The cobalt dinitrogen complexes [(EP$_3^{\text{th}}$)Co($\mu$-N$_2$)$_2$Mg(THF)$_4$], with triphos ligand scaffolds (EP$_3^{\text{th}}$, E = N or CMe), were prepared via two electron reductions of the Co(I) precursors [CoCl(EP$_3^{\text{th}}$)]. Both complexes showed high degrees of N$_2$ activation owing to the formation of a rare M-N=N-Mg-NN-M bridging-magnesium core. These systems showed further N$_2$ functionalisation reactivity by silylation, forming silyldiazenido complexes [(EP$_3^{\text{th}}$)Co(NNSiMe$_3$)].

Harnessing the abundance of atmospheric N$_2$ for direct chemical transformations is a significant scientific challenge. Industrially, N$_2$ is reacted to form ammonia via the Haber-Bosch process, but the high energetic demands of this method have sparked the development of discrete transition metal-based catalysts that are capable of fixing nitrogen under ambient conditions.$^{1-3}$ Fe and Mo systems have received the most attention, due to their biomimetic origins,$^4$ yet, such catalysts are still far from industrial applications. Other metals are therefore of interest, that could activate N$_2$ sufficiently for catalytic transformations. Cobalt has shown particular promise, with high turnovers of catalytic N$_2$ to N(SiMe$_3$)$_3$ conversion achieved by a bimetallic Co-Co complex (fig. 1),$^5$ and catalytic NH$_3$ formation (up to 15.9 eq) using a [PNP]Co(N$_2$)] complex.$^8$ These recent examples demonstrate the significant potential of Co, and therefore warrant its further attention for N$_2$ fixation.

Despite the reported cobalt-mediated catalysis, investigations into direct N$_2$ functionalisation at a cobalt centre for mechanistic studies remains relatively unexplored. Peters and co-workers first observed N$_2$ functionalisation of a Co(I) complex in 2003, forming methyl- and silyl-diazenido Co(II) species, supported by an anionic B-triphos ligand.$^6$ Since then, there have been very few examples of well-characterised N$_2$-functionalised complexes. The most recently reported example has been the silylation product reported by Deng in 2018$^7$ (fig. 1). Herein, we investigate N$_2$ coordination and functionalisation of new Co(-I) systems supported by neutral triphos ligands, varying from typical Co(II)/Co(I) systems (scheme 1).

Our group has been investigating the N-triphos ligand motif [(N(CH$_2$PR$_3$)$_3$)]$^{9-13}$ and recently, we reported a Mo/N-triphos N$_2$ complex. This complex showed moderate N$_2$ activation that was comparable to the C-triphos analogue, but with a varied reactivity profile.$^{13}$ Of the many triphos derivatives, N-triphos is advantageous (particularly over the similar C-triphos system), due to the ease of synthetic tunability of the steric and electronic ligand parameters, and the accessible lone pair on the apical nitrogen provides an additional reactive site.$^{11,12}$ We sought to investigate the relatively unexplored potential of cobalt for N$_2$ activation using the neutral N-triphos (N(CH$_2$PPh$_3$)$_3$ or NPh$_3^{\text{th}}$) and C-triphos ([MeC(CH$_2$PPh$_3$)$_3$] or MeCP$_2^{\text{th}}$) scaffolds.

![Fig. 1 Notable previous examples of Co-mediated N$_2$ fixation or functionalisation.$^{1-7}$](image)

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**Scheme 1.** Novel Co-N$_2$ complexes in this work, with N$_2$ functionalisation by silylation.
The Co(II)-chloride complex, [CoCl(NP$_3$)$_2$] (1), served as a useful precursor for N$_2$ reductions, and was prepared via Zn reduction of a solution of CoCl$_2$ and NP$_3$ in THF (scheme 2). Complex 1 was isolated in a 55% yield and high purity from the reaction mixture following filtration and crystallisation via vapour diffusion of hexane into a THF solution (fig. S5). An IR spectrum of this solution taken after 2 days showed a characteristic N-N band at 1878 cm$^{-1}$, indicating the formation of a new dinitrogen complex. Filtration of this solution and removal of solvent in vacuo yielded a dark red/brown solid. The $^{31}$P NMR spectrum of this complex displayed a series of well-defined resonances: three phenyl multiplets at 7.38, 6.96 and 6.86 ppm, and a characteristic singlet at 3.86 ppm, corresponding to the backbone (SI fig. 5). The diamagnetic nature of this spectrum points towards a two electron reduction to generate a Co(i)/d$^{10}$ species. Additionally, two broadened resonances appeared at 3.79 and 1.45 ppm, confirming THF coordination to Mg. The $^{31}$P$^1$(H) NMR spectrum of 2 showed a signal at 17.5 ppm (fig. S5, SI) and was indicative of a single phosphorus environment, with the ligand still fully chelated to the Co centre. This $^{31}$P NMR resonance was broadened at 298 K; this suggests fluxionality within complex 2, which was confirmed by low temperature NMR spectroscopy, that showed a sharpening of this resonance. Single crystals of 2 were grown by vapour diffusion of hexane into a THF solution. X-ray analysis of 2 revealed a rare dumbbell-like complex with a stabilising central Mg$^{2+}$ cation bridging between two activated cobalt dinitrogen complexes (fig. 3). Only a handful of N$_2$ complexes reported in the literature contain a central M-NN-Mg-NN-M core (M = Co, Fe, Mo, W), of which there are just 5 cobalt complexes. These include either Co(0) centres supported by an anionic B-triphos or a β-diketiminate ligand, or Co(i) tris(PR$_3$)$_3$ centres (R = Ph,$_2$$_2$,$_2$$_2$. Only two of these were crystallographically characterised (the ([Co(PMe$_3$)$_3$] and [Co(B-triphos)] species), highlighting the unusual nature of the molecular structure of 2.

The central Co-N-Mg-N-Co moiety of 2 (fig. 3) shows almost linear Co-N-M bonds [174.3(5) and 174.5(5)°], but a bent N-N-Mg bond [153.7(5) and 159.6(5)°], which is typical for Lewis acid-functionalised N$_2$ ligands. The cis geometry of this bending around Mg is unique to 2 (compared to the other crystallised Co species$^{6,16}$), but this is just in the solid state. It is likely that 2 is fluxional in solution, as evidenced by the variable temperature $^{31}$P NMR spectroscopy (fig. S5, SI).

The crystal structure also reveals that the NN bond lengths [1.157(6) and 1.156(7) Å] are significantly elongated relative to free N$_2$ (NN = 1.0975 Å$^{20}$), indicating a high degree of N$_2$ activation. This is further supported by the low IR stretching frequency assigned to 2 ($\tilde{v}_{\text{NN}}$ = 1878 cm$^{-1}$). The $^{15}$N-labelled isotopologue (2-$^{15}$N) was additionally prepared (via a similar route in scheme 2, under a $^{15}$N$_2$ atmosphere), which showed a

![Fig. 2 X-ray crystal structure of complex 1](image1)

![Fig. 3 X-ray crystal structure of complex 2. Disorder of the coordinated THF has been omitted for clarity](image2)
strong IR band at 1816 cm$^{-1}$ which was assigned to the $^{15}$N$_2$ stretch and shifted relative to the $^{14}$N$_2$ complex (fig. 4). The strong dinitrogen activation in 2 is attributed to the interaction of the central Lewis acidic Mg cation, which imparts a 'push-pull' type weakening of the NN bond (increased metal back-bonding to the NN bond [push]) as a result of withdrawal of electron density at the distal nitrogen bound to the Lewis acid [pull]).

Attempts to crystallise 5 were unsuccessful, but selected crystals obtained from preparations via route 1 were screened, revealing crystallographic unit cells of $\left\{\left\{\text{MeCP}\right\}_{3}\text{Co}\right\}_{2}\left\{\mu-\text{N}_2\right\}$ and $\left\{\text{Co}\left\{\text{MeCP}\right\}_{3}\right\}_{2}\text{N}_2$. This is in parallel to the side-products 3 and 4 only forming via the alternative route shown in scheme 2.

In situ reactivity studies of the highly activated N$_2$ complexes 2 and 5 were performed, with respect to N$_2$ functionalisation. Firstly, the degree of N$_2$ activation was modulated by exchange with alkali metals. In situ reactions of 2 with alkali metals (Li, Na or K) in THF resulted in Mg exchange to form mononuclear complexes, $\left\{\text{NP}^{\text{ph}}\text{Co}\right\}_{2}\left\{\mu-\text{N}_2\right\}$ and $\left\{\text{NP}^{\text{ph}}\text{N}_2\right\}$ (scheme 4). Further reaction of 2-K with 18-crown-6 resulted in the formation of $\left\{\text{NP}^{\text{ph}}\text{Co}\right\}_{2}\left\{\mu-\text{N}_2\right\}\left\{\text{K}(18\text{-crown-6})\right\}$ (2-K[18C6]), by encapsulation of K$^+$. These alkali metal exchanges were monitored by IR spectroscopy, showing a change in N$_2$ environment by a shifted N≡N stretch (table S1, SI). C-triphos analogues to 2-K and 2-K[18C6] were additionally prepared (scheme 4), with IR spectroscopic indicating similar reactivity to form 5-K and 5-K[18C6] (table S1). The Li$^+$ and Na$^+$ exchanges resulted in N$_2$ stretches at higher frequencies; this lower degree of N$_2$ activation is expected for replacement of the stronger Mg$^2+$ Lewis acid for the weaker M$^+$alkali metal cations. The K$^+$ adducts showed increased N$_2$ activation (noted by lower N≡N stretch).
strecthing frequencies), and is rationalised by possible multiple K' interactions to the N2 ligand (both end-on and side-on interactions have been previously observed for K'-stabilised [Co-N2] complexes.\textsuperscript{22} However, encapsulation of the K' adducts by crown-ethers resulted in the least activated systems, due to withdrawal of the N2-activating metal cation interaction.

Silylation reactions of 2 and 5 were also investigated. Reaction of 2 or 5 with 2.5 eq Me3SiCl in THF resulted in the formation of silyldiazenido complexes \{[EPC\textsubscript{n}Co(NNSiMe\textsubscript{3})] (E = N) or 7 (E = CMe), scheme 4\}. The silyldiazenido complex was characterised by IR spectroscopy, showing a disappearance of the N=NN stretch and revealing a new, lower frequency N=N stretch at 1678 cm\textsuperscript{-1} (6) or 1672 cm\textsuperscript{-1} (7) (fig. 5). These stretching frequencies are indicative of N2 functionalisation and mono-silylation, especially in comparison to the reported Co/B-triphos silyldiazenido complex (\nu\textsubscript{NN} = 1654 cm\textsuperscript{-1}, fig. 1).\textsuperscript{6} These stretches were confirmed as the functionalised NN bonds by repeating the silylation with the \textsuperscript{15}N isotopologue complex 2-\textsuperscript{15}N, which showed a similarly shifted IR N=N stretch at 1622 cm\textsuperscript{-1} (6-\textsuperscript{15}N).

Further XRD characterisation of 6 and 7 could not be obtained but selected single crystals from crystallisation attempts revealed unit cells relating to 1 (or the C-triphos analogue). [CoCl(triphos)] is a rational side-product to the silylation of the N2 complex, due to Cl ions (by-products) that likely interact with the highly reactive silyldiazenido species. However, further 29Si NMR spectroscopic characterisation of 6 showed a signal at -7.6 ppm (with a correlating \textsuperscript{1}H NMR signal at 0.28 ppm) that was assigned to the [Co-NNSiMe\textsubscript{3}] species, further confirming the N2 functionalisation reactivity.

In conclusion, we have shown that high degrees of N2 activation can be achieved for cobalt complexes with neutral triphos ligands, owing to a rare Mg-bridging interaction to two Co-(i) centres. Both the N-triphos and C-triphos ligands behave in an analogous manner, showing similar reduction pathways, side-product formations and N2 activations. Furthermore, they have been demonstrated to facilitate N2 silylation, and our future studies are directed towards achieving catalytic turnovers by optimisation of the silylation conditions.

Imperial College London is acknowledged for financial support. We thank Dr Andrew Ashley (Imperial College London) for the generous use of \textsuperscript{15}N\textsubscript{2} gas, and Dr Andrew J P White (Imperial College London) for crystallography discussions.

Conflicts of interest
There are no conflicts to declare.

Notes and references