellipsoids are set at 50% probability.\textsuperscript{102}

**Scheme 18** CO\textsubscript{2} fixation and activation by dinitrogen-bridged nickel complexes 37 and 38.\textsuperscript{109–111}
18-crown-6 facilitated the isolation of the Fe(−I) complex 36 (Scheme 17), the structure of which was confirmed by X-ray crystallography (Fig. 3). Attempting this reaction at temperatures above −78 °C resulted in decomposition to a complex mixture of products. The treatment of 35 with an excess of both KC₈ and HBArF₄·OEt₂ ([HBArF₄]⁻ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) at −95 °C in diethyl ether under a dinitrogen atmosphere allowed for the catalytic generation of ammonia, albeit with modest turnover numbers (3.3 ± 1.1 equivalents of NH₃ per Fe). Reactions at temperatures above −95 °C were ineffective, which is attributed to the poor binding of N₂ to 35 at elevated temperatures.¹⁰²

Fig. 4 Molecular structure of 40. Hydrogen atoms and co-crystallised hexane omitted and carbon atoms of β-diketiminate ligands are depicted as wireframe for clarity. Anisotropic displacement ellipsoids are set at 50% probability.¹¹²

Scheme 19 Reactivity of "slipped" Co(I) β-diketiminate complex 42 with CO₂ and N₂O.¹¹⁴,¹¹⁵

Fig. 5 Molecular structure of T-shaped Ni(II) complex 48 (top), and the species obtained after treating with CO₂ (49, bottom). Hydrogen atoms, co-crystallised naphthalene (48) and disorder in carboxylate group (49) omitted, and iPr groups (49) are depicted as wireframe for clarity. Anisotropic displacement ellipsoids are set at 50% probability.¹²⁷

Scheme 20 (a) Formation of isocyanate from reaction of CO₂ with iron-silylamide complex 46. (b) Transposition reaction of Ni complex 47 with CO₂ to generate Ni(II) isocyanate.¹²⁴,¹²⁵
Carbon dioxide activation

One common example of carbon dioxide activation by low-coordinate 3d metals is the co-polymerisation of CO$_2$ and epoxides by Zn$\beta$-diketiminate complexes, with a significant number of reports on this subject.$^{103-108}$ The reaction is postulated to be an example of Lewis acid catalysis, and recent work has shown that introducing electron withdrawing CF$_3$ groups into the ligand framework can drastically increase turnover frequency for these catalysts.$^{106-108}$

A Ni complex (37), closely related to the Fe and Co complexes $^{27a-c}$ shown in Scheme 15, was synthesised by Limberg and co-workers by reduction of the corresponding nickel(II) bromide with potassium triethylborohydride under a nitrogen atmosphere.$^{109}$ This complex can be further reduced to the Ni(0) species $^{38}$ by reaction with KC$_8$. Both complexes were able to activate carbon dioxide, undergoing reductive coupling and cleavage to generate Ni(i)CO ($^{39}$), Ni(ii)CO$_3$ ($^{40}$), and Ni(ii)C$_2$O$_4$Ni(ii) ($^{41}$) species (Scheme 18).$^{110,111}$ Complex $^{40}$ forms a macrocyclic structure in the solid state, consisting of six nickel and six potassium cations, which was characterised by X-ray diffraction (Fig. 4). All of the Ni(i) centres in this structure are square planar and possess low spin configurations. Complex $^{40}$ was also synthesised by reacting a Ni(0)CO complex with either N$_2$O or O$_2$, a highly unusual example of CO oxidation at nickel.$^{112}$ The iron dinitrogen complex $^{27a}$ (Scheme 15) reacted with CO$_2$ in a similar manner, affording the first four-coordinate iron dicarbonyl complex, and a carbonate-bridged diiron complex.$^{113}$

Similar reactivity towards CO$_2$ was demonstrated by the Co(i) $\beta$-diketiminate complex $^{42}$, which features a highly unusual slipped $\kappa_1$N$_9^6$-arene coordination mode.$^{114,115}$ The reaction between this compound and CO$_2$ affords the monocarbonyl complex $^{43}$ and dicobalt carbonate complex $^{44}$ (Scheme 19). The mechanism has been probed by DFT calculations, and is considered to proceed via the oxo-bridged dimer $^{45}$, which was synthesised independently by reaction of $^{43}$ with N$_2$O. The reaction between $^{45}$ and CO$_2$ afforded $^{44}$ as the sole product (Scheme 19).$^{115}$

Reactions between low-coordinate metal amides and carbon dioxide can afford isocyanates, carbodiimides, or (often) a mixture of the two. While the reaction has been performed with metals from the s-,$^{116,117}$ p-,$^{118-120}$ and f-block,$^{121,122}$ zinc- and iron-based systems have shown some of the greatest selectivities,$^{123,124}$ with a recent iron silylamide ($^{46}$) affording the corresponding isocyanate with $>95\%$ selectivity at CO$_2$ pressures as low as 0.01 atm (Scheme 20a).$^{124}$ A related reaction is seen with the PNP-pincer Ni(i) complex $^{47}$,$^{125}$ which undergoes a transposition of the ligand N atom on reaction with CO$_2$ to afford a POP-pincer and Ni(i) isocyanate (Scheme 18b).$^{126}$
The T-shaped Ni(I) complex 48, which features a rigid acridane-based ligand, was recently investigated by Yoo and Lee. This species was obtained by reduction of the corresponding Ni(II) chloride by sodium naphthalenide, and proved capable of activating a diverse range of small molecules under mild conditions. Notably, 48 reduced carbon dioxide under ambient conditions, affording the carboxylate-bridged species 49 (Fig. 5). The complex can also reduce ethene to an ethane bridge, and causes homolytic bond cleavage of a range of molecules; including dihydrogen, methanol, phenol, diphenyl disulfide, methyl iodide, hydrazine, and acetonitrile.

Reactivity towards carbon monoxide

The activation of carbon monoxide by low-coordinate 3d species is less explored than that of CO$_2$ or N$_2$, with the majority of low-coordinate complexes simply binding CO to give the corresponding metal carbonyls. Examples of more interesting reactivity include the chromium dinitrogen complex 34, which reacts with CO to afford the bridged complex 50, a relatively rare example of an isocarbonyl complex. Compound 50 features activated CO molecules bridging through both the carbon and oxygen atoms with a diamagnetic mixed valent Cr(II)/Cr(0) core (Scheme 21a). The three-coordinate Ni(0) carbonyl complex 51 (Scheme 21b) is capable of oxidising CO in the presence of N$_2$O or O$_2$ to give the macrocyclic carbonate complex 40, previously seen in Scheme 18 and Fig. 4 as the result of CO$_2$ activation.

The Fe(II) complexes 16 and 55 reduce CO with complete scission of the C=O bond, affording the highly unusual squaraines 56a–b, iron carboxylates 57a–b, and Fe(CO)$_5$. The cobalt(II) complexes 52a and 52b reacted with CO to afford sterically encumbered ketones. These reactions proceeded cleanly at room temperature affording either a benzophenone (53) or a keto-fluorenone (54) depending on the flanking aryl group (Scheme 22).

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Scheme 23 Reactions of Fe(II) m-terphenyl complexes with CO. (a) Mes and Xyl substituted compounds (16 and 55) react to give squaraines (56a–b), iron carboxylates (57a–b), and Fe(CO)$_5$. (b) Naphthyl substituted 58 reacts with CO to afford iron-carbene 59. (c) Proposed mechanism for the reaction between 16 or 55 with CO.
aines 56a–b, with concomitant formation of the Fe(II) carboxylate complexes 57a–b and Fe(CO)_5 (Scheme 23a, Fig. 6). This reaction proceeds cleanly at room temperature and 1 bar pressure, and is both the first example of reductive cleavage of CO by a low-coordinate iron complex and C_4 ring formation from CO with complete C=O bond cleavage. The squaraines 56a–b feature broken conjugation due to the steric bulk of the aryl substituents, which forces them out-of-plane with the C_4O_2 ring. This results in less delocalisation into the aromatic rings, giving an unusually high C=O IR stretching frequency (56a = 1673 cm^-1) and carbonyl chemical shift (56a δ_c = 269.7 ppm) in comparison to other squaraines. Reactions with ^13CO proved that all four carbon atoms in the central squaraine ring are derived from CO, and monitoring by IR spectroscopy has suggested that ketene or ketenyl (C≡C=O) intermediates may be formed during the reaction. The analogous reaction using the related m-terphenyl complex 58, which features flanking 1-naphthyl substituents, has facilitated the isolation of Fe(II) carbene 59 (Scheme 23b), which is postulated to be an intermediate in the formation of squaraines from 16 and 55. It is proposed that the reaction halts at 59 due to the increased steric demands of the flanking naphthyl groups, which prevent further reaction. Indeed, naphthyl-substituted m-terphenyl complexes are known to display conformational isomerism due to restricted rotation, and the results of DFT calculations support the notion that these flanking groups halt the reaction at species 59. Based upon these observations, a mechanism was proposed that accounts for the formation of these products, and fits all the available mechanistic data (Scheme 23c).

**Conclusions and outlook**

Although the use of low-coordinate, first-row metal complexes in catalysis and small molecule activation is a relatively young field, this strategy shows considerable promise for achieving reactivity that would be challenging by other means. Already, a vast array of diverse and exciting transformations has been discovered, and we feel confident that this research area will continue to grow and develop in the future. One thing we noted while composing this perspective is the relatively narrow range of 3d metals that dominate this area. Cobalt, nickel and iron are by far the most thoroughly investigated elements, with manganese, chromium and copper appearing less frequently, for example. It is possible that the less-explored elements could yield as-yet unseen reactivity, and we hope to see more work in this area in the future.

It is highly likely that the preparation of new bulky ligands with different electronic properties will be key to the development of future low-coordinate catalysts and reagents. Of particular interest are the relatively new class of cyclic (alkyl)(amino)carbenes (CAACs), which are more σ-donating and π-accepting than N-heterocyclic carbenes and the recently developed [2,6-(2,4,6-i-Pr_3C_6H_2)_2C_6H_3]−, an incredibly sterically encumbering m-terphenyl ligand, which was recently exploited in the synthesis of several Sn–Sn bonded compounds.

Finally, we note the increasing interest in mechanistic investigations of these catalysts, with more researchers undertaking kinetic measurements of these systems rather than simply viewing the reaction as a “black box”. Hopefully this will lead to a greater understanding of the factors that underpin the reactivity of low-coordinate metal species and allow for the future rational design of improved catalytic systems.

**Conflicts of interest**

There are no conflicts to declare.
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